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A Comprehensive Approach to (S)-(−)-2-Methyl-1-Butanol as a Convenient Precursor for Synthesis of Chiral Liquid Crystals[1]

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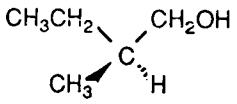
The chemistry of S-(−)-2-methyl-1-butanol leading to chiral liquid crystals (CLC) and their intermediates is summarized and new facile synthetic methods are described. Efficiency of the presented methods is discussed and illustrated with syntheses of several known and new CLC as well as the corresponding chiral intermediates. The newly synthesized chiral compounds display cholesteric and smectic phases.

Keywords: (S)-(−)-2-methyl-1-butanol, (S)-(+)-2-methyl-1-butyl benzenesulfonate, chiral liquid crystals, smectic C

INTRODUCTION

Chiral liquid crystals (CLC) have found numerous practical applications in various fields.[2] Therefore, there has been continuous interest in developing new materials[3] and reliable synthetic methods based on inexpensive reagents.

Historically CLC, and cholesteric liquid crystals in particular, have been associated with cholesterol and other natural steroidal molecules containing chiral centers. However, the cholesteric mesophase is not necessarily attributed to steroidal substances.[4] Introduction of a chiral center into typical nematogens such as Schiff bases[5] or biphenyl derivatives[6] can produce CLC. Branching at the chiral center unfavorably affects the stability of the mesophase and such compounds sometimes do not exhibit liquid crystalline properties. Nevertheless, chiral host additives added to ordinary nematic phases convert them to cholesteric type mesophases.[7] In short, in all CLC the presence of at least one chiral center or another element of dissymmetry[8] in the molecule is required. The nature of the chiral center should distort the linear alignment of the molecules as little as possible. The latter requirement eliminates the vast majority of potential chiral reagents. Among several chiral precursors, (S)-(−)-2-methyl-1-butanol (**1**) remains one of the most accessible and inexpensive reagents[9] used for preparation of various optically active compounds including



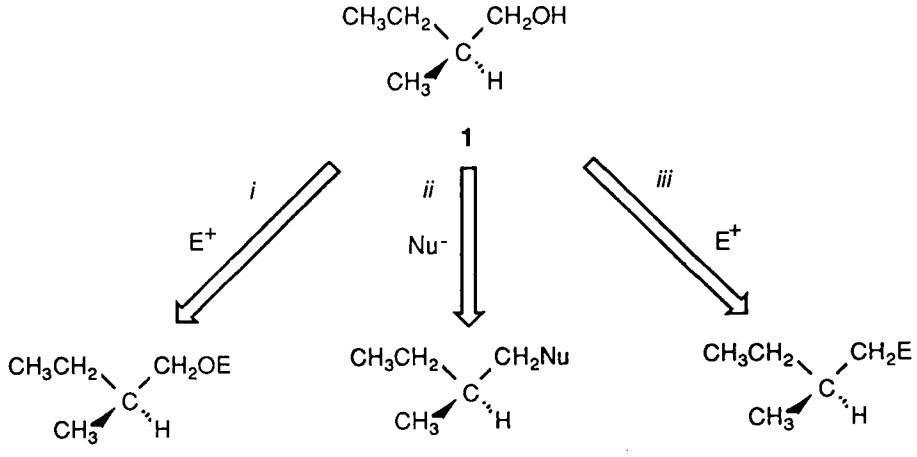
1

CLC. Typically, **1** is converted into an ester or a chiral alkylating agent which is then used for introduction of the chiral center into a molecular framework of ordinary mesogens. In most cases, **1** has been converted to (S)-(+)-1-bromo-2-methylbutane (**2**), but the reported yields of this process are inconsistent, ranging from 29 to 90%.[10] The product is relatively unstable and undergoes rearrangement and racemization.[10a] Much better results for alkylation reactions are obtained with (S)-2-methyl-1-butyl alkane/arenesulfonates[11], which are available in almost qualitative yield from **1**.

Most of the known synthetic applications of **1** have been reported either in the patent literature or in journals where details have not been provided. In this paper we systematize the approach to the chemistry of (S)-(−)-2-methyl-1-butanol and illustrate the potential of this underexploited CLC precursor.

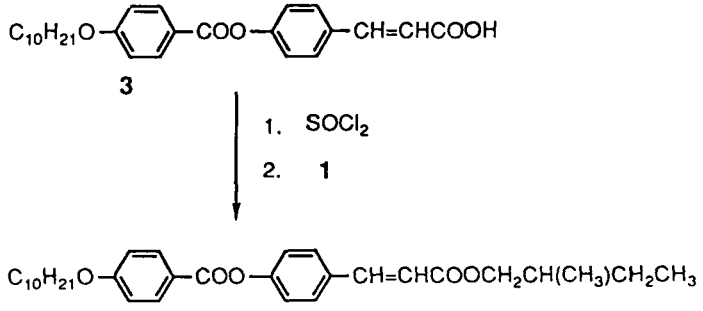
RESULTS AND DISCUSSION

(S)-(−)-2-Methyl-1-butanol (1) possesses two easily functionalizible sites which can be utilized in three different fashions: (*i*) the nucleophilic oxygen, which can react with electrophilic reagents to form chiral esters or ethers, and the C1-carbon which can act either as (*ii*) an electrophile or as (*iii*) a nucleophile depending on the attached substituent (Scheme 1). All three processes are very important for preparation of CLC and their intermediates. Schemes 2–10 show the applicability of the above general scheme illustrated by our results.



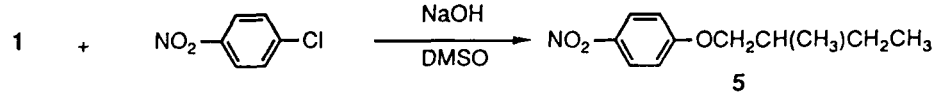
Scheme 1

Route *i* in Scheme 1 encompasses numerous examples of rather routine esterification reactions described previously in the literature.[12] One of the most important representatives from this group is the first ferroelectric liquid crystal DOBAMBC.[13] Since DOBAMBC shows several disadvantages such as low stability and a yellowish color typical of Schiff bases, we decided to synthesize a colorless carboxy analog of DOBAMBC **4** (Scheme 2). The compound is a low temperature monotropic smectic C. The mesogenic properties of **4** will be shown later in Table II.



Scheme 2

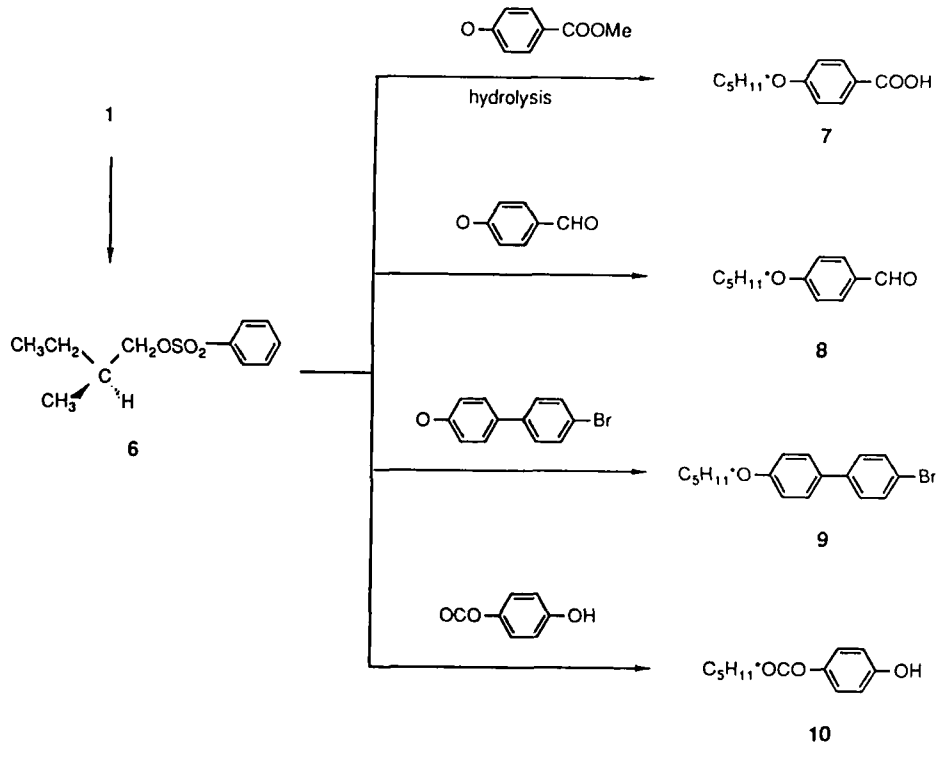
The nucleophilic oxygen in **1** can also be employed in etherification reactions involving conversion of the alcohol to its alkoxide. The latter can be conveniently generated *in situ* in DMSO in the presence of powdered NaOH. Thus, reaction between **1** and 4-chloronitrobenzene carried out under these conditions gives (S)-(+)-4-(2-methyl-1-butoxy)nitrobenzene (**5**) in an 87% yield (Scheme 3). Reduction of **5** yields (S)-(+)-4-(2-methyl-1-butoxy)aniline,[14] a chiral intermediate for Schiff bases, azo and azoxy compounds.[15]



