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The Synthesis of Optically Active Cyanohydrin Esters and Their Use as High Ps Dopants for Ferroelectric Displays†

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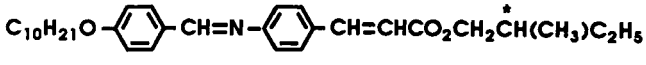
This paper describes the reasoning underlying the design and synthesis of a range of cyanohydrin esters, specifically as high Ps dopants of host S_C materials, for use in fast switching ferroelectric displays. Full synthetic details are given for the preparation of optically pure cyanohydrin esters from naturally occurring *L*-amino-acids; examples derived from (a) a *D*-amino-acid, (b) lactic acid are also given. Such materials provide excellent dopants which in suitable S_C hosts provide mixtures with wide S_C^* ranges, good Ps values and long pitches, which switch rapidly at room temperature and may be multiplexed at video frame rates.

Keywords: ferroelectric materials, high Ps dopants, chiral cyanohydrin esters

Meyer *et al.*[1] proposed in 1975 that ferroelectric properties could be exhibited by certain low symmetry, crystalline and fluid, smectic liquid crystal phases and they demonstrated that this was so by the synthesis and examination of the physical properties of optically active DOBAMBC (I). The S_C^* phase is the most fluid phase to offer such ferroelectric properties and therefore gives the greatest potential for electro-optic device applications, and although S_I and S_F phases are also ferroelectric, most attempts to produce suitable materials for device applications are directed towards S_C^* phases.

(I) 

K 76°C (S_I 63°C) S_C 95°C S_A 117°C I

Compounds such as (I) have small Ps values because the molecule does not possess a large dipole at any point in its structure and although it is not essential, and indeed may be undesirable, to have a high Ps value for the mixture used in a

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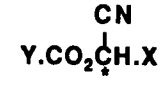
device, it is still important to have materials of high Ps value (as dopants) which can be used at low concentrations in compatible host materials to give the phase range, phase type and other properties required for the specific application. In this way a moderate Ps value for the final mixture can be achieved by the addition of the high Ps dopant which, because it is required in only a small amount, will only slightly modify the phase behavior and optical properties of the host system.

To achieve high Ps values it is best to have a strongly dipolar group situated close to or, ideally, directly attached to the chiral centre. If the chiral centre is also itself directly coupled to the molecular core, then one would anticipate that the whole unit (core and chiral centre) will be strongly linked in any molecular rotation and the effect of a tilted core and dipolar centre moving independently will be minimized. A further requirement from the point of view of commercial use is that the optically active systems should be readily available, chemically stable and not involve the time-consuming, unpredictable and costly process of optical resolution. Two possibilities are available to meet this requirement, (a) to prepare chiral compounds from achiral starting materials by asymmetric synthesis, and (b) to prepare chiral compounds from readily available (usually naturally occurring) chiral precursors. The first of these approaches is becoming increasingly relevant as more and better general asymmetric syntheses are devised to give products of higher and higher enantiomeric excesses. The second approach, however, has the advantage of starting with material which is already 100% optically pure and, so long as reactions can be used which are mild enough to prevent racemizations, the product should be of high optical purity. A further valuable factor which offers some freedom in devising S_C^* device mixtures is to be able to provide both enantiomeric forms of the chiral dopant. In this way the Ps value of a mixture can be varied by using different proportions of the (*R*) and (*S*) forms (keeping the total amount of dopant used constant) without altering the transition temperatures of the mixture. We therefore had the following objectives in mind in thinking of a suitable dopant structure:

(a) strongly dipolar group attached to a chiral centre,
(b) chiral centre close to the molecular core,
(c) compounds prepared without the necessity for optical resolution,
(d) compounds available in both enantiomeric forms,
(e) compounds stable to racemization.

These requirements are met by compounds of type (**II**)[2] where **Y** can be a core system and **X** can be a terminal chain, or *vice versa*. The compounds we report at

(II) 

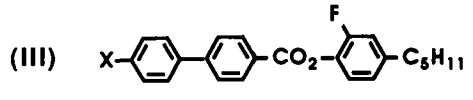
this stage in our work are those with **Y** as the core system and **X** as an alkyl chain. The general reaction scheme for their preparation is shown in Scheme 1 where the starting materials are the following commercially available α-amino-acids[3]: *L*-valine

[(*S*)-(+)-2-amino-3-methylbutanoic acid], *L*-leucine [(*S*)-(+)-2 amino-4-methylpentanoic acid], *L*-isoleucine [(2*S*, 3*S*)-(+)-2-amino-3-methylpentanoic acid] and *L*-norleucine [(*S*)-(+)-2-aminohexanoic acid]. Initial work revealed that the dopants derived from *L*-valine had some advantage (see Table II) and so *D*-valine was chosen as the amino-acid to use for the preparation of an enantiomeric dopant, although the *D*-forms of all the other amino-acids are also commercially available.

The route in Scheme 1 shows that an amino-acid (**1**) is converted into the sodium salt of the hydroxy-acid (**2**) by a stereospecific (retention of configuration) diazotization procedure as described by Mori *et al.*[4] It was not necessary to isolate the hydroxy-acid because the sodium salt could be obtained following the procedure of Winitz *et al.*,[5] and was then readily converted into the benzyl ester (**3**) as a way of protecting the acid function. The hydroxy-compound (**3**) was then esterified with a suitable "core" acid[6] (those used are **A-M**) by using the DCC method of esterification, and the benzyl group was then removed by hydrogenolysis. The acid function in compound **5** was then converted *via* the amide into the cyano function to give the final products **7**. The optical purities of the final products were checked by using nmr spectroscopy with a chiral shift reagent (tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]-europium(III)).

The full range of cyanohydrin esters prepared is listed in Table I along with their transition temperatures and values of specific rotation. The majority of the esters are not mesomorphic, but they have moderate melting points; one is a liquid and the others melt in the range of 32–98.5°C. Four examples of esters containing three ring units were prepared with the intention of promoting mesogenic character, and although this was achieved it was at the expense of higher melting points. All of the compounds prepared were laevorotatory apart from two of the three examples derived from lactic acid.

Considerable effort has been made to optimize the potential of mixtures containing these esters for use in ferroelectric display devices and preliminary reports have already been given of this work,[7–10] and further work is still continuing in previously disclosed host systems such as HI (**III**) and in other novel systems. A sample of some of these results is shown in Table II for a two- and three-ring



HI is a 1:1:1 mixture of compounds X = C_8H_{17}, $C_7H_{15}O$, $C_8H_{17}O$

HI transitions: S_I 28°C S_C 107°C S_A 113°C N 152°C I

lactate derivative and for a series of valine, leucine and norleucine derivatives. It is clear that the cyanohydrin esters depress the S_C–S_A transition temperature of the host mixture quite significantly and even the most mesogenic of these compounds (*i.e.*, **M7Lac**) affects the S_C–S_A transitions to a similar extent. The S_A–N transition is however far less sensitive to the effect of the dopant and for the three-ring example (**M7Lac**) this transition is raised quite markedly. The extrapolated Ps values are reasonably similar for the two-ring compounds, but the length of the

TABLE I

Transition temperatures (°C) and specific rotations (°) in $CHCl_3$

	Transitions
$C_8H_{17}O.Ph.Ph.CO_2CH(CN)CH(CH_3)_2$[a]	K 67 I
$C_8H_{17}O.Ph.Ph.CO_2CH(CN)CH_2CH(CH_3)_2$	K 46 I
$C_8H_{17}O.Ph.Ph.CO_2CH(CN)CH(CH_3)CH_2CH_3$	K 74 I
$C_8H_{17}O.Ph.Ph.CO_2CH(CN)CH_2CH_2CH_2CH_3$	K 59 I
$C_9H_{19}.Ph.Ph.CO_2CH(CN)CH(CH_3)_2$	K 32 I
$C_9H_{19}.Ph.Ph.CO_2CH(CN)CH_3$	K 55 I
$C_7H_{15}.Ch.Ph.CO_2CH(CN)CH(CH_3)_2$	Liquid K < −20 I
$C_7H_{15}.Ch.Ch.CO_2CH(CN)CH(CH_3)_2$	K 84 I
$C_7H_{15}.Pm.Ph.CO_2CH(CN)CH(CH_3)_2$	K 81 I
$C_8H_{17}O.Ph.Ph.CH_2CO_2CH(CN)CH(CH_3)_2$	K 60 I
$C_8H_{17}O.Ph.Ph.CH_2CH_2CO_2CH(CN)CH(CH_3)_2$	K 56 I
$C_8H_{17}O.Ph.Ph.Ch.CO_2CH(CN)CH(CH_3)_2$	K 122 (S_B 113 S_A 114) I
$C_5H_{11}.Ch.Ph.Ph.CO_2CH(CN)CH(CH_3)_2$	K 89 (S_B 74 S_A 75) I
$C_6H_{13}O.Ph.CO_2.Ph.CO_2CH(CN)CH(CH_3)_2$	K 54 I
$C_8H_{17}O.Ph.Ph.CO_2.Ph.CO_2CH(CN)CH(CH_3)_2$	K 102 S_C 145 S_A 155 I
$C_{10}H_{21}O.Ph.Ph.CO_2CH(CN)CH_3$	K 98.5 I
$C_9H_{19}O.Ph.Ph.CO_2.Ph.CO_2CH(CN)CH_3$	K 121 (S_B 119) S_C 132 S_A 181 I

[a] enantiomer of this compound was also prepared.
monotropic transition.

