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Enantioselective Synthesis of Chiral Liquid Crystalline Compounds from Monoterpenes

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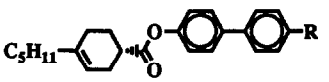
Key words: enantioselective synthesis, liquid crystal, monoterpene, chiral

Abstract: Chiral liquid crystalline compounds **1-9** have been synthesized enantioselectively from monoterpenes The optical purities of (*S*)-(-)- and (*R*)-(+)-perillalcohol (**16**, **27**), (*S*)-(-)- and (*R*)-(+)-1-pentyl-4-hydroxymethyl-1-cyclohexene (**33**, **34**) and (2*S*,5*S*)-2-pentyl-5-hydroxymethyl-1-cyclohexanone (**53**) have been determined by ^{1}H NMR analysis using chiral shift reagents The mesomorphic phases and transition temperatures of compounds **2**,**3**,**5**,**6**,**7**,**8** and **9** have been characterized.

Introduction

A great deal is already known about the requirements of benzene, cyclohexane, or heterocyclic rings for thermotropic liquid crystals However, there has been little exploration for the function of a 1,4-disubstituted cyclohexene ring, which is able to impart chirality to a liquid crystal. Of special interest is that optically active liquid crystal molecules are widely used in electronic devices, and indeed, liquid crystals with chiral smectic C phase have received particular attention because of their role in bi-stable, fast-switching surface stabilized ferroelectric liquid crystal (SSFLC) displays [1,2] There are many possible compounds that can be explored the structure of the ring with chiral center(s), the position of the double bond in a cyclohexene ring, and the terminal groups can all be varied Some of the compounds or their mixtures will likely be desirable ferroelectric materials for practical applications In light of this fact, we have undertaken a research program with the aim to synthesize enantioselectively some liquid crystalline compounds containing a 1,4-disubstituted cyclohexene (*i e.* **1-8**) or a 2,5-disubstituted cyclohexanone (*i e.* **9**) in the rigid core, in order to explore the mesogenic character of these compounds and to open up the possibility of introducing a new class of liquid crystals In the *trans*-ester **9**, the liquid-crystalline properties may be present due to their rod-shaped molecule, whereas, in the *cis*-ester **10**, such properties may be absent due to the pseudo-axial position of the alkyl group which excludes the possibility of their rod-like form. The alkyl chains in **5-8** contain a double bond and a branch It is known that liquid crystals with alkenyl side chains are stable as long as the double bond is not conjugated.[3,4] The branched methyl group is not necessarily desirable, because it might reduce the nematic range of the liquid crystals The reason for the incorporation of the 2-propenyl chain into **5-8** is due

to the fact that the starting materials, (*S*)-(-)-β-pinene and (*R*)-(+)-α-pinene, are readily available commercially Here, we wish to describe the synthesis of these molecules by starting from commercially available and inexpensive monoterpenes.



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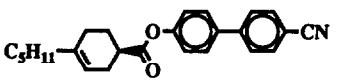
2, R = OC_8H_{17}



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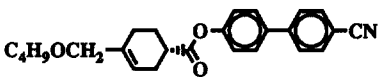

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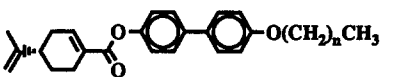

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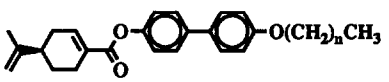
6, n = 7



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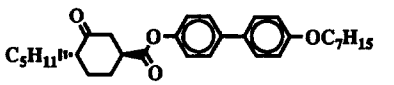
8, n = 7



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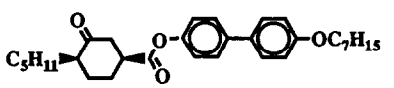