Scheme 3

Route *ii* (Scheme 1) involves reactions between various nucleophilic reagents with derivatives of **1** in which substituents at C-1 affect the electrophilicity of the carbon. As mentioned earlier, the alcohol can be converted almost quantitatively into the corresponding sulfonate esters and these can be used as alkylating reagents. Due to the considerably lower cost of pure benzenesulfonyl chloride relative to *p*-toluenesulfonyl chloride, we have employed (S)-(+)-2-methyl-1-butyl benzenesulfonate (**6**) as the alkylating agent of choice. As an additional bonus, its preparation is extremely simple and the product can be used without further purification.

Scheme 4 shows several 0-alkylation reactions using sulfonate **6** leading to the chiral intermediate ethers **7**, **8** and **9** as well as ester **10**. Compounds **7**[16] and **8**[5c]



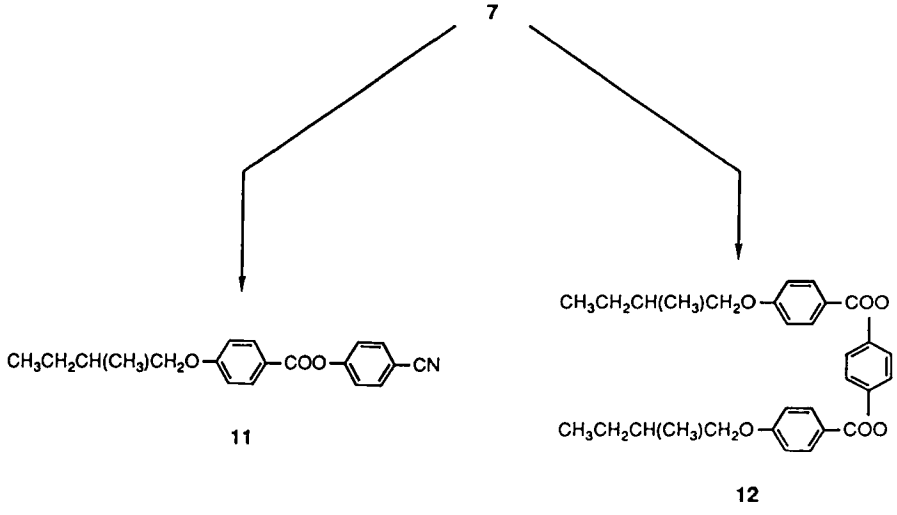
Scheme 4

have been previously synthesized from the corresponding phenolate and bromide **2** with moderate overall yields. The substitution of sulfonate **6** for **2** provides a simpler and more reliable procedure for preparation of these compounds in high yields. This method can also be applied for synthesizing esters under nonacidic conditions.

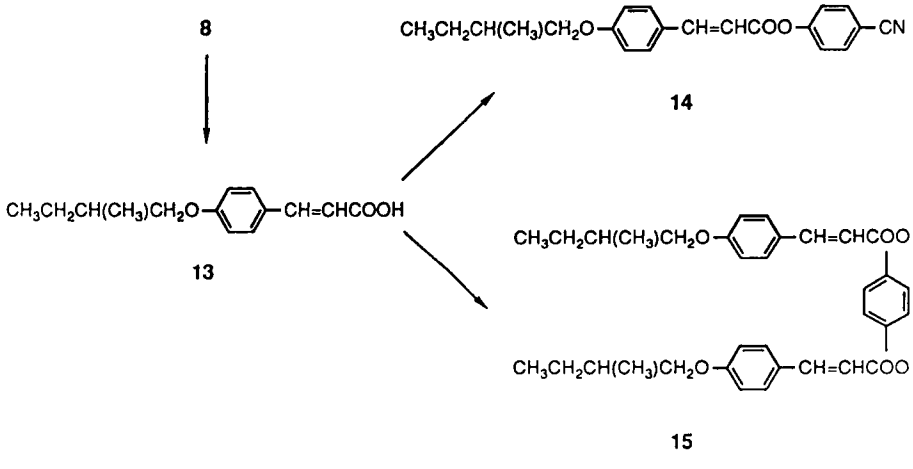
Each of the products in Scheme 4 bears a functional group (carboxyl, aldehyde, bromo and hydroxyl) which was subsequently utilized for synthesis of various chiral products. For example, (S)-(+)-4-(2-methyl-1-butoxy)benzoic acid (**7**) was used for preparation of previously known esters **11**[16] and **12**[17] (Scheme 5).

(S)-(+)-4-(2-Methyl-1-butoxy)benzaldehyde (**8**) was converted by the Knoevenagel-Doebner method[18] to (S)-(+)-4-(2-methyl-1-butoxy)cinnamic acid (**13**) (Scheme 6).

This acid is a new compound with a cholesteric mesophase: K 138.5 CH 146.5 I. Its acid chloride in reaction with *p*-cyanophenol and with hydroquinone gave the respective esters **14** and **15**. As expected, the introduction of a —CH=CH— linking group between the benzene ring and the carbonyl group in **13**, **14** and **15** increases thermal stability of the mesophase. Although the parent acid **7** and ester **11** are isotropic[16a] their cinnamic analogs **13** and **14** show a cholesteric phase. Both esters **12** and **15** are cholesteric liquid crystals, however, the mesophase in **15** is shifted toward the higher temperature range and is wider by 45°C than in **12** (Table I).