TABLE II

Transition temperatures and other physical properties of several cyanohydrin esters as 10% mixtures in HI (III)

	S_C–S_A (°C)	S_A–N (°C)	Ps[b] ($nCcm^{-2}$)	N_p^*[c] (μm)	pPs[d] ($\mu mnCcm^{-2}$)	SP
C_9H_{19}.Ph.Ph.$CO_2CH(CN)CH_3$	67(−4.0)[a]	112(−0.1)[a]	180	0.20	36	+
$C_9H_{19}O$.Ph.Ph.$CO_2PhCO_2CH(CN)CH_3$	78(−2.9)	133(+2.0)	70	0.58	41	+
$C_8H_{17}O$.Ph.Ph.$CO_2CH(CN)CH(CH_3)_2$	74(−3.3)	111(−0.2)	164	0.53	87	+
$C_8H_{17}O$.Ph.Ph.$CO_2CH(CN)CH_2CH(CH_3)_2$	59(−4.8)	110(−0.3)	125	0.22	28	+
$C_8H_{17}O$.Ph.Ph.$CO_2CH(CN)(CH_2)_3CH_3$	72(−3.5)	112(−0.1)	139	0.27	38	+

values in parentheses are the effect on the stated transition temperature of the host in °C/% added.
polated spontaneous polarization from 10 wt.% solution in **HI** (see text, **(III)**), measured at 10°C below the S_C–S_A transition.
l cematic pitch extrapolated from mixtures in E7 at room temperature.
r(Ps).
of polarization of the S_C^* phase.
of N* helical pitch.

TABLE III

Properties of a long pitch mixture (LPM10) formulated from a cyanohydrin Ester **A7Val** in **H1**

T_{N-I}/°C	132	N_p^*/μm	15
T_{S_A-N}/°C	96	Δn	0.18
$T_{S_C-S_A}$/°C	75	$\Delta\epsilon$	−1.9
$T_{S_?-S_C}$/°C	0	τ_r/μs	13
Ps/nCcm^{-2} at 25°C	21	50V pulse (min. width)/μs	125
Cone angle/°	23	AC to latch/Vpk	20

The composition of mixture LPM10 is 85 wt% **H1(III)**; 5% **A7Val**; 10% ME805F (2-fluoro-4-pentylphenyl 4'-octoxybenzoate) (added to suppress lower smectic phases and to reduce the S_A phase range).

helical pitch N_p is variable. In order to assess the utility of compounds from such a variety of parameters, our collaborators at RSRE (Malvern) have proposed that the product $N_p \times$ Ps (*i.e.*, *p*Ps) is a good criterion of a compound's suitability since both a long helical pitch and a high Ps value are desirable properties. On this basis it can be seen that compound **A7Val** is the best, and most of the subsequent physical measurements were made for this compound and its enantiomer (which shows identical results to those given in Table II for **A7Val**, apart from the sense of helical pitch (*L*) and sign of polarization (−)).

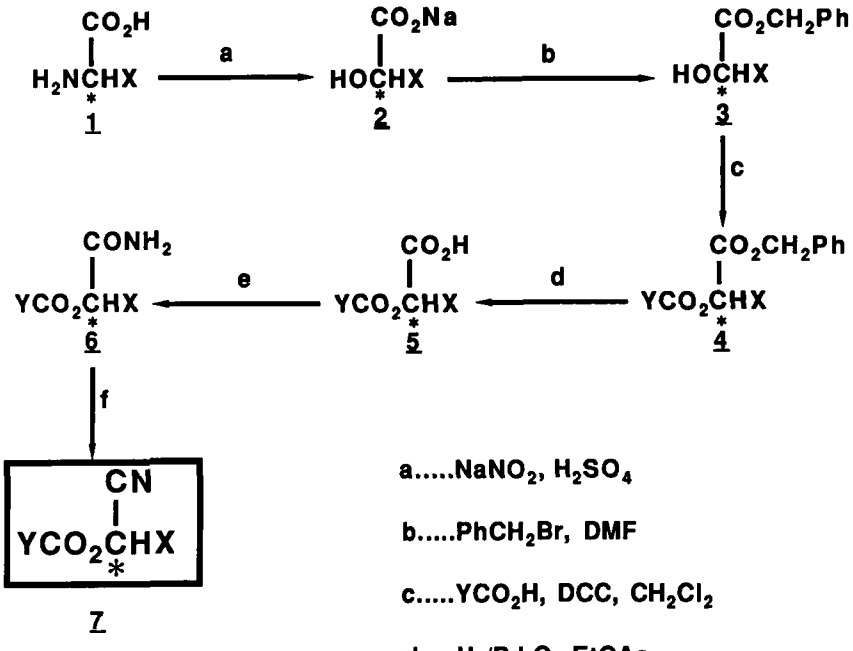
Numerous mixtures have been prepared based on **A7Val** and Table III gives the values for one of these.[8] This mixture shows the desired sequence of phases ($I \rightarrow N^* \rightarrow S_A \rightarrow S_C^*$) to enable good alignment to be obtained, gives a 0–75°C S_C range and fast switching times.

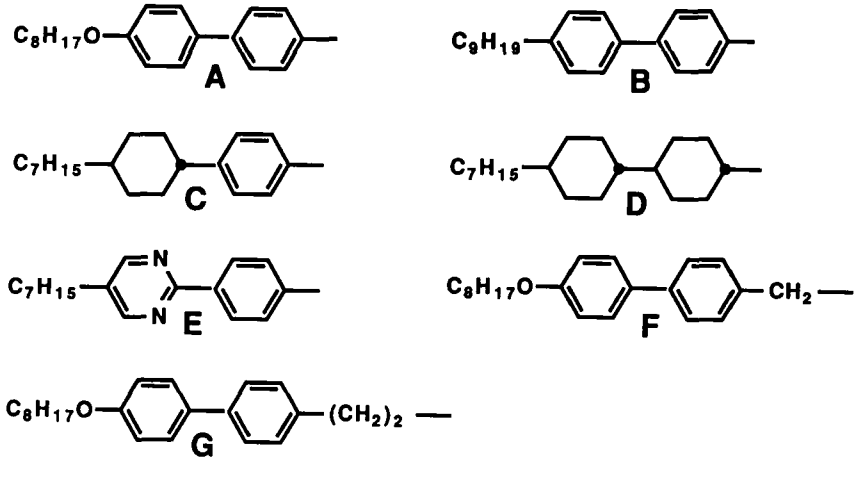
The cyanohydrin esters of the type reported here have therefore been shown to meet the objectives for a suitable molecular structure as outlined earlier and in suitable hosts, such as the one illustrated here, they are excellent dopants for the provision of mixtures with appropriate Ps values with long N* helical pitch which do not require pitch compensation. Such mixtures give rapid switching at room temperature and permit multiplexing at video frame rates.

Experimental

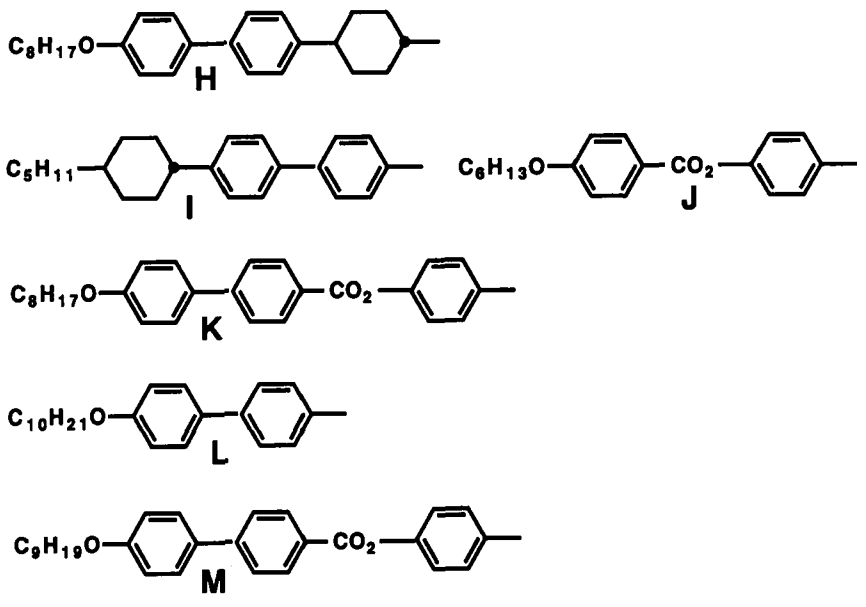
(S)-(−)-*Sodium 2-hydroxy-3-methylbutanoate* (*2Val*) A cold solution of sodium nitrite (26.4 g, 0.384 mol) in water (105 ml) was added dropwise to a stirred, cold solution of (*S*)-(+)-valine (30.0 g, 0.256 mol) in 0.5M-sulphuric acid (390 ml) during 3 hours, controlling the temperature between 0°C and −2°C. The reaction mixture was left stirring at room temperature overnight, then adjusted to pH 6 by adding solid sodium bicarbonate. The solution was acidified to pH 3 with 40%-orthophosphoric acid, and the crude product was extracted into tetrahydrofuran (THF) (2 × 200 ml). The combined THF solutions were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure at 50°C to give an oil.