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Results and Discussion

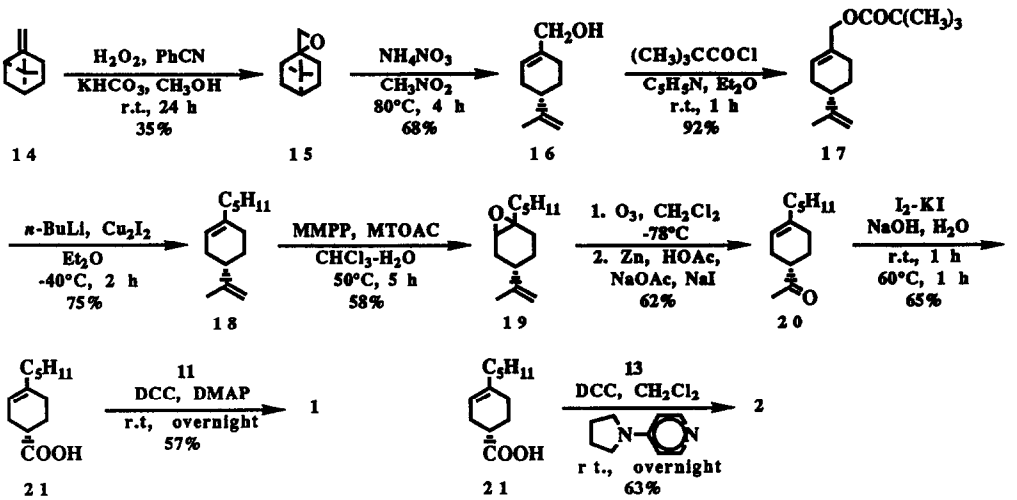
Enantioselective Synthesis of Chiral Liquid Crystalline Compounds Containing a 1,4-Disubstituted Cyclohexene Ring.

Our synthesis of (*S*)-(-)-4'-(4"-cyanobiphenyl) 4-pentyl-3-cyclohexene-1-carboxylate (**1**) and (*S*)-(-)-4'-(4"-octoxybiphenyl) 4-pentyl-3-cyclohexene-1-carboxylate (**2**) were elaborated from naturally occurring (*S*)-(-)-β-pinene (**14**) and (*S*)-(-)-perillalcohol (**16**) As outlined in Scheme 1, the chiral liquid crystals **1** and **2** can be assembled by esterification of (*S*)-(-)-4-pentyl-3-cyclohexene-1-carboxylic acid (**21**) with appropriate phenols, **11** and **13**

11. R = CN
12. R = OC_7H_{15}
13. R = OC_8H_{17}

(*S*)-(-)-β-Pinene (**14**) was epoxidized with 1 equivalent of 30% hydrogen peroxide and 0 5 equivalent of benzonitrile to give (*S*)-(-)-β-pinene epoxide (**15**) in 35% yield.[5] The ring opening of (*S*)-(-)-β-pinene epoxide (**15**) was accomplished by treatment with ammonium nitrate to afford (*S*)-(-)-perillalcohol (**16**) in 68% yield [6] The optical purity of **16** was found to be 88% ee determined by ^{1}H NMR spectroscopic method using chiral shift reagent complex Ag(fod) and Pr(hfc)$_3$ (*vide infra*) (*S*)-(-)-Perillalcohol (**16**) was converted in 92% yield to (*S*)-(-)-perillyl pivalate (**17**)[7] by treatment of an excess pivaloyl chloride in the presence of pyridine The nucleophilic displacement reaction of pivalate **17** with lithium dibutylcuprate proceeded to afford (*S*)-(-)-1-pentyl-4-(2-propenyl)-1-cyclohexene (**18**) in 75% yield [8]