Scheme 5



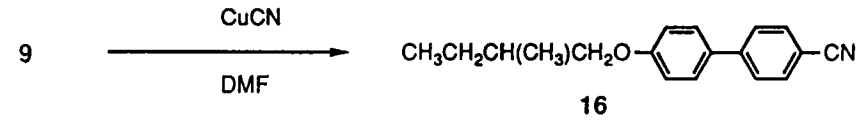
Scheme 6

TABLE I

compound	*K*	*Ch*	*I*
12	127	161[a]	
13	138.5	146.5	
14	79	93.5	
15	162	241	

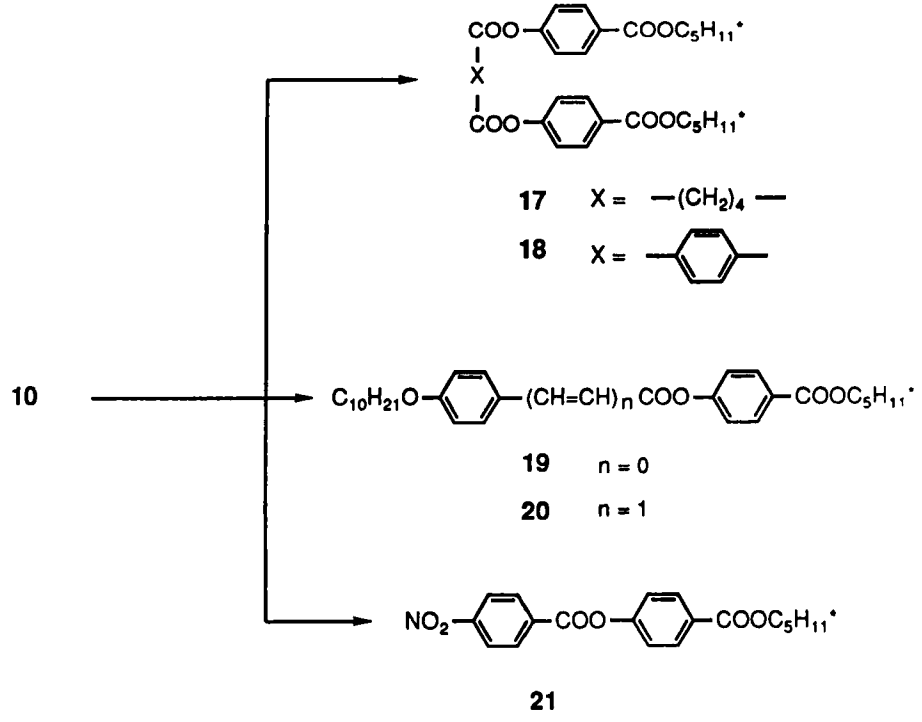
[a]Lit.[17] *K* 122 *Ch* 164 I

The bromobiphenyl **9** is also a new compound which can serve as a starting material for formation of a new C—C bond using various coupling techniques.[19] We converted it to cyanobiphenyl **16** (Scheme 7) in 50% overall yield based on **1**. Compound **16** was previously obtained by a related reaction of toluenesulfonate of **1** and 4-cyano-4′-hydroxybiphenyl in only 18% overall yield.[20]



Scheme 7

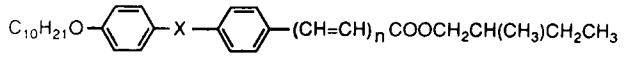
Hydroxyester **10** reacts with appropriate acid chlorides to form esters **17**, **18**, **19**, **20** and **21** (Scheme 8). Compound **17** is not a liquid crystal though it might serve as a nematogen-like chiral additive. Ester **18** is a known[21] CLC displaying smectic and cholesteric phases as well as a short range "blue phase" upon cooling from the isotropic liquid.



Scheme 8

Recently synthesized compounds **19**,[22] **20**[23] and the previously mentioned **4** formally belong to the important big family of colorless, stable DOBAMBC analogs. These and related esters are currently gaining a lot of attention[22–25] due to com-

TABLE II[a]



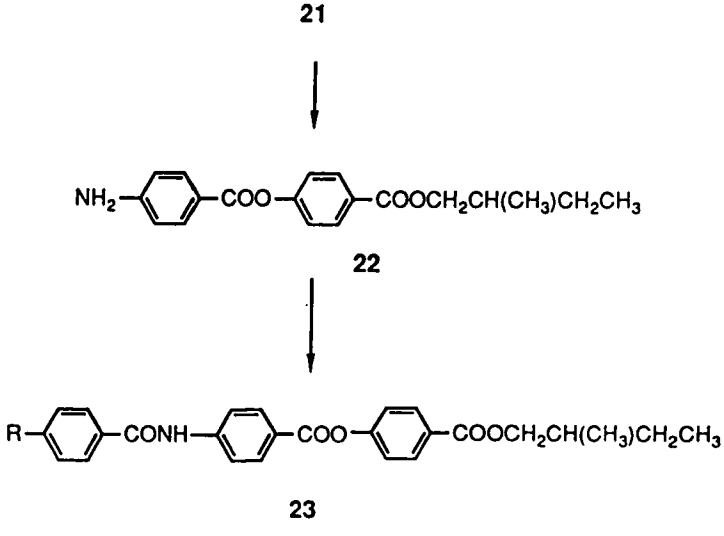
compound	X	n	K	S_C	S_A	I
4	COO	1	52	(45)		94[b]
19	COO	0	49	(36)		59[c]
20	CH=CHCOO	0	59	69		96[d]
DOBAMBC	CH=N	1	76	92		117[c]

[a]Smectic phases were identified based on microphotographs in G. W. Gray and J. W. G. Goodby *Smectic Liquid Crystal Tetures and Structures* (Leonard Hill, London, 1984); and D. Demus and L. Richter, *Textures of Liquid Crystals* (VEB, Leipzig, 1980); [b]lit.[26] *K* 52 S_C (44.5) S_A 92.5 *I*; [c]lit.[22] *K* 52 S_C (35) S_A 59.5 *I*; [d]lit.[23] *K* 60.2 S_C 71.1 S_A 95.2 *I*; [e]Reference[13].

monly appearing low temperature chiral S_C phases and potential applications in electrooptical fast switching devices. Mesogenic properties of esters **4**, **19**, and **20** are summarized in Table II.

According to data in Table II, it appears that all investigated compound display a chiral smectic C phase. The "carboxy" analog of DOBAMBC **4** is a low temperature monotropic smectic C, while its regioisomer **20** is an enantiotropic smectic C.

The nitro ester **21** can be reduced to the corresponding chiral amine **22**, another potentially useful starting point for the introduction of common linking groups such as azomethine, azo, and azoxy. Using this amine, we prepared three new chiral



Scheme 9

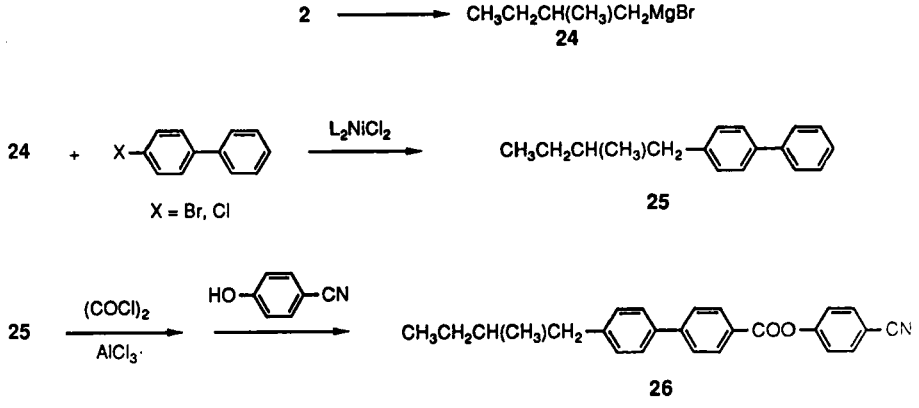
TABLE III

compound	*R*	*K*	*S*	*Ch*	*I*
23a	Br	215			(213)
23b	MeO	188	202		229
23c	*n*-PrO	186	236		

amides **23** (Scheme 9) which display relatively high temperature cholesteric and smectic mesophases (Table III).

(S)-(+)-2-Methyl-1-butyl arenesulfonate can also be used for synthesis of (S)-(+)-1-bromo-2-methylbutane[11a] (**2**) which is quite indispensible in some reactions. Although the direct bromination of **1** with PBr_3 appears to be a simple one step process, the two step route from **1** to **2** via **6** is more efficient and reliable. Thus, sulfonate **6** cleanly reacts with lithium bromide in acetone to give pure chiral bromide **2** in 70% overall yield.

Route *iii* in Scheme 1 is based on the reactions of organometallic reagents derived from **1** with electrophiles. A common goal in the synthesis of CLC via this route is the direct attachment of the (S)-2-methyl-1-butyl group to the aromatic system. Kumada *et al.* have described a cross-coupling reaction of alkylmagnesium reagents with aryl halides in the presence of nickel-phosphine complexes leading to alkylarenes with good yields.[19a] Under these conditions, the bromide **2** is converted to its Grignard reagent **24** and reacted with either 4-bromo- or 4-chlorobiphenyl, giving (S)-(+)-4-(2-methyl-1-butyl)biphenyl **25** in 55% and 86%, respectively (Scheme 10). This method is more reliable than the method reported by Gray.[27]



Scheme 10

Hydrocarbon **25** has been chlorocarbonylated according to the standard procedure[28] and the crude acyl chloride subsequently reacted with *p*-cyanophenol to give **26**[27] in 50% yield.