The crude product was dissolved in water (105 ml) and decolourized with charcoal at room temperature. A concentrated solution of sodium hydroxide was added





Scheme 1 (cont. on next page)



Val...$CH(CH_3)_2$

Leu...$CH_2CH(CH_3)_2$

Iso...$CH(CH_3)CH_2CH_3$

Nor...$(CH_2)_3CH_3$

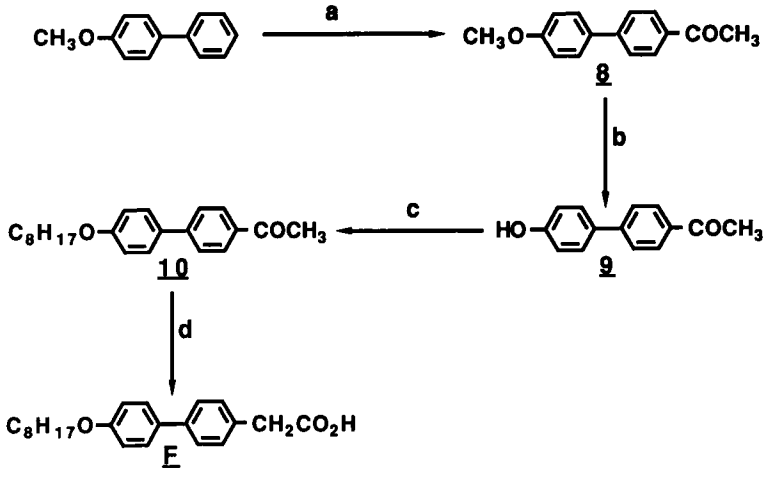
Lac...CH_3

Scheme 1 (cont'd)

dropwise to the cold solution adjusting the pH to 4.5–5.0. Acetone (3 times the volume of the aqueous solution) was added and the precipitate which formed was filtered off and dried (*in vacuo*, $CaCl_2$). Yield 22.0 g, 61%; $[\alpha]_D^{20} = -13.95°$ (H_2O); ν_{max} (KCl) 3320, 2970, 2940, 2880, 1590, 1450, 1185, 1135, 1020 cm^{-1}.

(S)-(−)-*Sodium 2-hydroxy-4-methylpentanoate* (***2Leu***) was prepared similarly from (*S*)-(+)-leucine; yield 63%; $[\alpha]_D^{20} = -25.3°(H_2O)$; ν_{max} (KCl) 3060, 2950, 2880, 1615, 1460, 1405, 1140, 1085 cm^{-1}.

(S)-(−)-*Sodium 2-hydroxy-3-methylpentanoate* (***2Iso***) was prepared similarly from (2*S*,3*S*)-(+)-isoleucine; yield 40%; $[\alpha]_D^{20} = -6.7°(H_2O)$;$\nu_{max}$ (KCl) 3480, 3350, 2970, 2940, 2880, 1590, 1360, 1185, 1160, 1120 cm^{-1}.



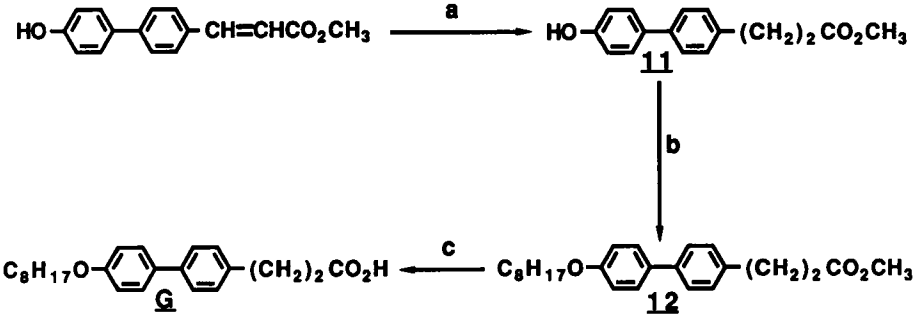
a....CH_3COCl, CH_2Cl_2

b....HBr, CH_3CO_2H

c....$C_8H_{17}Br$, K_2CO_3, $CH_3CH_2COCH_3$

d....S, morpholine; NaOH, EtOH; HCl

Scheme 2

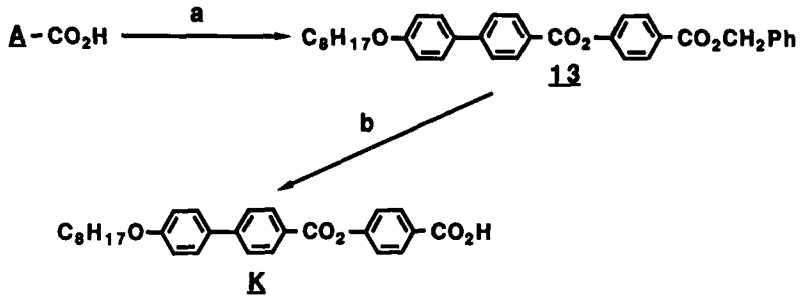


a....H_2/Pd-C, THF

b....$C_8H_{17}Br$, K_2CO_3, $CH_3CH_2COCH_3$

c....KOH, EtOH, H_2O; CH_3CO_2H

Scheme 3



a....benzyl 4-hydroxybenzoate, DCC, CH_2Cl_2

b....H_2/Pd-C, $CH_3CO_2CH_2CH_3$

Scheme 4

(S)-(−)-*Sodium 2-hydroxyhexanoate* (***2Nor***) was prepared similarly from (*S*)-(+)-norleucine; yield 66%; ν_{max}(KCl) 3400–3260, 2960, 2940, 2880, 1580, 1370, 1135, 1080, 840 cm^{-1}.

(S)-*Benzyl 2-hydroxy-3-methylbutanoate* (***3Val***) A mixture of (*S*)-(−)-sodium 2-hydroxy-3-methylbutanoate (**2Val**) (10.0 g, 72 mmol), benzyl bromide (12.2 g, 72 mmol) and sieve-dried dimethylformamide (DMF) (120 ml) was stirred at room temperature for 24 hours. The DMF was removed under reduced pressure (at 50–55°C) and the remaining suspension was diluted with ether (100 ml) and filtered. The filtrate was washed successively with water, sodium bicarbonate solution, and water, and dried ($MgSO_4$). After distilling off the solvent (below 55°C), the crude product was distilled at 135–140°C/0.6–0.65 mmHg (Kugelrohr). Yield 14.4 g, 96%; ^{1}Hnmr ($CDCl_3$) δ 0.70–1.35(6H, m), 1.74–2.36(1H, m), 3.00(1H, d), 4.04(1H, t), 5.19(2H, s), 7.38(5H, s); ν_{max} (film) 3500, 2970, 2940, 2880, 1730, 1500, 1460–1260, 1140, 1060, 850, 700 cm^{-1}.

(S)-*Benzyl 2-hydroxy-4-methylpentanoate* (***3Leu***) was prepared similarly from compound **2Leu**; yield 82%; bp 135°C/0.5 mmHg; ^{1}Hnmr ($CDCl_3$) δ 0.90 (6H, d), 1.40–2.20(3H, m), 3.58(1H, s), 4.34(1H, t), 5.34(2H, s), 7.60(5H, s); ν_{max} (film) 3450, 2960, 2880, 1735, 1500, 1455, 1270, 1215, 1140, 1090, 750, 700 cm^{-1}.

(S)-*Benzyl 2-hydroxy-3-methylpentanoate* (***3Iso***) was prepared similarly from compound **2Iso**; yield 53%; bp 140–150°C/0.7–0.75 mmHg; ^{1}Hnmr ($CDCl_3$) δ 0.70–1.10(6H, m), 1.10–1.50(2H, q), 1.60–2.20(1H, m), 2.95(1H, d), 4.24(1H, t), 5.39(2H, s), 7.60(5H, s); ν_{max} (film) 3460, 2970, 2940, 2880, 1735, 1500, 1460, 1215, 1140, 756, 700 cm^{-1}.

(S)-*Benzyl 2-hydroxyhexanoate* (***3Nor***) was prepared similarly from compound **2Nor**; yield 52%; bp 140–150°C/0.25 mmHg; ν_{max} (film) 3450, 2960, 2880, 1730, 1500, 1455, 1200, 1130, 1085, 910 cm^{-1}.

(S)-*1-(Benzyloxycarbonyl)-2-methylpropyl 4'-octoxybiphenyl-4-carboxylate (**A4Val**)* A solution of *N,N'*-dicyclohexylcarbodiimide (DCC) (7.5 g, 36 mmol) in sieve-dried dichloromethane (50 ml) was added slowly (20 min) to a stirred mixture of 4'-octoxybiphenyl-4-carboxylic acid (**A**) (10.8 g, 33 mmol), (*S*)-benzyl 2-hydroxy-3-methylbutanoate (**3Val**) (6.9 g, 33 mmol) and 4-(*N*-pyrrolidino)pyridine (N-PPY) (0.49 g, 3.3 mmol) in sieve-dried dichloromethane (250 ml). The reaction mixture was stirred for 6 hours at room temperature. The *N,N'*-dicyclohexylurea was filtered off and the filtrate was washed successively with water, 5%-aqueous acetic acid, and water, and finally dried ($MgSO_4$). After removal of the solvent, the crude diester was purified by column chromatography [silica gel; eluting with dichloromethane—light petroleum (bp 60–80°C) (4:1)] to give a viscous liquid product which solidified after a long time. Yield 12.5 g, 74%; mp 27°C; ^{1}Hnmr ($CDCl_3$) δ 0.90–2.80(22H, m), 4.00(2H, t), 5.16–5.36(3H, d), 7.06(2H, d), 7.42(5H, s), 7.70(4H, q), 8.22(2H, d); ν_{max} (film) 2930, 2860, 1755, 1725, 1610, 1500, 1250, 1185, 1110, 830, 775 cm^{-1}.