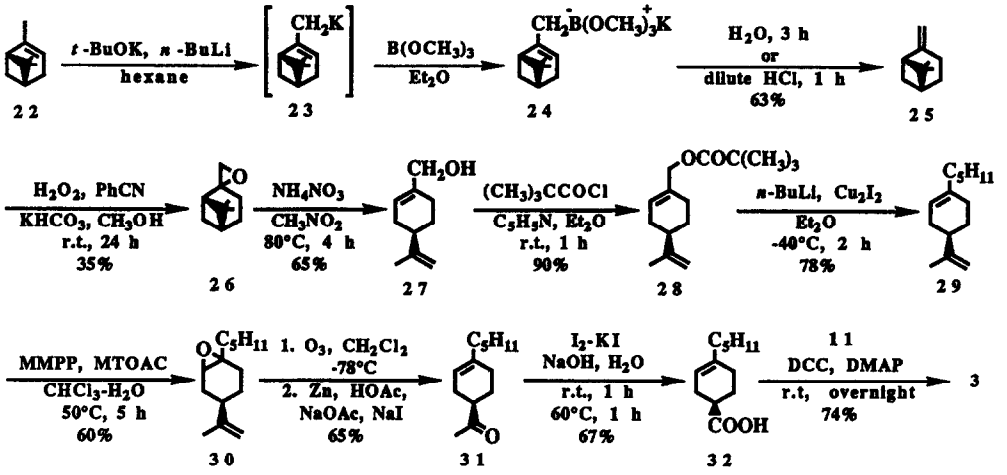
Scheme 1



In view of the possible complication due to the chemoselectivity of the two double bonds of **18** upon ozonolysis, the trisubstituted double bond must be first protected before the cleavage of the terminal double bond by ozonolysis Epoxide functionality was chosen as a masked trisubstituted double bond which can be regenerated under reductive condition Thus, the trisubstituted double bond of **18** was selectively protected as an epoxide by treatment with MMPP in the two-phase system of chloroform and water at 50°C in the presence of the phase-transfer catalyst, methyltrioctylammonium chloride (MTOAC).[9] (*S*)-(-)-1-Pentyl-4-(2-propenyl)cyclohexane-1,2-epoxide (**19**) was a mixture of two diastereomers. Then epoxide **19** was converted to (*S*)-(-)-1-pentyl-4-acetyl-1-cyclohexene (**20**) by ozonolysis of the terminal double bond accompanied with the deoxygenation of the epoxide by reductive workup with zinc dust in acetic acid in 62% yield [10] Finally, (*S*)-(-)-4-pentyl-3-cyclohexene-1-carboxylic acid (**21**) was obtained from (*S*)-(-)-1-pentyl-4-acetyl-1-cyclohexene (**20**) in 65% by a haloform reaction[11,12] with iodine-potassium iodide-10% sodium hydroxide using dioxane as cosolvent. Esterification of acid **21** with 4-hydroxy-4'-cyanobiphenyl (**11**) or 4-hydroxy-4'-*n*-octoxybiphenyl (**13**), respectively, in the presence of DCC and DMAP or 4-pyrrolidinopyridine yielded the desired optically active liquid crystals **1** (57%) and **2** (63%).

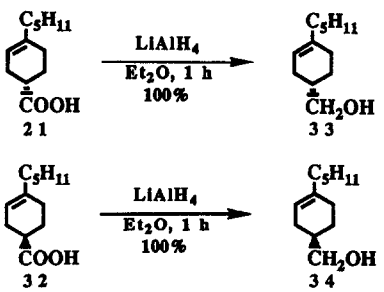
Using a procedure similar to the synthesis of (*S*)-(-)-liquid crystalline compound **1**, (*R*)-(+)-4'-(4''-cyanobiphenyl) 4-pentyl-3-cyclohexene-1-carboxylate (**3**) can be synthesized The commercially unavailable (+)-β-pinene (**25**) was however prepared from commercially available (+)-α-pinene (**22**). (Scheme 2)[13]