CONCLUSION

This paper has comprehensively described the use of (S)-(−)-2-methyl-1-butanol (**1**) in synthesis of chiral liquid crystals (CLC). **1** is an inexpensive source of chiral carbon which can be efficiently converted into several important building blocks such as **5**, **7**, **8**, **9**, **10**, **22**, and **25** which are applicable for further exploration of CLC. Using these precursors, we synthesized two new series of liquid crystls: (**i**) cinnamic acid **13** and its two derivatives **14** and **15**, which possess cholesteric mesophases; (**ii**) chiral amides **23**, which display a cholesteric phase (**23a**), smectic phase (**23c**) or both (**23b**). We also synthesized a new DOBAMBC analog **4**, which shows a monotropic chiral S_C phase. The presented methods could also be extended to other chiral alcohols used in syntheses of CLC.

EXPERIMENTAL

Melting points were determined by Boetius PHMK05 apparatus with a microscope attachment. ^{1}H NMR spectra were recorded at 90MHz on a Varian EM-390 spectrometer (ppm, in $CHCl_3$, Me_4Si as a reference). IR spectra were obtained in $CHCl_3$ on a FTIR Nicolet 7000 series instrument. Specific rotations were determined in $CHCl_3$ solutions, with Perkin-Elmer 241 MC Polarimeter. (S)-(−)-2-Methyl-1-butanol **1** ($[\alpha]_D^{25} = -5.84$, neat was obtained from Aldrich. Mass spectra data were obtained with a Hewlett-Packard 5985B GCMS instrument by electron impact or chemical ionization techniques. The values in parentheses represent the relative intensities of the major fragments.

4-(4-Decyloxybenzoyloxy)cinnamic acid 3. 4-(4-Decyloxybenzoyloxy) benzaldehyde[29] (2.0 g, 5.2 mmol) and malonic acid (1.0 g, 9.6 mmol) were refluxed in 20 ml of pyridine containing a catalytical amount of piperidine. After 1 h the reaction mixture was cooled down and poured into a mixture of ice and hydrochloric acid. Crude acid was filtered off and after three recrystallizations from ethyl acetate gave 1.5 g (68% yield) of **3**: *K* 151 *N* 246 *I*; ^{1}H NMR (acetone-d_6) δ 8.11 (*d*, *J* = 9 Hz, 2H), 7.77 (*d*, *J* = 9 Hz, 2H), 7.69 (*d*, *J* = 16 Hz, 1H), 7.33 (*d*, *J* = 9 Hz, 2H), 7.09 (*d*, *J* = 9 Hz, 2H), 6.52 (*d*, *J* = 16 Hz, 1H), 4.12 (*t*, *J* = 7 Hz, 2H), 1.95–0.86 (*m*, with maximum at 1.28, 19H); EIMS, m/z 424 (M^+, 3), 262(74), 261(100), 138(30), 122(30), 121(74), 120(32); HRMS, m/z (calcd for $C_{26}H_{32}O_5$: 424.2250) 424.2261; Anal. Calcd for $C_{26}H_{32}O_5$: *C*, 73.56; *H*, 7.60. Found: *C*, 73.53; *H*, 7.60.

(S)-(+)-2-Methyl-1-butyl 4-(4-decyloxybenzoyloxy)cinnamate 4. Acid **3** (1.0 g, 2.4 mmol) was refluxed with thionyl chloride (5 ml) for 1 h. Excess $SOCl_2$ was then evaporated and the crude oily acid chloride was added to a solution of **1** (0.5 ml) in chloroform (5 ml). The mixture was refluxed for 2 h, the solvent was evaporated and the crude product was purified on silica gel (hexanes eluent). After low-temperature recrystallization from heptane 0.8 g (68% yield) of white crystals were obtained: *K* 52 S_C (45) S_A 94 *I*, (lit.[25] *K* 52 S_C (44.5) S_A 92.5 *I*); $[\alpha]_D^{25} = +2.3$ (2.4); ^{1}H NMR δ 8.13 (*d*, *J* = 9 Hz, 2H), 7.71 (*d*, *J* = 16 Hz, 1H), 7.59 (*d*, *J* =

9 Hz, 2H), 7.24 (*d*, *J* = 9 Hz, 2H), 6.97 (*d*, *J* = 9 Hz, 2H), 6.43 (*d*, *J* = 16 Hz, 1H), 4.15–4.00 (*m*, 4H), 1.95–0.85 (*m*, with maxima at 1.28 and 0.97, 28H); IR 2929, 1731, 1707, 1639, 1604, 1511, 1315, 1069 cm^{-1}; EIMS, m/z 494(M^+, 2), 262(68), 261(100), 121(63); HRMS, m/z (calcd for: $C_{31}H_{42}O_5$: 494.3032) 494.3034; Anal. Calcd for $C_{31}H_{42}O_5$: *C*, 75.27; *H*, 8.56. Found: *C*, 75.21; *H*, 8.57.

(S)-(+)-4-(2-Methyl-1-butoxy)nitrobenzene 5. A warm solution of 4-chloronitrobenzene (15.7 g, 0.10 mol) and (S)-(−)-2-methyl-1-butanol (10.6 g, 0.12 mol) in DMSO (20 ml) was added at once to a vigorously stirred suspension of powdered sodium hydroxide (5.0 g, 0.125 mol) in DMSO (10 ml) at 60°C. After 3 h of stirring at 60°C and 10 min at 70°C, the reaction mixture was cooled and poured into water (100 ml). The crude product was extracted with methylene chloride (3x); the combined organic extracts were dried over magnesium sulfate and after evaporation of the solvent the yellow residue was vacuum distilled (121–122°C/0.45 mm Hg) to give 18.0 g (86% yield) of **5**: $[\alpha]_D^{25}$ = +13.3 (14.5), (lit.[30] $[\alpha]^{25}$ = +2.327); ^1H NMR δ 8.18 (*d*, *J* = 9 Hz, 2H), 6.94 (*d*, *J* = 9 Hz, 2H), 3.90 (*d*, *J* = 3 Hz, 1H), 3.8 (*d*, *J* = 3 Hz, 1H), 1.99 – 0.95 (*m* with maximum at 1.10, 1.05 and 0.96, 9H); IR (neat) 2963, 1607, 1594, 1514, 1340, 1262, 1111, 845, 752, 654 cm^{-1}; EIMS, m/z 209 (M^+, 5), 140(9), 139(10), 109(100), 71(29), 70(28), 55(22); HRMS, m/z (calcd for $C_{11}H_{15}NO_3$: 209.1052) 209.1056. The optically active alcohol **1** may be recovered during fractional distillation as the first low boiling fraction.

(S)-(+)-2-Methyl-1-butyl benzenesulfonate 6. To a mixture of pyridine (16 ml) and (S)-(−)-2-methyl-1-butanol (10.6 ml, 0.1 mol) cooled in an ice bath, benzenesulfonyl chloride (14.0 ml, 0.11 mol), was added at such a rate that the temperature did not exceed +5°C. The mixture was stirred for an additional 1 h and poured on ice (200 g) and concentrated hydrochloric acid (1:1). The product was extracted twice with chloroform. The combined extracts were dried over Na_2SO_4 and evaporated to yield 23–24.5 g of colorless or yellowish oil which was used in further reactions. GLC showed about a 96% purity of this material: $[\alpha]_D^{22}$ + 4.05 (neat); ^1H NMR δ 7.91 (*d*, *J* = 9 Hz, 2H), 7.66–7.54 (*m*, 3H), 3.89 (*d*, *J* = 3 Hz, 1H), 3.85 (*d*, *J* = 3 Hz, 1H), 1.96–0.85 (*m*, 9H); IR 1590, 1470, 1458, 1370, 1200, and 765 cm^{-1}; EIMS, m/z 143(9), 142(10), 141(32), 78(17), 77(67), 70(100) 57(15).