(S)-*1-(Benzyloxycarbonyl)-3-methylbutyl 4'-octoxybiphenyl-4-carboxylate* (***A4Leu***) was prepared similarly from compounds **A** and **3Leu**; yield 78% (liquid); ^{1}Hnmr ($CDCl_3$) δ 0.80–2.40(24H, m), 4.06(2H, t), 5.34(2H, s), 5.44(1H, t), 7.16(2H, d), 7.50(5H, s), 7.80(4H, q), 8.36(2H, d); ν_{max} (film) 2930, 2860, 1755, 1720, 1605, 1500, 1296–1250, 1185, 1105, 830, 775 cm^{-1}.

(S)-*1-(Benzyloxycarbonyl)-2-methylbutyl 4'-octoxybiphenyl-4-carboxylate* (***A4Iso***) was prepared similarly from compounds **A** and **3Iso**; yield 33% (liquid); ^{1}Hnmr ($CDCl_3$) δ 0.70–2.40(24H, m), 4.10(2H, t), 5.36(3H, m), 7.20(2H, d), 7.60(5H, s), 7.86(4H, q), 8.40(2H, d); ν_{max} (film) 2930, 2860, 1755, 1720, 1605, 1500, 1250, 1185, 1110, 830, 775 cm^{-1}.

(S)-*1-(Benzyloxycarbonyl)pentyl 4'-octoxybiphenyl-4-carboxylate* (***A4Nor***) was prepared similarly from compounds **A** and **3Nor**; yield 21% (liquid); ^{1}Hnmr ($CDCl_3$) δ 0.60–2.20(24H, m), 4.06(2H, t), 5.34(2H, s), 5.42(1H, t), 7.16(2H, d), 7.50(5H, s), 7.80(4H, q), 8.40(2H, d); ν_{max} (film) 2930, 2860, 1760, 1725, 1610, 1500, 1275, 1250, 1185, 1110, 830, 775 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl 4'-octoxybiphenyl-4-carboxylate (**A5Val**)* Compound **A4Val** (12.5 g, 24.2 mmol) was dissolved in ethyl acetate (160 ml) containing 5% Pd-on-charcoal (200 mg); the mixture was stirred overnight under an atmosphere of hydrogen and the reaction was monitored by using tlc. After hydrogenolysis was complete (~550 ml uptake of hydrogen), the catalyst was filtered off and the filtrate was evaporated to dryness to give a solid product (the product gave one spot on tlc and was used without further purification). Yield 9.7 g, 95%; mp 80–83°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.10–1.50(16H, m), 1.80(2H, m), 2.45(1H, m), 4.00(2H, t), 5.15(1H, d), 6.95(2H, d) 7.55(2H, d), 7.65(2H, d), 8.10 (2H, d), 9.00–9.50(1H, s); ν_{max} (KCl) 3400, 2930, 2860, 1720, 1710, 1605, 1500, 1290, 1270, 1250, 1195, 1115, 825, 775 cm^{-1}.

(S)-*1-Carboxy-3-methylbutyl 4'-octoxybiphenyl-4-carboxylate* (***A5Leu***) was prepared similarly from compound **A4Leu**; yield ~100%; mp 65–67°C; ^{1}Hnmr ($CDCl_3$)

δ 0.90–2.40(24H, m), 4.20(2H, t), 5.60(1H, t), 7.22(2H, d), 7.90(4H, q), 8.50(2H, d), 10.70(1H, s); ν_{max} (KCl) 3320, 2960, 2920, 2860, 1780, 1725, 1605, 1500, 1250, 1195, 1110, 835, 770 cm^{-1}.

(S)-*1-Carboxy-2-methylbutyl 4'-octoxybiphenyl-4-carboxylate* (***A5Iso***) was prepared similarly from compound **A4Iso**; yield ~100%; mp 48–49°C; ^{1}Hnmr ($CDCl_3$) δ 0.80–2.40(24H, m), 4.18(2H, t), 5.46(1H, d), 7.24(2H, d), 7.90(4H, q), 8.44(2H, d), 8.82(1H, s); ν_{max} (KCl) 2930, 2860, 1720, 1605, 1500, 1275, 1250, 1190, 1110, 830, 775 cm^{-1}.

(S)-*1-Carboxypentyl 4'-octoxybiphenyl-4-carboxylate* (***A5Nor***) was prepared similarly from compound **A4Nor**; yield 98%; mp 72–74°C; ^{1}Hnmr ($CDCl_3$) δ 0.80–2.40(24H, m), 4.10(2H, t), 5.50(1H, t), 7.20(2H, d), 7.80(4H, q), 8.40(2H, d), 10.40(1H, s); ν_{max} (KCl) 2940, 2860, 1745, 1715, 1600, 1500, 1290, 1280, 1195, 1095, 830, 775 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl 4'-octoxybiphenyl-4-carboxylate* (***A6Val***)
The carboxylic acid **A5Val** (9.4 g, 22.1 mmol) was initially converted into the acid chloride by reacting with oxalyl chloride (5.75 g, 44 mmol) and sieve-dried DMF (2 drops) in sodium-dried benzene (25 ml) for 3 hours at room temperature. The excess of oxalyl chloride and the solvent were removed by distillation under reduced pressure. The crude acid chloride residue was dissolved in diglyme (10 ml) and added to an aqueous solution of ammonia (d = 0.88 g ml^{-1}, 100 ml) with stirring. After the addition, the reaction mixture was stirred for 30 min at room temperature, then the product was filtered off, washed with water and dried (*in vacuo*, $CaCl_2$); yield 9.4 g, ~100%, mp 95–97°C; ν_{max} (KCl) 3390, 3200, 2930, 2850, 1725, 1670, 1605, 1500, 1280, 1190, 1110, 830, 770 cm^{-1}.

(S)-*1-Carbamoyl-3-methylbutyl 4'-octoxybiphenyl-4-carboxylate* (***A6Leu***) was prepared similarly from compound **A5Leu**; yield 76%; mp 92–94°C; ν_{max} (KCl) 3480, 3360, 3200, 2920, 2860, 1710, 1690, 1605, 1500, 1275, 1195, 1105, 835, 770 cm^{-1}.

(S)-*1-Carbamoyl-2-methylbutyl 4'-octoxybiphenyl-4-carboxylate* (***A6Iso***) was prepared similarly from compound **A5Iso**; yield 91%; mp 84–87°C; ν_{max} (KCl) 3470, 3180, 2930, 2860, 1720, 1675, 1605, 1500, 1270, 1190, 1100, 825, 770 cm^{-1}.

(S)-*1-Carbamoylpentyl 4'-octoxybiphenyl-4-carboxylate* (***A6Nor***) was prepared similarly from compound **A5Nor**; yield 97%; mp 95–96°C; ν_{max}(KCl) 3930, 3820, 3205, 2930, 2860, 1720, 1690, 1605, 1500, 1280, 1190, 1125, 825, 770 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl 4'-octoxybiphenyl-4-carboxylate* (***A7Val***)
A mixture of thionyl chloride (26.3 g, 221 mmol) and sieve-dried DMF (100 ml) was added dropwise (30 min) to a vigorously stirred solution of the amide **A6Val** (9.0 g, 22.1 mmol) in sieve-dried DMF (100 ml). After the addition, the reaction mixture was left stirring at room temperature for 8 hours. The reaction mixture was poured into ice-water and the product was extracted into ether (2 × 300 ml); the combined ethereal extracts were washed successively with a saturated solution of $NaHCO_3$, and water, and then dried ($MgSO_4$). After removal of the solvent, the product was purified by column chromatography [silica gel; eluting with ethyl

acetate-light petroleum (bp 40–60°C) (1:3)] and then recrystallized (light petroleum bp 40–60°C). Yield 8.3 g, 97%; mp 67°C; $[\alpha]_D^{20} = -3.1°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.10–1.55(16H, m), 1.80(2H, m), 2.30(1H, m), 4.00(2H, t), 5.45(1H, d), 7.00(2H, d), 7.55(2H, d), 7.65 (2H, d), 8.10(2H, d); *m/z* 408, 407 (M^+), 295, 214, 197; ν_{max} (KCl) 2970, 2940, 2860, 1740, 1616, 1500, 1280, 1190, 1110, 830, 770 cm^{-1}.