Scheme 2



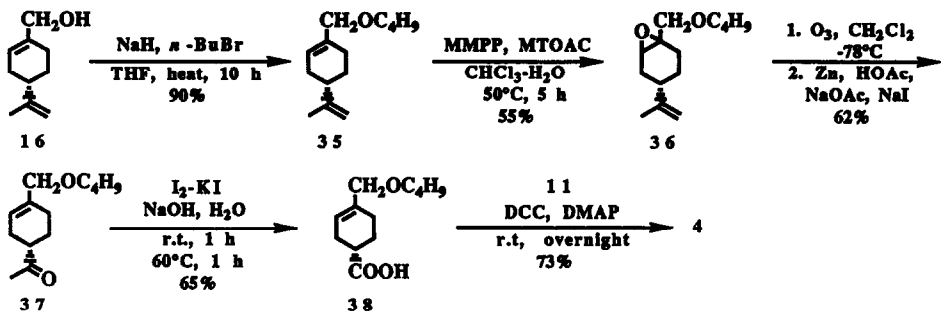
In order to determine the optical purities of chiral acids **21** and **32**, both of the acids were converted in quantitative yield to the corresponding alcohols **33** and **34** by reduction with lithium aluminum hydride (Scheme 3). The optical purities of **33** and **34** were determined as 77% ee and 83% ee, respectively, by ^{1}H NMR spectroscopic method using chiral lanthanide shift reagent Eu(hfc)$_3$ (*vide infra*).

Scheme 3



The synthesis of (*S*)-(-)-4'-(4"-cyanobiphenyl) 4-butoxymethyl-3-cyclohexene-1-carboxylate (**4**) can be achieved by an extension of the similar methodology for the synthesis of (*S*)-(-)-4'-(4"-cyanobiphenyl) 4-pentyl-3-cyclohexene-1-carboxylate (**1**) (*S*)-(-)-Perillyl butyl ether (**35**) was prepared in 90% yield by reaction of (*S*)-(-)-perillalcohol (**16**) and *n*-butyl bromide in the presence of sodium hydride [14] In an almost identical manner as the synthesis of **1**, compound **4** was synthesized from **35** (Scheme 4)

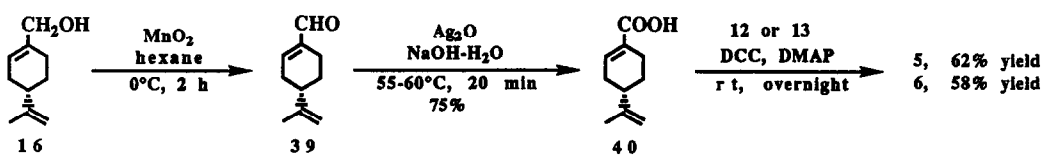
Scheme 4



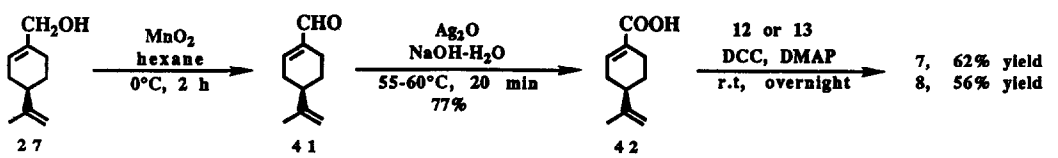
(*S*)-(-)-4'-(4"-Heptoxybiphenyl) 4-(2-propenyl)-1-cyclohexene-1-carboxylate (**5**) and (*S*)-(-)-4'-(4"-octoxybiphenyl) 4-(2-propenyl)-1-cyclohexene-1-carboxylate (**6**) were easily synthesized by esterification of (*S*)-(-)-4-(2-propenyl)-1-cyclohexene-1-carboxylic acid (**40**) with appropriate phenols **12** and **13** The chiral acid **40** is structurally related to (*S*)-(-)-perillalcohol (**16**) and could be achieved by oxidation of (*S*)-(-)-perillalcohol (**16**) (Scheme 5). The conversion of (*S*)-(-)-perillalcohol (**16**) to (*S*)-(-)-perillaldehyde (**39**) was carried out by stirring **16** with an excess of manganese dioxide The aldehyde so prepared was unstable and polymerized under prolonged standing at room temperature. Therefore, it was further oxidized to the corresponding acid **40** without purification The oxidation of **39** with Ag_2O provided acid **40** in 75% yield [15] Esterification of **40** with appropriate phenols **12** and **13**, respectively, in the presence of DCC and DMAP afforded **5** (62%) and **6** (58%).