(S)-(+)-1-Bromo-2-methylbutane 2. Crude **6**, prepared from 0.1 mol of **1**, lithium bromide (45 g, 0.5 mol) and acetone (50 ml) were stirred overnight at room temperature. When GC showed no starting material, the reaction mixture was poured into water (200 ml) and the crude bromide was extracted with pentane (3x). The combined pentane extracts were dried over magnesium sulfate, the solvent was evaporated and the residue was distilled under reduced pressure (40–41°C/40 mm Hg; lit.[10d] 38°C/39 mm Hg) to give 10.5 g (70% yield) of pure product: $[\alpha]_D^{22}$ = +4.00 (neat), (lit.[10c] $[\alpha]_D^{25}$ = +4.05). Distillation under atmospheric pressure causes rearrangement of the bromide and loss of its optical purity.

(S)-(+)-4-(2-Methyl-1-butoxy)benzoic acid 7. Methyl 4-hydroxybenzoate (15.2 g, 0.1 mol), crude **6** (prepared from 0.1 mol of **1**), and anhydrous potassium carbonate (20.0 g) were refluxed for 6 h in acetone (20 ml). After cooling, the inorganic salts were filtered off and washed with acetone (3x). The acetone was

evaporated from the filtrate to yield a yellowish oil. The oil was dissolved in methanol (60 ml) then combined with sodium hydroxide (8.0 g, 0.2 mol) in methanol (50 ml) and the mixture was refluxed for 40 min. The methanol was evaporated, the residue was dissolved in a small amount of water and extracted with ether. The aqueous solution was acidified with concentrated HCl and the crude acid **7** was filtered off. Recrystallization of the crude product from hexane-benzene and then from water-ethanol gave 9.4 g (45% yield) of pure **7** as colorless crystals: mp 114–115°C; $[\alpha]_D^{22} = +9.9$ (3.60); (lit.[16] mp. 116–118°C, $[\alpha]_D^{33} = +6.4$); ^{1}H NMR δ 7.94 (*d*, *J* = 9 Hz, 2H), 6.93 (*d*, *J* = 9 Hz, 2H), 3.91 (*d*, *J* = 3 Hz, 1H), 3.84 (*d*, *J* = 3 Hz, 1H), 1.98–0.96 (*m* with maxima at 1.12, 1.06 and 0.99, 9H).

(S)-(+)-4-(2-Methyl-1-butoxy)benzaldehyde 8. 4-Hydroxybenzaldehyde (15.0 g, 0.123 mol), crude **6** (prepared from 0.1 mol of **1**), and anhydrous potassium carbonate (24.0 g, 0.174 mol) were refluxed for 4 h in acetonitrile (60 ml) until GC analysis showed the complete conversion of **6**. The mixture was diluted with water and the product was extracted (3x) with chloroform. The extract was dried over magnesium sulfate. Vacuum distillation of the dark oil left after evaporation of the solvent yielded 13.6 g (71% yield) of a colorless fraction collected at 110–112°C/0.6 mm Hg: $[\alpha]_D^{22} = +10.6$ (11.3), (lit.[5c] bp 113–115°C/0.09 mm Hg, $[\alpha]_D^{22} = +5.13$); ^{1}H NMR δ 9.92 (*s*, 1H), 7.89 (*d*, *J* = 9 Hz, 2H), 6.95 (*d*, *J* = 9 Hz, 2H), 3.92 (*d*, *J* = 3 Hz, 1H), 3.85 (*d*, *J* = 3 Hz, 1H), 1.99–0.95 (*m* with maxima at 1.13, 1.03, and 1.00, 9H).

(S)-(+)-4-Bromo-4'-(2-methyl-1-butoxy)biphenyl 9. 4-Bromo-4'-hyroxybiphenyl (25.0 g, 0.1 mol) in DMSO (75 ml) was added to a suspension of powdered sodium hydroxide (4.0 g, 0.1 mol) in DMSO (15 ml). After stirring for a short time the warm mixture turned homogeneous. Crude **6** (prepared from 0.1 mol of **1**) was added in such a manner that the reaction temperature did not exceed 90°C and then the mixture was maintained for additional 45 min at 90°C. The hot mixture was poured into 300 ml of cold water; the solidified product was filtered off and dried. Two recrystallizations from ethanol yielded 24.2 g (76% yield) of white crystals of the product: mp. 128–129°C; $[\alpha]_D^{22} = +7.5$ (4.2); ^{1}H NMR δ 7.59–7.35 (*m* with maxima at 7.52, 7.51, 7.47, 7.44, and 7.42, 6H), 6.96 (*d*, *J* = 9 Hz, 2H), 3.88 (*d*, *J* = 3 Hz, 1H), 3.79 (*d*, *J* = 3 Hz, 1H), 1.98–0.96 (*m* with maxima at 1.13, 1.03, and 0.98, 9H); IR 1603, 1518, 1484, 1391, 1043, 1011, 1000, 927 cm^{-1}; EIMS, m/z 318 and 320 (M^+, 19), 250(87) and 248(100); Anal. Calcd for $C_{17}H_{19}BrO$; *C*, 63.96; *H*, 6.00; Found: *C*, 63.99; *H*, 5.97.

(S)-(+)-2-Methyl-1-butyl 4-hydroxybenzoate 10. To a stirred suspension of powdered sodium hydroxide (4.2 g, 0.105 mol) in DMSO (10 ml) was added a warm solution of 4-hydroxybenzoic acid (15.2, 0.11 mol) in DMSO (80 ml). To the resulting homogeneous solution of the sodium salt was added crude **6** (prepared from 0.1 mol of **1**) and the reaction mixture was maintained for 4.5 h at 80–90°C. The mixture was poured in 500 ml of cold water and the organic product was extracted with chloroform (3x). The extract was dried with magnesium sulfate, the solvent was evaporated and the residue was distilled under vacuum at 152–154°C/0.4 mm Hg (lit.[31] 170°C/0.6mm Hg) to give 11.2 g (54% yield) of colorless oil:

$[\alpha]_D^{22}$ = +6.3 (7.8), (lit.[21] $[\alpha]_D^{25}$ = +6.3, lit.[31] $[\alpha]_D^{25}$ = +5.5, *c* = 0.03); ^{1}H NMR δ 7.95 (*d*, *J* = 9 Hz, 2H), 6.93 (*d*, *J* = 9 Hz, 2H), 4.19 (*d*, *J* = 3 Hz, 1H), 4.12 (*d*, *J* = 3 Hz, 1H), 1.98–0.90 (*m*, with maxima at 1.09, 1.02, and 0.92, 9H), IR 3300, 1705, 1610, 1514, 1275, 1160, 1115, and 1042, cm^{-1}; EIMS, m/z 208(M^+, 3.5), 139(20), 138(57), 121(100). Since the ester shows slight decomposition during vacuum distillation it can be used in reactions with acid chlorides without distillation.

(S)-(+)-4-[4-(2-Methyl-1-butoxy)benzoyloxy]benzonitrile 11. Acid **7** (4.2 g, 20 mmol) as refluxed for 1 h with thionyl chloride (10 ml). Excess $SOCl_2$ was evaporated and the crude acid chloride was added to a solution of *p*-cyanophenol (2.6 g, 22 mmol) in chloroform (20 ml) containing pyridine (5 ml). The mixture was refluxed for 3 h, cooled down and poured into diluted hydrochloric acid. The organic phase was separated, dried over magnesium sulfate and the solvent was evaporated. The crude product was twice recrystallized from ethanol to give 4.9 (80% yield) of the product: mp 89°C; $[\alpha]_D^{22}$ = +8.4 (7.36), (lit.[16a] mp. 88–88.5°C, $[\alpha]_D^{22}$ = +6.4); ^{1}H NMR δ 8.12 (*d*, *J* = 8 Hz, 2H), 7.72 (*d*, *J* = 9 Hz, 2H), 7.35 (*d*, *J* = 9 Hz, 2H), 6.98 (*d*, *J* = 9 Hz, 2H), 3.91 (*d*, *J* = 3 Hz, 1H), 3.84 (*d*, *J* = 3 Hz, 1H), 1.98–0.96 (*m* with maxima at 1.13, 1.06 and 1.00, 9H); IR 2233, 1736, 1603, 1512, 1260, 1165, 1062, and 847 cm^{-1}; EIMS, m/z 309(M^+, 1), 191(M^+-OC6H4CN, 100), 121(98). Anal. Calcd for-$C_{19}H_{19}NO_3$: *C*, 73.76; *H*, 6.19; *N*, 4.53. Found: *C*, 73.43; *H*, 6.29; *N*, 4.55.