(S)-(−)-*1-Cyano-3-methylbutyl 4'-octoxybiphenyl-4-carboxylate* (***A7Leu***) was prepared similarly from compound **A6Leu** and was recrystallized from petroleum fraction (bp 40–60°C); yield 95%; mp 46°C; $[\alpha]_D^{20} = -17.5°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.55(16H, m), 1.80(2H, m), 1.95(3H, m), 4.00(2H, t), 5.65(1H, t), 7.00(2H, d), 7.55(2H, d), 7.65(2H, d), 8.10(2H, d); *m/z* 422, 421(M^+), 309, 214, 197; ν_{max} (KCl) 2970, 2940, 2860, 1735, 1610, 1500, 1470, 1280, 1190, 1110, 830, 770 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylbutyl 4'-octoxybiphenyl-4-carboxylate* (***A7Iso***) was prepared similarly from compound **A6Iso** and was recrystallized from petroleum fraction (bp 40–60°C); yield 93%; mp 74°C; $[\alpha]_D^{20} = -5.4°$($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.75(18H, m), 1.85(2H, m), 2.10(1H, m), 4.00(2H, t), 5.10(1H, d), 7.00(2H, d), 7.55(2H, d), 7.65(2H, d), 8.10(2H, d); *m/z* 422, 421(M^+), 309, 214, 197; ν_{max}(KCl) 2970, 2940, 2860, 1740, 1610, 1500, 1280, 1190, 1110, 830, 770 cm^{-1}.

(S)-(−)-*1-Cyanopentyl 4'-octoxybiphenyl-4-carboxylate* (***A7Nor***) was prepared similarly from compound **A6Nor** and was recrystallized from petroleum fraction (bp 40–60°C); yield 91%; mp 59°C; $[\alpha]_D^{20} = -10.6°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 0.95–1.65(17H, m), 1.80(2H, m), 2.05(2H, m), 4.00(2H, t), 5.05(1H, t), 7.00(2H, d), 7.55(2H, d), 7.65(2H, d), 8.05(2H, d); *m/z* 422, 421(M^+), 309, 214, 197; ν_{max}(KCl) 2960, 2930, 2860, 1740, 1605, 1500, 1270, 1200, 1110, 835, 770 cm^{-1}.

The following compounds of type **4** were prepared by using the method described for compound **A4Val**.

(S)-*1-(Benzyloxycarbonyl)-2-methylpropyl 4'-nonylbiphenyl-4-carboxylate* (***B4Val***) [from 4'-nonylbiphenyl-4-carboxylic acid (**B**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 91% (liquid); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.45(18H, m), 1.65(2H, m), 2.40(1H, m), 2.65(2H, t), 5.15(1H, d), 5.20(2H, q), 7.25(2H, d), 7.35(5H, s), 7.55(2H, d), 7.65(2H, d), 8.15(2H, d); ν_{max} (film) 3030, 2925, 2850, 1755, 1725, 1610, 1500, 1255, 1110, 775, 740, 695 cm^{-1}.

(S)-*1-(Benzyloxycarbonyl)-2-methylpropyl 4-*(trans-*4-heptylcyclohexyl)benzoate* (***C4Val***) [from 4-(*trans*-4-heptylcyclohexyl)benzoic acid (**C**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 58%; mp 38–40°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 0.95–1.60(23H, m), 1.90(4H, d), 2.37(1H, m), 2.55(1H, t), 5.13(1H, d), 5.70(2H, q), 7.27(2H, d), 7.35(5H, s), 8.00(2H, d); ν_{max}(KCl) 2960, 2920, 2850, 1750, 1720, 1610, 1355, 1275, 1240, 1115, 755, 700 cm^{-1}.

(S)-*1*-(*Benzyloxycarbonyl*)-*2*-*methylpropyl* trans-4-(trans-*4*-*heptylcyclohexyl*)*cyclohexanecarboxylate* (***D4Val***) [from *trans*-4-(*trans*-4-heptylcyclohexyl)cyclohexanecarboxylic acid (**D**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 77%; mp 35°C; ^{1}Hnmr ($CDCl_3$) δ 0.70–2.35(42H, m), 4.90(1H, d), 5.15(2H, q), 7.35(5H, s); ν_{max} (film) 2920, 2850, 1755, 1740, 1450, 1130, 740, 695 cm^{-1}.

(S)-*1*-(*Benzyloxycarbonyl*)-*2*-*methylpropyl* 4-(*5*-*heptylpyrimidin*-*2*-*yl*)*benzoate* (***E4Val***) [from 4-(5-heptylpyrimidin-2-yl)benzoic acid (**E**)]; [silica gel; eluting with dichloromethane-ethyl acetate (3:1)]; yield 88%; mp 65–66°C; ^{1}Hnmr ($CDCl_3$) δ 0.85–1.45(17H, m), 1.67(2H, m), 2.40(1H, m), 2.65(2H, t), 5.15(1H, d), 5.23(2H, q), 7.35(5H, s), 8.20(2H, d), 8.55(2H, d), 8.67(2H, s); ν_{max} (KCl) 2970, 2930, 2860, 1760, 1715, 1430, 1290, 1255, 1135, 1110, 1015, 765, 700 cm^{-1}.

(S)-*1*-(*Benzyloxycarbonyl*)-*2*-*methylpropyl* 4'-*octoxybiphenyl*-*4*-*ylethanoate* (***F4Val***) [from 4'-octoxybiphenyl-4-ylethanoic acid (**F**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 40–60°C) (2:1)]; yield 83% (liquid); ^{1}Hnmr ($CDCl_3$) δ 0.85–1.55(19H, m), 1.80(2H, m), 2.25(1H, m), 3.75(2H, s), 4.00(2H, t), 4.90(1H, d), 5.15(2H, q), 6.95(2H, d), 7.30(7H, m), 7.50(4H, d); ν_{max} (film) 3040, 2930, 2860, 1745, 1610, 1500, 1250, 1130, 810, 700 cm^{-1}.

(S)-*1*-(*Benzyloxycarbonyl*)-*2*-*methylpropyl* 3-(*4'*-*octoxybiphenyl*-*4*-*yl*)*propanoate* (***G4Val***) [from 3-(4'-octoxybiphenyl-4-yl)propanoic acid (**G**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (2:1)]; yield 85%; mp 45°C; ^{1}Hnmr ($CDCl_3$) δ 0.85–1.55(19H, m), 1.80 (2H, m), 2.23(1H, m), 2.75(2H, m), 3.00(2H, t), 4.00(2H, t), (4.90) (1H, d), 5.18(2H, q), 6.95(2H, d), 7.25(2H, d), 7.35(5H, s), 7.50 (4H, q); ν_{max} (KCl) 2930, 2860, 1750, 1730, 1610, 1505, 1255, 1130, 700 cm^{-1}.

(S)-*1*-(*Benzyloxycarbonyl*)-*2*-*methylpropyl* trans-*4*-(*4'*-*octoxybiphenyl*-*4*-*yl*)*cyclohexanecarboxylate* (***H4Val***) [from *trans*-4-(4'-octoxybiphenyl-4-yl)cyclohexanecarboxylic acid (**H**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 69%; mp 55°C; ^{1}Hnmr ($CDCl_3$) δ 0.85–2.25(29H, m), 2.30(1H, m), 2.50(2H, m), 4.00(2H, t), 4.95(1H, d), 5.17(2H, q), 6.95(2H, d), 7.25(2H, d), 7.35(5H, s), 7.50(4H, q); ν_{max} (KCl) 2930, 2860, 1750, 1730, 1610, 1505, 1250, 1135, 825, 815, 760, 705 cm^{-1}.

(S)-*1*-(*Benzyloxycarbonyl*)-*2*-*methylpropyl* 4'-(trans-*4*-*pentylcyclohexyl*)*biphenyl*-*4*-*carboxylate* (***I4Val***) [from 4'-(*trans*-4-pentylcyclohexyl)biphenyl-4-carboxylic acid (**I**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 66%; mp 60°C; ^{1}Hnmr ($CDCl_3$) δ 0.85–1.65(22H, m), 1.92(4H, t), 2.40(1H, m), 2.55(1H, t), 5.15(1H, d), 5.23(2H, q), 7.35(7H, t), 7.57(2H, d), 7.65(2H, d), 8.15 (2H, d); ν_{max} (KCl) 2920, 2850, 1755, 1730, 1610, 1500, 1260, 1130, 830, 700 cm^{-1}.

(S)-*1*-(*Benzyloxycarbonyl*)-*2*-*methylpropyl* 4-(*4*-*hexoxybenzoyloxy*)*benzoate* (***J4Val***) [from 4-(4-hexoxybenzoyloxy)benzoic acid (**J**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 79% (liquid); ^{1}Hnmr ($CDCl_3$) δ 0.85–1.65(15H, m), 1.80(2H, m), 2.40 (1H, m), 4.00(2H, t), 5.15(1H,

d), 5.22(2H, q), 6.98(2H, d), 7.35(7H, t) 8.15(4H, q); ν_{max} (film) 2970, 2940, 2880, 1755, 1740, 1730, 1605, 1515, 1255, 1205, 1160, 1060, 765, 700 cm^{-1}.

(S)-*1-(Benzyloxycarbonyl)-2-methylpropyl 4-(4'-octoxybiphenyl-4-carbonyloxy)benzoate* (***K4Val***) [from 4-(4'-octoxybiphenyl-4-carbonyloxy)benzoic acid (**K**)]; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 63%; mp 73°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.60(21H, m), 1.82(2H, m), 2.40(1H, m), 4.00(2H, t), 5.15(1H, d), 5.23(2H, q), 7.00(2H, d), 7.35(5H, s), 7.60(2H, d), 7.70 (2H, d), 8.20(2H, d), 8.25(2H, d); ν_{max} (KCl) 2930, 2860, 1755, 1740, 1730, 1600, 1505, 1280, 1250, 1190, 1160, 1075, 1060, 835, 770 cm^{-1}.

The following compounds of type **5** were prepared by using the method described for compound **A5Val**.