(*R*)-(+)-4'-(4"-Heptoxybiphenyl) 4-(2-propenyl)-1-cyclohexene-1-carboxylate (**7**) and (*R*)-(+)-4'-(4"-octoxybiphenyl) 4-(2-propenyl)-1-cyclohexene-1-carboxylate (**8**) were synthesized in an identical manner as their (-)-enantiomers **5** and **6** from (*R*)-(+)-perillalcohol (**27**) (Scheme 6).

Scheme 5



Scheme 6



Synthesis of Chiral Liquid Crystalline Compound Containing a *trans*-2,5-Disusbstituted Cyclohexanone Ring — (1*S*,4*S*)-4'-(4"-Heptoxybiphenyl) 4-Pentyl-3-cyclohexanone-1-carboxylate (9).

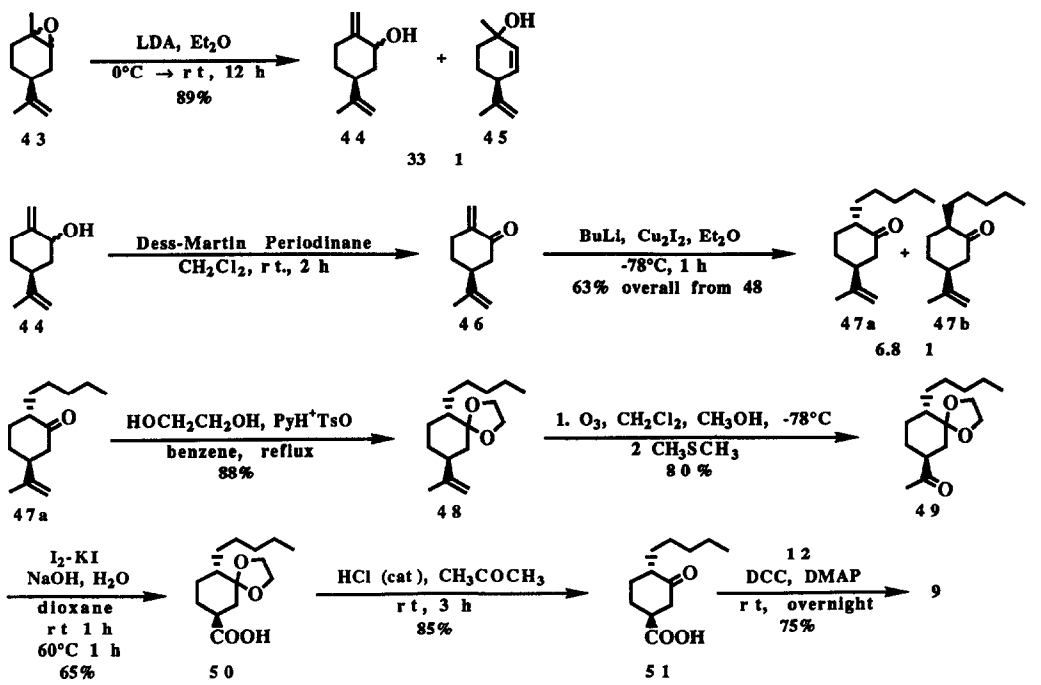
The synthetic plan for (1*S*,4*S*)-4'-(4"-heptoxybiphenyl) 4-pentyl-3-cyclohexanone-1-carboxylate (**9**) was elaborated upon the transformation of the naturally occurring (*S*)-(-)-limonene oxide (**43**) By treating **43** with LDA, the desired allylic alcohol **44** was obtained in 89% yield.[16] Nonetheless, the product was a