(S,S)-(+)-1,4-Bis[4-(2-methyl-1-butoxy)benzoyloxy]benzene 12. Crude acid chloride of **7** was reacted with hydroquinone as described above. Crystallization of the crude product from ethanol gave 78% yield of the pure product: *K* 127 *Ch* 161 *I*; $[\alpha]_D^{25}$ = +10.6 (0.7), (lit.[17] *K* 122 *Ch* 164 *I*; $[\alpha]_D^{25}$ = +7.53, *c* = 0.3); ^{1}H NMR δ 8.15 (*d*, *J* = 9 Hz, 4H), 7.25 (*s*, 4H), 6.95 (*d*, *J* = 9 Hz, 4H), 3.92 (*d*, *J* = 3 Hz, 2H), 3.85 (*d*, *J* = 3 Hz, 2H), 1.98–0.95 (*m*, with maxima at 1.13, 1.05 and 0.99, 18H); IR 1731, 1606, 1512, 1182, 1074 cm^{-1}; EIMS, m/z 490(M^+, 24), 192(64), 191(100), 122(40), 121(77), 93(32).

(S)-(+)-4-(2-Methyl-1-butoxy)cinnamic acid 13. The aldehyde **8** (9.6 g, 0.05 mol), malonic acid (6.25 g, 0.06 mol), pyridine (10 ml) and piperidine (0.4 ml) were refluxed for 1 h. The reaction mixture was cooled down and poured into mixture of ice and hydrochloric acid. The crude product was filtered off and recrystallized from aqueous methanol to give 8.7 g (74% yield) of pure **13**: *K* 138.5 *Ch* 146.5 *I*; $[\alpha]_D^{22}$ = +16.2 (6.8); ^{1}H NMR δ 7.76 (*d*, *J* = 16 Hz, 1H), 7.50 (*d*, *J* = 9 Hz, 2H), 6.90 (*d*, *J* = 9 Hz, 2H), 6.30 (*d*, *J* = 16 Hz, 1H), 3.86 (*d*, *J* = 3 Hz, 1H), 3.78 (*d*, *J* = 3 Hz, 1H), 2.0–0.94 (*m* with maxima at 1.06, 1.01, and 0.98, 9H); IR 1687, 1604, 1512, 1259, 1172, 1046, 985, 877, and 831 cm^{-1}; EIMS, m/z 234(M^+, 18), 164(100); Anal. Calcd for $C_{14}H_{18}O_3$: *C*, 71.77; *H*, 7.74. Found: *C*, 71.90; *H*, 7.61.

(S)-(+)-4-[4-(2-Methyl-1-butoxy)cinnamoyloxy]benzonitrile 14. The cinnamic acid **13** (4.68 g, 20 mmol) was refluxed for 1 h with thionyl chloride (10 ml). Excess $SOCl_2$ was removed under vacuum, then the crude acid chloride was combined with *p*-cyanophenol (2.38 g, 20 mmol) and refluxed in chloroform (25 ml) for 40

min. At this point pyridine (1 ml) was added and the reaction mixture was left at reflux for additional 2 h. Evaporation of chloroform left crude cyanoester **14** which was decolorized with charcoal in methanol. Two recrystallizations from hexane-benzene gave 4.30 g (64% yield) of the product: *K* 79 *Ch* 93.5 *I*; $[\alpha]_D^{22}$ = +9.4 (4.5); ^{1}H NMR δ 7.83 (*d*, *J* = 16 Hz, 1H), 7.73 (*d*, *J* = 9 Hz, 2H), 7.54 (*d*, *J* = 9 Hz, 2H), 7.31 (*d*, *J* = 9 Hz, 2H), 6.96 (*d*, *J* = 9 Hz, 2H), 6.79 (*d*, *J* = 16 Hz), 1H), 3.88 (*d*, *J* = 3 Hz, 1H), 3.79 (*d*, *J* = 3 Hz, 2H), 1.95–0.94 (*m* with maxima at 1.06, 1.01, and 0.98, 9H); IR 2233, 1734, 1632, 1603, 1512, 1505, 1115, and 926 cm^{-1}; EIMS, m/z 335(M^+, 6), 217(M^+-OC_6H_4CN, 100), 147(66), 119(18), 118(14); HRMS, m/z (calcd for $C_{21}H_{21}NO_3$: 335.1521) 335.1514; Anal. Calcd for $C_{21}H_{21}NO_3$: *C*, 75.20; *H*, 6.31; *N*, 4.18. Found: *C*, 75.41; *H*, 6.25; *N*, 4.46.

(*S*,*S*)-(+)-*1,4-Bis*[*4-(2-methyl-1-butoxy)cinnamoyloxy*]*benzene 15.* Crude acid chloride of **13** was reacted with hydroquinone as described above. Two recrystallizations from acetone yielded 80% yield of colorless crystals: *K* 162 *Ch* 241 *I*; $[\alpha]_D^{22}$ = +11.9 (3.5); ^{1}H NMR δ 7.91 (*d*, *J* = 16 Hz, 2H), 7.60 (*d*, *J* = 9 Hz, 4H), 7.23 (*s*, 4H), 6.97 (*d*, *J* = 9 Hz 4H), 6.51 (*d*, *J* = 16 Hz, 2H), 3.92 (*d*, *J* = 3 Hz, 2H), 3.84 (*d*, *J* = 3 Hz, 2H), 1.98–0.93 (*m* with maxima at 1.12, 1.06, and 1.02, 18H); IR 1730, 1603, 1513, 1501, 1289, 1170, 1132, 1045, and 927 cm^{-1}; EIMS, m/z 542(M^+, 9) 219(25), 218(63), 217(100), 147(74), 119(49), 91(37); Anal. Calcd for $C_{34}H_{38}O_6$: *C*, 75.25; *H*, 7.06. Found: *C*, 74.98; *H*, 7.01.

(*S*)-(+)-*4-Cyano-4'-(2-methyl-1-butoxy)biphenyl 16.* Compound **16** was prepared from the bromo derivative **9** by heating it with CuCN in DMF.[32] A short path vacuum distillation (170°C/0.4 mm Hg) followed by recrystallization from ethanol gave 66% of white crystals: mp 53.5°C, $[\alpha]_D^{22}$ = +11.4 (7.60); (lit.[6b,20] 53.5°C, $[\alpha]_D^{20}$ = +10); ^{1}H NMR δ 7.66 (*s*, 4H), 7.54 (*d*, *J* = 9 Hz, 2H), 7.00 (*d*, *J* = 9 Hz, 2H), 3.88 (*d*, *J* = 3 Hz, 1H), 3.81 (*d*, *J* = 3 Hz, 1H), 1.95–0.95 (*m* with maxima at 1.09, 1.00, and 0.93, 9H); IR 2229, 1606, 1525, 1495, 1180, 1040 and 926 cm^{-1}; EIMS, m/z 265(M^+, 14), 196(16), 195(100).