(S)-*1-Carboxy-2-methylpropyl 4'-nonylbiphenyl-4-carboxylate* (***B5Val***) (from **B4Val**); yield 87%; mp 72–73°C; ^{1}Hnmr ($CDCl_3$) δ 0.85(3H, t), 1.00–1.55 (21H, m), 1.65(2H, m), 2.45 (1H, m), 2.65(2H, t), 5.15(1H, d), 7.28(2H, d), 7.52(2H, d), 7.65(2H, d), 8.12(2H, d), 10.95(1H, s); ν_{max} (KCl) 2930, 2850, 1710, 1610, 1285, 1110, 1020, 770 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl 4-*(trans-*4-heptylcyclohexyl)benzoate* (***C5Val***) (from **C4Val**); yield ~100%; mp 71°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.60 (20H, m), 1.90(4H, d), 2.05(1H, s), 2.40(1H, m), 2.52(1H, t), 5.15(1H, d), 7.30(2H, d), 8.00(2H, d), 11.00(1H, s); ν_{max} (KCl) 2920, 2850, 1715, 1610, 1285, 1110, 1020, 750, 710 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl* trans-*4-*(trans-*4-heptylcyclohexyl)cyclohexanecarboxylate* (***D5Val***) (from **D4Val**); yield 93%; mp 68–70°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 0.95–2.15(38H, m), 2.30(1H, m) 4.90(1H, d), 10.35(1H, s); ν_{max} (KCl) 3490, 3370, 2920, 2850, 1715, 1695, 1470, 1225, 1185 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl 4-(5-heptylpyrimidin-2-yl)benzoate* (***E5Val***) (from **E4Val**); yield ~100%; mp 88°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.55 (14H, m), 1.70(2H, t), 2.48(1H, m), 2.65(2H, t), 5.15(1H, d), 8.20(2H, d), 8.40(2H, d), 8.75(2H, s), 10.20(1H, s); ν_{max} (KCl) 3420, 2930, 2860, 1760, 1715, 1435, 1285, 1260, 1115, 765 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl 4'-octoxybiphenyl-4-ylethanoate* (***F5Val***) (from **F4Val**); yield 79%; mp 80–81°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 0.95–1.55(16H, m), 1.80(2H, m), 2.28(1H, m), 3.78(2H, s), 4.00(2H, t), 4.92(1H, d), 6.98(2H, d), 7.35(2H, d), 7.50(4H, q); ν_{max} (KCl) 3440, 3120, 2930, 2860, 1735, 1725, 1610, 1500, 1250, 1025, 810 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl 3-(4'-octoxybiphenyl-4-yl)propanoate* (***G5Val***) (from **G4Val**); yield 98%; mp 74–75°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.02 (6H, d), 1.20–1.55(10H, m), 1.80(2H, m), 2.28(1H, m), 2.80(2H, m), 3.05(2H, t), 4.00(2H, t), 4.90(1H, d), 6.95(2H, d), 7.25(2H, d), 7.50(4H, q); ν_{max} (KCl) 3400, 2930, 2860, 1740, 1715, 1610, 1500, 1250, 1180, 1155, 830 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl* trans-*4-(4'-octoxybiphenyl-4-yl)cyclohexanecarboxylate* (***H5Val***) (from **H4Val**); yield 93%; mp 125°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H,

t), 1.10(6H, d), 1.20–1.90(16H, m), 2.05(2H, d), 2.20(2H, m), 2.33(1H, m), 2.55(2H, m), 4.00(2H, t), 4.95(1H, d), 6.95(2H, d), 7.25(2H, d), 7.52(4H, q), 9.70(1H, s); ν_{max} (KCl) 3500, 3390, 2930, 2860, 1735, 1715, 1610, 1500, 1250, 1180, 1050, 820 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl 4'-*(trans-*4-pentylcyclohexyl)biphenyl-4-carboxylate* (***I5Val***) (from **I4Val**); yield ~100%: mp 148°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.60(19H, m), 1.92(4H, t), 2.40–2.60(2H, m), 5.17(1H, d), 7.30(2H, d), 7.55(2H, d), 7.63(2H, d), 8.15(2H, d), 9.75(1H, s); ν_{max} (KCl) 3400, 2930, 2850, 1725, 1715, 1610, 1285, 1115, 770 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl 4-(4-hexoxybenzoyloxy)benzoate* (***J5Val***) (from **J4Val**); yield 99%; mp 62–63°C; ^{1}Hnmr ($CDCl_3$) δ 0.93(3H, t), 1.00–1.60(12H, m), 1.82(2H, m), 2.43(1H, m), 4.03(2H, t), 5.15(1H, d), 6.97(2H, d), 7.30(2H, d), 8.15(4H, q), 9.45(1H, s); ν_{max} (KCl) 3430, 2940, 2880, 1740, 1725, 1610, 1515, 1260, 1165, 1060, 765, 695 cm^{-1}.

(S)-*1-Carboxy-2-methylpropyl 4-(4'-octoxybiphenyl-4-carbonyloxy)benzoate* (***K5Val***) (from **K4Val**); yield 70%; mp 117°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.60(16H, m), 1.82(2H, m), 2.45(1H, m), 4.00(2H, t), 5.15(1H, d), 6.95(2H, d), 7.32(2H, d), 7.60(2H, d), 7.68(2H, d), 8.18(2H, d), 8.22(2H, d), 9.25(1H, s); ν_{max} (KCl) 2930, 2860, 1735, 1725, 1605, 1505, 1260, 1190, 1165, 1070, 1015, 830, 770 cm^{-1}.

The following compounds of type **6** were prepared by using the method described for compound **A6Val**.

(S)-*1-Carbamoyl-2-methylpropyl 4'-nonylbiphenyl-4-carboxylate* (***B6Val***) (from **B5Val**); yield 88%; mp 77°C; ν_{max} (KCl) 3390, 3200, 3050, 2920, 2850, 1725, 1670, 1610, 1400, 1280, 1110, 770 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl 4-*(trans-*4-heptylcyclohexyl)benzoate* (***C6Val***) (from **C5Val**); yield 93%, a sticky solid which was used without being analyzed.

(S)-*1-Carbamoyl-2-methylpropyl* trans-*4-*(trans-*4-heptylcyclohexyl)cyclohexanecarboxylate* (***D6Val***) (from **D5Val**); yield ~100%; ν_{max} (KCl) 3410, 3140, 3050, 2920, 2850, 1735, 1670, 1645, 1405, 1180, 1020 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl 4-(5-heptylpyrimidin-2-yl)benzoate* (***E6Val***) (from **E5Val**); yield 92%; mp 120°C; ν_{max} (KCl) 3390, 3200, 2930, 2860, 1725, 1680, 1615, 1430, 1275, 1120, 1020, 870, 760 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl 4'-octoxybiphenyl-4-ylethanoate* (***F6Val***) (from **F5Val**); yield 97%; mp 147–148°C; ν_{max} (KCl) 3390, 3200, 2930, 2860, 1735, 1665, 1610, 1500, 1245, 1140, 1020, 810 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl 3-(4'-octoxybiphenyl-4-yl)propanoate* (***G6Val***) (from **G5Val**); yield 91%; mp 115°C; ν_{max} (KCl) 3420, 3210, 2940, 2870, 1740, 1670, 1615, 1510, 1250, 825 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl* trans-*4-(4'-octoxybiphenyl-4-yl)cyclohexanecarboxylate* (***H6Val***) (from **H5Val**); yield 93%; mp 155°C; ν_{max} (KCl) 3390, 3200, 2930, 2860, 1730, 1665, 1610, 1500, 1250, 1175, 1025, 820 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl 4'-*(trans-*4-pentylcyclohexyl)biphenyl-4-carboxylate* (***I6Val***) (from **I5Val**); yield 98%; mp 137°C; ν_{max} (KCl) 3380, 3180, 2930, 2850, 1720, 1680, 1610, 1400, 1275, 1180, 1100, 1000, 830, 770 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl 4-(4-hexoxybenzoyloxy)benzoate* (***J6Val***) (from **J5Val**); yield 89%; mp 130°C; ν_{max} (KCl) 3420, 3330, 3220, 2940, 2860, 1730, 1680, 1605, 1515, 1255, 1210, 1160, 1075, 845, 765 cm^{-1}.

(S)-*1-Carbamoyl-2-methylpropyl 4-(4'-octoxybiphenyl-4-carbonyloxy)benzoate* (***K6Val***) (from **K5Val**); yield 97%; mp 155°C; ν_{max} (KCl) 3500, 3160, 2930, 2860, 1740, 1705, 1685, 1605, 1505, 1215, 1195, 1160, 1065, 830, 770 cm^{-1}.

The following compounds of type **7** were prepared using the method described for compound **A7Val**.