mixture of two diastereomers inseparable by TLC (hexane/ethyl acetate 10 1) The ratio of the two diastereomers was 1.1.65 as substantiated by an NMR study. A small amount of the elimination product from the more substituted carbon, namely (3*S*)-6-hydroxy-6-methyl 3-(2-propenyl)-1-cyclohexene (**45**), was also isolated in 2 7% yield. The ratio of **44** to **45** was 33:1

Allylic alcohol **44** was successfully oxidized to α,β-unsaturated ketone **46** by using Dess-Martin periodinane [17] Enone **46** was an unstable oil which polymerized upon prolonged standing at room temperature. It must be noted that the solvent should not be removed completely to prevent the sensitive enone from polymerization In considering the ready polymerization of **46**, care must be taken in the subsequent workup process to ensure that the dilute solution of **46** was kept at low temperature For the purpose of drying, anhydrous benzene should be added for an azeotropic distillation Enone **46** was too unstable for isolation, and therefore no other physical data could be obtained for further characterization

Michael addition reaction of enone **46** with Bu_2CuLi derived from butyllithium and cuprous iodide afforded two diastereomers of (5*S*)-2-pentyl-5-(2-propenyl)-1-cyclohexanone (**47**) in 63% overall yield from **44** Ketone **47a** was refluxed with ethylene glycol in benzene catalyzed with pyridinium tosylate[18,19], and water separation by a Dean-Stark trap with Drierite on the side arm was used to aid in water removal until the starting ketone was almost consumed (about 1 day) to afford ketal **48** (Scheme 22) Ozonolysis of **48** at -78℃, followed by reductive workup with dimethyl sulfide provided methyl ketone **49** as an oil The yield of **49** was 80% overall from **47** Iodoform reaction of **49** gave the chiral carboxylic acid **50** in 65% yield

Scheme 7

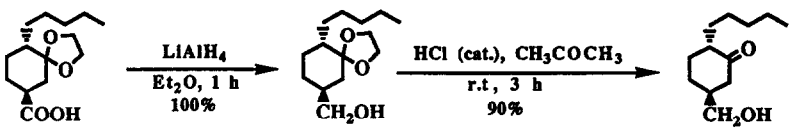


Once the acid formation had been accomplished, removal of the ketal protecting group was destined to occur prior to manipulation of esterification. The ketal protecting group was removed by treatment with a

catalytic amount of hydrochloric acid. Finally, esterication of acid **51** with **12** in the presence of DCC and DMAP yielded the desired optically active liquid crystal **9** in 75% yield.

In order to determine the optical purity of (1*S*,4*S*)-4-pentyl-3-cyclohexanone-1-carboxylic acid (**51**), it was converted to (2*S*,5*S*)-2-pentyl-5-hydroxymethyl-1-cyclohexanone (**53**) via **52** (Scheme 8). Thus, (1*S*,4*S*)-4-pentyl-3-cyclohexanone-1-carboxylic acid ethylene acetal (**51**) was first reduced to (2*S*,5*S*)-2-pentyl-5-hydroxymethyl-1-cyclohexanone ethylene acetal (**52**) in quantitative yield with lithium aluminum hydride After that, the ketal protecting group was removed by treatment with a catalytic amount of hydrochloric acid in 90% yield. The optical purity was determined as 94% ee by ^{1}H NMR spectroscopic method using chiral lanthanide shift reagent Eu(hfc)$_3$ (*vide infra*).

Scheme 8



50 **52** **53**

Determination of Enantiomeric Purities of (*S*)-(-)- and (*R*)-(+)-Perillalcohols (16 and 27), (*S*)-(-)- and (*R*)-(+)-1-Pentyl-4-hydroxymethyl-1-cyclohexenes (33) and (34), and (2*S*,5*S*)-2-Pentyl-5-hydroxymethyl-1-cyclohexanone (53).