(*S*,*S*)-(+)-*Bis*[*4-(2-methyl-1-butoxycarbonyl)phenyl*] *adipiate 17.* Crude hydroxyester **10** (obtained from 0.05 mol of **6**) was combined with adipoyl chloride (3.7 g, 20 mmol) and refluxed for 4 h in chloroform. At this point pyridine (5 ml) was added and the reflux was continued for 1 h and the reaction mixture was poured into dilute hydrochloric acid. The organic phase was separated, dried over magnesium sulfate and the resulting oil was passed through a short silica gel column. The eluent was concentrated and the residue was crystallized twice from methanol to give 2.0 g (15% yield) of pure **17**: mp 45°C; $[\alpha]_D^{22}$ = +4.5 (1.25); ^{1}H NMR δ 8.08 (*d*, *J* = 9 Hz, 4H), 7.16 (*d*, *J* = 9 Hz, 4H), 4.21 (*d*, *J* = 3 Hz, 2H), 4.14 (*d*, *J* = 3 Hz, 2H), 2.83–2.49 (*m*, 4H), 2.02–0.83 (*m*, with maxima at 1.93, 1.09, and 0.99, 22H); IR 1757, 1714, 1605, 1279, 1162, 1114, 1046, and 877 cm^{-1}; CIMS, m/z 527(MH^+, 13), 440(13), 439(47), 319(28), 209(57), 167(19), 139(100), 121(33), 111(67); Anal. Calcd for $C_{30}H_{38}O_8$: *C*, 68,42; *H*, 7.27; Found: *C*, 68.33; *H*, 7.30.

(*S*,*S*)-(+)-*Bis*[*4-(2-methyl-1-butoxycarbonyl)phenyl*]-*terephthalate 18.* The procedure, identical to that described above for **17**, furnished compound **18** in 10% yield after two recrystallizations from isopropanol: *K* 137 *S* 150 *Ch* 162 *I*; $[\alpha]_D^{22}$ =

+4.3 (1.2), (lit.[21] *K* 135 *S* 146 *Ch* 160 *I*; $[\alpha]_D^{25}$ = +3.9); ^{1}H NMR δ 8.37 (*s* 4H), 8.17 (*d*, *J* = 9 Hz, 4H), 7.34 (*d*, *J* = 9 Hz, 4H), 4.24 (*d*, *J* = 3 Hz, 2H), 4.18 (*d*, *J* = 3 Hz, 2H), 1.98–0.90 (*m* with maxima at 1.13, 1.06, and 1.01, 18H); IR 1740, 1716, 1605, 1529, 1161, 1120, 1015, and 874 cm^{-1}; CIMS, m/z 547(MH$^+$, 49), 477(55), 459(22), 435(15), 407(41), 389(17), 340(14), 339(65), 225(10), 209(47), 167(22), 139(100), 121(29).

(*S*)-(+)-*2-Methyl-1-butyl-4-(4-decyloxybenzoyloxy)benzoate 19.* The crude hydroxyester **10** (obtained via **6** from 0.1 mol of **1**) was combined with 4-decyloxybenzoyl chloride (30.0 g, 0.1 mol) was reluxed for 3 h in chloroform (80 ml). At this point pyridine (10 ml) was added, the reflux was continued for 1 h and the reaction mixture was poured into dilute hydrochloric acid. The organic phase was separated, dried over magnesium sulfate, the solvent was evaporated, and the crude product recrystallized from ethanol to yield 15.0 g (32% yield) of white crystals of **19**: *K* 49 S_C (36) S_A 59 *I*; $[\alpha]_D^{22}$ = +2.9 (1.84), (lit.[22] *K* 52 S_C (35) S_A 59.5 *I*); ^{1}H NMR δ 8.16 (*d*, *J* = 9 Hz, 2H), 8.13 (*d*, *J* = 9 Hz, 2H), 7.28 (*d*, *J* = 9 Hz, 2H), 6.95 (*d*, *J* = 9 Hz, 2H), 4.24 (*d*, *J* = 3 Hz, 1H), 4.17 (*d*, *J* = 3 Hz, 1H), 4.05 (*t*, *J* = 6 Hz, 2H), 1.95–0.79 (*m*, with maxima at 1.32, 1.09, 1.00, 28H); IR 1732, 1716, 1605, 1512, 1468, 1259, 1161, 1120, 1067, and 1008 cm^{-1}; CIMS, m/z 469(MH$^+$, 100), 399(41), 381(17), 262(14), 261(77). Anal. Calcd for $C_{29}H_{40}O_5$: *C*, 74.32; *H*, 8.60. Found: *C*, 74.42; *H*, 8.48.

(*S*)-(+)-*2-Methyl-1-butyl-4-(4-decyloxycinnamoyloxy)benzoate 20.* Compound **20** was obtained in 38% yield according to the preceding procedure: *K* 59 S_C 69 S_A 96 *I*, (lit.[23] *K* 60.2 S_C 71.1 S_A 95.2 *I*); $[\alpha]_D^{22}$ = +3.7 (0.55); ^{1}H NMR δ 8.10 (*d*, *J* = 9 Hz, 2H), 7.84 (*d*, *J* = 15 Hz, 1H), 7.52 (*d*, *J* = 9 Hz, 2H), 7.24 (*d*, *J* = 9 Hz, 2H), 6.93 (*d*, *J* = 9 Hz, 2H), 6.43 (*d*, *J* = 15 Hz, 1H), 4.23 (*d*, *J* = 3 Hz, 1H), 4.14 (*d*, *J* = 3 Hz, 1H), 4.01 (*t*, *J* = 7 Hz, 2H), 1.95–0.83 (*m* with maxima at 1.33, 1.09, 1.00 and 0.93, 28H); IR 1718, 1716, 1603, 1512, 1505, 1276, 1161, 1135, 1114, 984, 926, and 872 cm^{-1}; CIMS, m/z 496(MH$^+$ + 1, 23), 495(MH$^+$, 68), 425(32), 287(100); Anal. Calcd for $C_{31}H_{42}O_5$: *C*, 75.27; *H*, 8.56. Found: *C*, 75.03; *H*, 8.32.

(*S*)-(+)-*2-Methyl-1-butyl 4-(4-aminobenzoyloxy)benzoate 22.* Crude hydroxyester **10** (obtained from 0.1 mol of **1** via **6**), 4-nitrobenzoyl chloride (18.5 g, 0.1 mol), and pyridine (9 ml) were refluxed for 5 h in chloroform (80 ml). The reaction mixture was poured into cold water and the organic material was extracted with chloroform. The chloroform extracts were washed with dilute hydrochloric acid and aqueous sodium carbonate, dried with $MgSO_4$ and evaporated to give an oil. The oil was reduced during 4 h with iron powder (35 g, reduced with hydrogen) in a boiling mixture of acetic acid (5 ml) and water (50 ml). The reaction mixture was cooled, the black solid was filtered off and washed several times with hot methanol. The methanol extract was decolorized with charcoal. After three recrystallizations from methanol the overall yield of **22** was 11.5 g (35% overall yield): mp 125–127°C; $[\alpha]_D^{22}$ = +3.5 (2.80); ^{1}H NMR δ 8.13 (*d*, *J* = 9 Hz, 2 H), 7.98 (*d*, *J* = 9 Hz, 2H), 7.25 (*d*, *J* = 9 Hz, 2H), 6.69 (*d*, *J* = 9 Hz, 2H) 4.43 (bs, 2H), 4.24 (*d*, *J* = 3 Hz, 1H), 4.18 (*d*, *J* = 3 Hz, 1H), 1.98–0.90 (*m* with maxima at

1.09, 1.03, and 0.93, 9H); IR 3475, 3390, 1728, 1718, 1608, 1508, 1125, 973, and 893 cm^{-1}; CIMS, m/z 329(MH^+ + 1, 21), 328(MH^+, 100), 286(13), 258(56), 240(14), 120(61). Anal. Calcd for $C_{19}H_{21}NO_4$: *C*, 69.70; *H*, 6.47; *N*, 4.28. Found: *C*, 69.85; *H*, 6.51; *N*, 3.99.