(S)-(−)-*1-Cyano-2-methylpropyl 4'-nonylbiphenyl-4-carboxylate* (***B7Val***) (from **B6Val**); [silica gel; eluting with ethyl acetate-light petroleum (bp 40–60°C) (1:3)]; recrystallized from light petroleum (bp 40–60°C); yield 92%; K_1 29°C K_2 32°C I; $[\alpha]^{20} = -4.8°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.87(3H, t), 1.05–1.55(18H, m), 1.65(2H, t), 2.33(1H, m), 2.67(2H, t), 5.47(1H, d), 7.27(2H, d), 7.55(2H, d), 7.70(2H, d), 8.10(2H, d); *m/z* 405(M^+), 307, 292, 211, 165; ν_{max} (KCl) 2970, 2930, 2860, 1735, 1610, 1470, 1265, 1095, 1000, 835, 760 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl 4-*(trans-*4-heptylcyclohexyl)benzoate* (***C7Val***) (from **C6Val**); [silica gel; eluting with ethyl acetate-light petroleum (bp 40–60°C) (1:3)]; yield 92%; mp< −20°C; $[\alpha]_D^{20} = -16.8°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.00–1.60(23H, m) 1.90(4H, d), 2.30(1H, m), 2.55(1H, t), 5.43(1H, d), 7.30(2H, d), 7.97(2H, d); *m/z* 384, 383 (M^+), 302, 285, 177, 147, 131, 115, 90, 84, 54; ν_{max} (film) 2930, 2860, 1735, 1610, 1470, 1260, 1185, 1090, 1020, 855, 770, 710 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl* trans-*4-*(trans-*4-heptylcyclohexyl)cyclohexanecarboxylate* (***D7Val***) (from **D6Val**); [silica gel; eluting with ethyl acetate-light petroleum (bp 40–60°C) (1:3)] recrystallized from light petroleum (bp 40–60°C); yield 78%; mp 84°C; $[\alpha]_D^{20} = -28.1°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 0.95–1.90(38H, m), 2.05(2H, d), 2.15(1H, m), 2.32(1H, m), 5.20(1H, d); *m/z* 390, 389 (M^+), 306, 289, 261, 208, 125, 108, 97, 80; ν_{max} (KCl) 2930, 2850, 1740, 1475, 1445, 1175, 1145, 1025, 725 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl 4-(5-heptylpyrimidin-2-yl)benzoate* (***E7Val***) (from **E6Val**); [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; recrystallized from light petroleum (bp <40°C); yield 98%; K_1 78°C K_2 81°C I; $[\alpha]_D^{20} = -8.9°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.05–1.55(14H, m), 1.68(2H, m), 2.37(1H, m), 2.68(2H, t), 4.48(1H, d), 8.18(2H, d), 8.52(2H, d), 8.67(2H, s); *m/z* 380, 379 (M^+), 336, 308, 295, 281, 227, 214, 168; ν_{max} (KCl) 2970, 2930, 2860, 1725, 1610, 1580, 1545, 1435, 1285, 1255, 1095, 1015, 875, 760 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl 4'-octoxybiphenyl-4-ylethanoate* (***F7Val***) (from **F6Val**); [silica gel; eluting with dichloromethane-light petroleum (bp 40–60°C) (1:1)]; recrystallized from ethanol; yield 97%; mp 60°C; $[\alpha]_D^{20} = -44°$($CHCl_3$);

^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.10(6H, t), 1.20–1.70(10H, m), 1.82(2H, m), 2.15(1H, m), 3.75(2H, s), 4.00(2H, t), 5.22(1H, d), 6.97(2H, d), 7.32(2H, d), 7.50(4H, q); *m/z* 422, 421 (M^+), 309, 295, 183; ν_{max} (KCl) 2930, 2860, 1750, 1610, 1500, 1250, 1140, 1025, 805 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl 3-(4'-octoxybiphenyl-4-yl)propanoate* (***G7Val***) (from **G6Val**); [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (2:1)]; recrystallized from ethanol; yield 93%; mp 56°C; $[\alpha]_D^{20} = -30.6°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.07(6H, t), 1.20–1.60(10H, m), 1.80(2H, m), 2.10(1H, m), 2.75(2H, m), 3.00(2H, t), 4.00(2H, t), 5.17(1H, d), 6.95(2H, d), 7.22(2H, d), 7.50(4H, d); *m/z* 436, 435 (M^+), 323, 199, 182; ν_{max} (KCl) 2930, 2860, 1750, 1610, 1505, 1255, 1180, 1150, 825 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl* trans-*4-(4'-octoxybiphenyl-4-yl)cyclohexanecarboxylate* (***H7Val***) (from **H6Val**); [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; recrystallized from light petroleum (bp 40–60°C); yield 44%; K 122°C (S_B 113°C S_A 114°C)I; $[\alpha]_D^{20} = -17.6°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.15(6H, t), 1.25–1.75(15H, m), 1.82(2H, m), 2.05(2H, d), 2.18(2H, m), 2.40–2.65(2H, m), 4.00(2H, t), 5.25(1H, d), 6.95(2H, d), 7.25(2H, d), 7.50(4H, d); *m/z* 491, 490, 489 (M^+), 377, 295, 249, 209, 196, 183; ν_{max} (KCl) 2930, 2860, 1740, 1615, 1500, 1245, 1165, 1025, 825 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl 4'-*(trans-*4-pentylcyclohexyl)biphenyl-4-carboxylate* (***I7Val***) (from **I6Val**); [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; recrystallized from light petroleum (bp 40–60°C); yield 93%; K 89°C(S_B 74°C S_A 75°C) I; $[\alpha]_D^{20} = -4.9°$ ($CHCl_3$): ^{1}Hnmr ($CDCl_3$) δ 0.93(3H, t), 0.97–1.60(19H, m), 1.92(4H, m) 2.32(1H, m), 2.53(1H, m), 5.47(1H, d), 7.33(2H, d), 7.57(2H, d), 7.70(2H, d), 8.10(2H, d); *m/z* 432, 431 (M^+), 333, 318, 305, 292, 219, 178, 165; ν_{max} (KCl) 2930, 2860, 1725, 1610, 1450, 1280, 1255, 1095, 830, 770 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl 4-(4-hexoxybenzoyloxy)benzoate* (***J7Val***) (from **J6Val**); [silica gel; eluting with ethyl acetate-light petroleum (bp 40–60°C) (1:3)]; recrystallized from ethanol; yield 94%; mp 54°C; $[\alpha]_D^{20} = -13.9°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.95(3H, t), 1.15–1.65(12H, m), 1.88(2H, m), 2.38(1H, m), 4.10(2H, t), 5.50(1H, d), 7.03(2H, d), 7.37(2H, d), 8.20(4H, d); *m/z* 423 (M^+), 295, 205, 121; ν_{max} (KCl) 2940, 2880, 2860, 1725, 1610, 1515, 1470, 1270, 1165, 1065, 845, 765, 695 cm^{-1}.

(S)-(−)-*1-Cyano-2-methylpropyl 4-(4'-octoxybiphenyl-4-carbonyloxy)benzoate* (***K7Val***) (from **K6Val**); [silica gel; eluting with ethyl acetate-light petroleum (bp 40–60°C) (1:3)]; recrystallized from ethyl acetate; yield 84%; K 102°C S_C 145°C S_A 155°C I; $[\alpha]_D^{20} = -9.4°$ ($CHCl_3$); ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.10–1.65(16H, m), 1.80(2H, m), 2.32(1H, m), 4.00(2H, t), 4.95(1H, d), 7.00(2H, d), 7.37(2H, d), 7.60(2H, d), 7.70(2H, d), 8.15(2H, d), 8.25(2H, d); *m/z* 528, 527 (M^+), 309, 196, 168, 139, 121; ν_{max} (KCl) 2930, 2860, 1735, 1605, 1505, 1265, 1200, 1165, 1070, 1015, 830, 770 cm^{-1}.

4-Acetyl-4'-methoxybiphenyl (***8***) A solution of acetyl chloride (10.0 g, 0.127

mol) in molecular sieve-dried dichloromethane (20 ml) was added dropwise at room temperature under anhydrous conditions to a stirred mixture of 4-methoxybiphenyl (23.0 g, 0.125 mol) and anhydrous aluminium trichloride (19.0 g, 0.142 mol) in molecular sieve-dried dichloromethane (150 ml). The reaction mixture was heated under reflux for one hour and then poured onto a mixture of ice (200 g) and 36%-hydrochloric acid (50 ml). The organic layer was separated and the aqueous layer was washed with dichloromethane (50 ml). The combined organic layers were washed with water (2 × 50 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was recrystallized from propan-2-ol; yield 20.3 g, 72%; mp 153–154°C; ^{1}Hnmr ($CDCl_3$); δ 2.63(3H, s), 3.87(3H, s), 7.00(2H, d), 7.57(2H, d), 7.65(2H, d), 8.00(2H, d).

4-Acetyl-4′-hydroxybiphenyl (***9***) A mixture of 4-acetyl-4′-methoxybiphenyl (**8**) (10.0 g, 44.2 mmol), 60%-hydrobromic acid (34 ml) and glacial acetic acid (108 ml) was heated under reflux for 6 hours. Water (50 ml) and charcoal were then added to the hot mixture, which was boiled, filtered hot and the filtrate was then allowed to cool. The crude product was filtered off and recrystallized from ethanol-water (1:1); yield 3.8 g, 41%; mp 212°C; ^{1}Hnmr (DMSO) δ 2.53(3H, s), 6.95(2H, d), 7.40(2H, d), 7.55(2H, d), 7.90(2H, d), 9.12(1H, s); ν_{max} (KCl) 3600, 1655, 1600, 1585, 1445, 1300, 1270, 1200, 825 cm^{-1}.