Our first attempt to determine the enantiomeric purities of (*S*)-(-)- and (*R*)-(+)-perillalcohols, (**16**) and (**27**), relied on ^{1}H NMR spectroscopic method using Eu(dcm)$_3$ as chiral lanthanide shift reagent [20,21,22] Eu(dcm)$_3$ was added incrementally to the substrate in a $CDCl_3$ solution, but the resulting differences in the chemical shifts of corresponding groups of the enantiomeric compounds were not distinct. By lowering the temperature gradually from room temperature to -50°C, the resonances of the two enantiomers also cannot be differentiated. This unsatisfactory results were probably due to the fact that the hydroxyl group in perillalcohol is far away from the chiral center, so the influence of Eu(dcm)$_3$ was not sufficient to induce enantiomeric shift differences [23]

In order to circumvent this, we have made an attempt to use chiral binuclear complex of Pr(hfc)$_3$ and Ag(fod) for the determination of the optical purities of (*S*)-(-)- and (*R*)-(+)-perillalcohol, (**16**) and (**27**) [24] The spectra were obtained in $CDCl_3$ solutions by using 1·1 2 of Pr(hfc)$_3$:Ag(fod):substrate. Nonequivalences of the two methylene protons (CH_2OH) of both enantiomers were observed, and the absorptions of the methylene protons in the pair of enantiomers were separated at shifts of ~ 4 ppm from TMS The two diastereotopic methylene protons of (-)- enantiomer were separated by 0 35 ppm, and those of (+)-enantiomer were separated by ~ 0 1 ppm Peak areas of the signals were found to correspond to optical purities of 88% for the (-)-enantiomer and 89% for the (+)-enantiomer, respectively. The optical purity for commercial (-)-perillalcohol was determined as 94%

In 1-pentyl-4-hydroxymethyl-1-cyclohexene (**33**) and (**34**), the hydroxymethylene group is adjacent to the chiral center. Therefore, it is expected that a chiral lanthanide shift reagent would induce large differences in resonance frequencies ($\Delta\Delta\delta$) between the corresponding protons of enantiomers. In general, shifts for protons closer to the point of association are larger than those for protons further apart. The oxygen-containing methylene protons are closer to the lanthanide metal ion, and should therefore experiece the greatest shift.

We used (+)-Eu(hfc)$_3$[25] as the chiral shift reagent for the determination of the enantiomeric purities of (*S*)-(-)- and (*R*)-(+)-1-pentyl-4-hydroxymethyl-1-cyclohexenes, (**33**) and (**34**). By adding (+)-Eu(hfc)$_3$ incrementally to the substrate, a chemical shift nonequivalence was observed. The spectra were obtained in $CDCl_3$ solutions at room temperature. The magnitude of induced shift ($\Delta\delta$) and the magnitude of chemical-shift differences (nonequivalence) for enantiomeric nuclei ($\Delta\Delta\delta$) depended on the ratio of Eu(hfc)$_3$ to the substrate. At a molar ratio of complex to substrate of 0.8, the resonances of the methylene protons (CH_2OH) shifted from δ 3.5 ppm to δ 17-18 ppm.

The diastereotopic oxygen-containing protons of (*R*)-(+)- enantiomer **36** are differentially perturbed and are shifted from δ 3.5 ppm to downfield. The nonequivalence of the H_A and H_B signals reached a maximum when 0.8 equiv. of complex had been added and decreased as further complex was added. The maximum investigated appeared as a doublet at δ 17.3 ppm and 17.6 ppm, separating by 0.3 ppm. In contrast, in the (*S*)-(-)-enantiomer **33**, the two protons maintained the same chemical shifts, leaving a singlet which was overlapped with one of the protons of the (*R*)-(+)-enantiomer **34**. Peak areas of the expanded signals were found to correspond to optical purities of 83% for the (*R*)-(+)-enantiomer **34** and 77% for the (*S*)-(-)-enantiomer **33**.