(S)-(+)-2-Methyl-1-butyl 4-[4-(4-bromobenzamido)benzoyloxy]benzoate 23a. 4-Bromobenzoyl chloride (2.6 g, 12 mmol) was refluxed for 1 h with aminodiester **22** (3.3 g, 10 mmol) in boiling chloroform (20 ml). At this point pyridine (2 ml) was added and the mixture was refluxed for additional 1 h. The reaction mixture was diluted with ethanol (10 ml), cooled and the crude amidoester **23a** was filtered off. Two recrystallizations from chloroform/ethyl acetate afforded 3.3 g (65% yield) of **23a**; *K* 215 *Ch* (213) *I*; $[\alpha]_D^{22}$ = +16.4 (0.67); ^1H NMR δ 8.25 (*d*, *J* = 9 Hz, 2H), 8.15 (*d*, *J* = 9 Hz, 2H), 8.03–7.66 (*m*, 6H), 7.28 (*d*, *J* = 9 Hz, 2H), 4.24 (*d*, *J* = 3 Hz, 1H), 4.14 (*d*, *J* = 3 Hz, 1H), 1.99–0.96 (*m* with maxima at 1.08, 1.03, and 0.98, 9H); IR 3434, 1736, 1712, 1595, 1517, 1408, 1264, 1175, 1161, 1067, 1011, 927, and 847 cm^{-1}; CIMS, m/z 512 and 510(MH^+, 25), 442(13) and 440(15), 432(49), 304(31), 302(34), 224(32), 209(47), 139(100), 121(32); Anal. Calcd for $C_{26}H_{24}BrNO_5$: *C*, 61.18; *H*, 4.74; *N*, 2.74. Found: *C*, 61.53; *H*, 4.58; *N*, 2.70.

(S)-(+)-2-Methyl-1-butyl 4[4-(4-methoxybenzamido)benzoyloxy]benzoate 23b. The amidoester **23b** was obtained according to the preceding procedure. Two recrystallizations from acetone gave the product in 78% yield: *K* 188 *S* 202 *Ch* 229 *I*; $[\alpha]_D^{22}$ = +2.8 (1.03); ^1H NMR (acetone-d_6) δ 8.22–8.02 (*m*, 8H), 7.43 (*d*, *J* = 8 Hz, 2H), 7.04 (*d*, *J* = 8 Hz, 2H), 4.23 (*d*, *J* = 3 Hz, 1H), 4.15 (*d*, *J* = 3 Hz, 1H), 3.83 (*s*, 3H), 1.95–0.95 (*m* with maxima at 1.08, 1.03, and 0.96, 9H); IR 3432, 1734, 1715, 1685, 1605, 1514, 1500, 1308, 1265, 1173, 1161, and 1067 cm^{-1}; CIMS, m/z 463(MH^+ + 1, 34), 462(MH^+, 100), 427(12), 374(14), 256(13), 255(18.5), 254(74), 209(35), 167(17), 139(83), 121(27). Anal. Calcd for $C_{27}H_{27}NO_6$: *C*, 70.26; *H*, 5.90; *N*, 3.04. Found: *C*, 70.20; *H*, 5.94; *N*, 3.01.

(S)-(+)-2-Methyl-1-butyl 4-[4-(4-propyloxybenzamido)benzoyloxy]benzoate 23c. The amidoester **23c** was obtained in a 70% yield following the procedure employed for the preparation of **23a**: *K* 186 *S* 236 *I*; $[\alpha]_D^{22}$ = +2.7 (1.10); ^1H NMR δ 8.22 (*d*, *J* = 9 Hz, 2H), 8.15 (*d*, *J* = 9 Hz, 2H), 7.86 (*d*, *J* = 9 Hz, 2H), 7.81 (*d*, *J* = 9 Hz, 2H), 7.30 (*d*, *J* = 9 Hz, 2H), 6.99 (*d*, *J* = 9 Hz, 2H), 4.24 (*d*, *J* = 3 Hz, 1H), 4.14 (*d*, *J* = 3 Hz, 1H), 3.99 (*t*, *J* = 7 Hz, 2H), 1.99–0.95 (*m*, with maxima at 1.13, 1.03, and 0.96, 14H); IR 3438, 1733, 1718, 1684, 1604, 1513, 1499, 1309, 1265, 1174, 1161, 1067, and 1014 cm^{-1}; EIMS, m/z 489(4), 283(71), 282(100), 163(70), 121(66), 119(38), 30(30); Anal. Calcd for $C_{29}H_{31}NO_6$: *C*, 71.14; *H*, 6.38; *N*, 2.86. Found: *C*, 71.05; *H*, 6.40; *N*, 2.65.

(S)-(+)-4-(2-Methyl-1-butyl)biphenyl 25. A Grignard reagent was prepared from (S)-(+)-1-bromo-2-methylbutane (**2**, 9.8 g, 65 mmol) and magnesium (1.8 g) in anhydrous ether (25 ml). The solution was slowly added at room temperature under dry argon to a magnetically stirred suspension of [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.22 g, 0.4 mmol) in a solution of 4-chlorobiphenyl (10.0 g, 53 mmol) in anhydrous ether (40 ml). After 5 h at reflux, the green reaction mixture was carefully poured into a mixture of ice and dilute hydrochloric acid.

The etheral phase was separated, the aqueous layer was extracted with hexane (2x) and the combined organic phases were dried over magnesium sulfate. The solvents were evaporated and the crude product was distilled (129–130°C/0.35 mm Hg) to give 10.2 g (86% yield) of a white crystalline product: mp. 34.5–35°C; $[\alpha]_D^{25}$ = +12.4 (4.95), (lit.[27] mp. 25.5°C; $[\alpha]_D^{20}$ = +11.0); ^{1}H NMR δ 7.60–7.20 (*m*, 9H), 2.70–2.64 (*m*, 1H), 2.43–2.38 (*m*, 1H), 1.71–0.85 (*m*, with maxima at 0.95, 0.90 and 0.87, 9H); EIMS, m/z 224(M^+, 13), 167(100), 164(10), 152(16), 115(10).

(S)-(+)-4-[4'-(2-Methyl-1-butyl)biphenyl-4-carboxy]benzonitrile **26**. To a cooled to −5°C suspension of aluminum chloride (6.3 g) in methylene chloride (110 ml) oxalyl chloride (6.0 g, 47 mmol) was added and subsequently a solution of hydrocarbon **25** (10.2 g 45.5 mmol) in methylene chloride (25 ml) was added dropwise. The greenish reaction mixture was stirred at 0°C for additional 3.5 h and then poured into mixture of ice and hydrochloric acid. The organic layer was separated, dried over $MgSO_4$, and the solvent was evaporated. The crude acid chloride was added to a solution of *p*-cyanophenol (4.4 g, 37 mmol) and dry pyridine (10 ml) in chloroform (30 ml) and refluxed for 5 h. The reaction mixture was poured into dilute hydrochloric acid, the organic phase was separated and dried over magnesium sulfate. Evaporation of the solvent left crude crystalline product which was recrystallized twice from ethanol to give 8.4 g (50% overall yield) of white plates of **26**: *K* 100 *Ch* 197 *I*; $[\alpha]_D^{25}$ = +9.3 (4.0), (lit.[27] *K* 99.5 *Ch* 195.9 *I*); ^{1}H NMR δ 8.24 (*d*, *J* = 8 Hz, 2H), 7.77–7.73 (*m*, 4H), 7.58 (*d*, *J* = 8 Hz, 2H), 7.39 (*d*, *J* = 9 Hz, 2H), 7.27 (*d*, *J* = 9 Hz, 2H), 2.73–2.67 (*m*, 1H), 2.47–2.41 (*m*, 1H), 1.98–0.90 (*m*, with maxima at 0.96 and 0.91, 9H); IR 2963, 2233, 1740, 1605, 1506, 1272, 1060, 1017, 1006 cm^{-1}; EIMS, m/z 369(M^+, 24), 261(49), 252(71), 251(100), 194(40), 191(35), 167(45), 166(65), 165(71), 152(32), 121(43); CIMS, m/z 371(MH^+ + 1, 26), 370(MH^+, 100), 251(38).

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