4-Acetyl-4′-octoxybiphenyl (***10***) A mixture of 4-acetyl-4′-hydroxybiphenyl (**9**) (2.60 g, 12.2 mmol), 1-bromooctane (2.83 g, 14.7 mmol), anhydrous potassium carbonate (2.50 g, 18.4 mmol) and molecular sieve-dried butanone (50 ml) was heated under reflux under anhydrous conditions for 48 hours. The solvent was distilled off and the product was poured into water (100 ml). The crude product was extracted into dichloromethane (2 × 100 ml), and the combined extracts were washed with water and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was purified by column chromatography [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 3.7 g, 93%; mp 135–136°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.20–1.60(10H, m), 1.82(2H, m), 2.62(3H, s), 4.00(2H, t), 6.95(2H, d), 7.57(2H, d), 7.65(2H, d), 8.00(2H, d); ν_{max} (KCl) 2960, 2930, 2860, 1680, 1605, 1530, 1365, 1295, 1205, 820 cm^{-1}.

4′-Octoxybiphenyl-4-ylethanoic acid (***F***) (a) A mixture of 4-acetyl-4′-octoxybiphenyl (**10**) (3.60 g, 11.11 mmol), sulphur (0.53 g, 16.66 mmol) and morpholine (5 ml) was heated under reflux for 5 hours. The reaction mixture was cooled and poured into water (100 ml), then the product (4′-octoxybiphenyl-4-acetothiomorpholide) was filtered off, washed with water and dried (*in vacuo*, $CaCl_2$); yield 4.40 g, 93%; mp 105–108°C.

(b) A mixture of the morpholide (4.40 g, 10.35 mmol) and 10%-sodium hydroxide in ethanol (25 ml) was heated under reflux for 10 hours. The solvent was distilled off and the crude product was dissolved in hot water (500 ml) and the solution was filtered. The filtrate was acidified to Congo Red with 36%-hydrochloric acid. The crude acid was extracted into chloroform (2 × 100 ml), and the combined extracts were washed with water (2 × 50 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude acid was recrystallized from chloroform;

yield 1.95 g, 56%; mp 167°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.15–1.55(10H, m), 1.80(2H, m), 3.60(2H, s), 4.00(2H, t), 6.95(2H, d), 7.33(2H, d) 7.50(4H, q); ν_{max} (KCl) 3420, 2960, 2930, 2860, 1700, 1610, 1505, 1295, 1255, 810 cm^{-1}.

Methyl 3-(4'-hydroxybiphenyl-4-yl)propanoate (***11***) Methyl 3-(4'-hydroxybiphenyl-4-yl)acrylate[11] (2.82 g, 11.1 mmol) was dissolved in tetrahydrofuran (100 ml) containing 5% Pd-on-charcoal (400 mg); the mixture was stirred under an atmosphere of hydrogen and the reaction was monitored by using tlc. After hydrogenation was complete, the catalyst was filtered off and the filtrate was evaporated to dryness to give a solid product (the product gave one spot on tlc and was used without further purification). Yield 2.76 g, 97%; mp 133–135°C.

Methyl 3-(4'-octoxybiphenyl-4-yl)propanoate (***12***) A mixture of compound **11** (2.76 g, 10.8 mmol), 1-bromooctane (2.50 g, 13 mmol), anhydrous potassium carbonate (2.20 g, 16.2 mmol) and molecular sieve-dried butanone (50 ml) was heated under reflux under anhydrous conditions for 48 hours. The solvent was distilled off and the product was poured onto water (100 ml). The crude product was filtered off, washed with water and then dried (*in vacuo*, $CaCl_2$). The crude product was purified by column chromatography [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (2:1)]; yield 3.00 g, 76%; mp 108–111°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.20–1.55(10H, m), 1.82(2H, m), 2.68(2H, t), 3.00(2H, t), 3.70(3H, s), 4.00(2H, t), 6.95(2H, d), 7.25(2H, d), 7.50(4H, q); ν_{max} (KCl) 2960, 2930, 2860, 1740, 1610, 1500, 1255, 1160, 1000, 830, 820 cm^{-1}.

3-(4'-Octoxybiphenyl-4-yl)propanoic acid (***G***) A mixture of the methyl ester **12** (3.00 g, 8.15 mmol), potassium hydroxide pellets (3.00 g) and ethanol-water (5:1) (150 ml) was heated under reflux overnight. Ethanol was distilled off and the remaining suspension was dissolved in boiling glacial acetic acid (~500 ml). Ice (~500 g) was added to the solution and the precipitated acid was filtered off, washed with water and dried (*in vacuo*, $CaCl_2$); yield 2.74 g, 95%; mp 198–200°C; ^{1}Hnmr ($CDCl_3$/DMSO) δ 0.90(3H, t), 1.20–1.55(10H, m), 1.80(2H, m), 2.65(2H, t), 2.95(2H, t), 4.00(2H, t), 6.95(2H, d), 7.28(2H, d), 7.48(4H, q); ν_{max} (KCl) 3420, 2960, 2930, 2860, 1700, 1610, 1500, 1255, 830 cm^{-1}.

Benzyl 4-(4'-octoxybiphenyl-4-carbonyloxy)benzoate (***13***) This compound was prepared by following the method described for compound **A4Val**, using 4'-octoxybiphenyl-4-carboxylic acid (**A**) and benzyl 4-hydroxybenzoate; [silica gel; eluting with dichloromethane-light petroleum (bp 60–80°C) (4:1)]; yield 88%; mp 95–99°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.15–1.60(10H, m), 1.83(2H, m), 4.00(2H, t), 5.38(2H, s), 7.00(2H, d), 7.20–7.50(7H, m), 7.57(2H, d), 7.65(2H, d), 8.15(2H, d), 8.20(2H, d); ν_{max} (KCl) 2930, 2860, 1730, 1720, 1605, 1500, 1270, 1165, 1075, 830, 765 cm^{-1}.

4-(4'-Octoxybiphenyl-4-carbonyloxy)benzoic acid (***K***) Compound **13** (14.0 g, 26.1 mmol) was dissolved in ethyl acetate (600 ml) containing 5% Pd-on-charcoal (300 mg); the mixture was stirred overnight under an atmosphere of hydrogen and the reaction was monitored by using tlc. After hydrogenolysis was complete, the acid came out of solution; tetrahydrofuran (500 ml) was added to dissolve the acid

and the catalyst was filtered off and the filtrate was evaporated to dryness to give a solid product (the product gave one spot on tlc and was used without further purification); yield 11.1 g, 96%; mp 205–208°C; ^{1}Hnmr ($CDCl_3$) δ 0.90(3H, t), 1.15–1.60(10H, m), 1.83(2H, m), 3.30(1H, s), 4.05(2H, t), 7.00(2H, d), 7.30(2H, d), 7.63(2H, d), 7.75(2H, d), 8.10(2H, d), 8.23(2H, d); ν_{max} (KCl) 3080, 2920, 2850, 1740, 1690, 1600, 1495, 1430, 1270, 1215, 1195, 1160, 1080, 830, 765 cm^{-1}.

(S)-(−)-*Benzyl lactate* (***3Lac***) Redistilled (*S*)-(+)-lactic acid (18.0 g, 0.200 mol) was dissolved in methanol (360 ml) and water (40 ml) was added. The solution was titrated to pH 7.0 (pH meter or pH paper) with a 20% aqueous solution of caesium carbonate (ca. 160 ml). The solvent was removed under reduced pressure at 50°C and the residue was re-evaporated twice from DMF (2 × 100 ml) at the same temperature. The white solid caesium salt obtained was stirred with benzyl bromide (34.2 g, 0.200 mol) in DMF (300 ml) for 15 h. The caesium bromide was filtered off, the filtrate was concentrated and then ether was added to the residue (150 ml). The organic layer was washed successively with water (100 ml), saturated $NaHCO_3$ (500 ml) and water (100 ml) and finally dried ($MgSO_4$). After removal of the solvent, the residual liquid was distilled under reduced pressure to afford the product as a colorless liquid. Yield 28.8 g, 80%; bp 96°C/0.05 mmHg; $[\alpha]_D^{24}$ = −12.9° ($CHCl_3$).

The subsequent steps were similar to those described for the compounds from the amino-acids and the three final products had the following properties.

(S)-(+)-*1-Cyanoethyl 4'-nonylbiphenyl-4-carboxylate* (***B7Lac***); K 55°C I; $[\alpha]_D^{24}$ = +5.5° ($CHCl_3$).

(S)-(+)-*1-Cyanoethyl 4'-decoxybiphenyl-4-carboxylate* (***L7Lac***); K 98.5°C I; $[\alpha]_D^{24}$ = +6.5° ($CHCl_3$).

(S)-(−)-*1-Cyanoethyl 4-(4'-nonoxybiphenyl-4-carbonyloxy)benzoate* (***M7Lac***); K 121°C (S_C 119°C) S_B 132°C S_A 181°C I; $[\alpha]_D^{24}$ = −2.3°($CHCl_3$).

Physical measurements

Confirmation of the structures of intermediates and products was obtained by ^{1}Hnmr spectroscopy (Jeol JNM-GX270 spectrometer), infra-red spectroscopy (Perkin-Elmer 457 grating spectrometer) and mass spectroscopy (AEI MS902 spectrometer).

Transition temperatures were measured using a Mettler FP5 hot stage and control unit in conjunction with an Olympus BHSP 753 polarizing microscope.

Specific rotations of the optically active compounds were determined using an Optical Activity AA-10 automatic polarimeter.

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11. The preparation of this compound will be reported in a later paper.