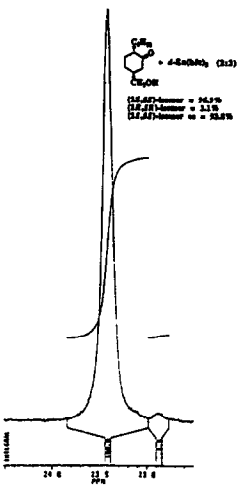


Fig 1 Expanded -CH_2OH NMR absorptions of **53** with *l*-Eu(hfc)$_3$ in $CDCl_3$

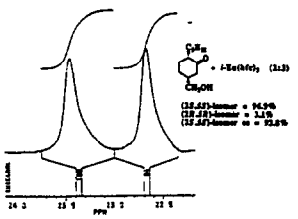


Fig.2. Expanded -CH_2OH NMR absorptions of **53** with *d*-Eu(hfc)$_3$ in $CDCl_3$

We have also made an attempt to use *d*-Eu(hfc)$_3$ and *l*-Eu(hfc)$_3$ for the determination of the optical purity of (2*S*,5*S*)-2-pentyl-5-hydroxymethyl-1-cyclohexanone (**53**) since its enantiomer was not available By comparing the two series of spectra, i.e the series of spectra obtained by adding *d*-Eu(hfc)$_3$ incrementally to a $CDCl_3$ solution of **53** at room temperature, and the series of spectra obtained for a $CDCl_3$ solution of **53** with increasing concentrations of *l*-Eu(hfc)$_3$, it is possible to assess the ee% of **53**. When the molar ratio of the substrate to the reagent was 2.3, the two methylene protons in the complex of (2*S*,5*S*)-substrate• *d*-Eu(hfc)$_3$ shifted from δ 3 6 ppm to ~23 ppm, maintaining as a singlet (Fig 1). Whereas, the resonances of the diastereotopic protons (H_A and H_B) in the complex of (2*S*,5*S*)-substrate• *l*-Eu(hfc)$_3$ appeared as a doublet and reached a maximum of ~0.8 ppm (Fig. 2) Thus, the shift of (2*R*,5*R*)-substrate• *d*-LSR was the same as that of (2*S*,5*S*)-substrate• *l*-LSR, where the resonance appeared as a doublet, one of which was overlapped with the singlet of the methylene protons in the complex of (2*S*,5*S*)-substrate• *d*-Eu(hfc)$_3$ The shift of

(2*R*,5*R*)-substrate• *l*-LSR was the same as that of (2*S*,5*S*)-substrate• *d*-LSR, and the resonance appeared as a singlet, which was overlapped with one of the doublet of the methylene protons in the complex of (2*S*,5*S*)-substrate• *l*-Eu(hfc)$_3$. In this way, peak areas of the expanded signals corresponded to optical purities of 94% for compound **53**.

Mesomorphic Phases and Transition Temperatures of Chiral Liquid Crystalline Compounds 2, 3, 5, 6, 7, 8 and 9.

The mesomorphic phases and transition temperatures of compounds **2**, **3**, **5**, **6**, **7**, **8** and **9** have been characterized by the use of polarizing microscopy. The transition temperatures listed in Table 1 were determined from DSC (differential scanning calorimeter) measurements.

The mesomorphic 1,4-disubstituted cyclohexene with a double bond in the 3-position (*viz.* **2,3**) are characterized by low melting points and wide mesomorphic ranges. Compound **2** has a very rich phase behavior, and there is a chiral smectic C phase from 123.4 to 133℃ which is the most widely examined ferroelectric phase for electro-optical applications Unfortunately, the P_s is only -0 53 nC/cm^2 when the temperature is 131℃.

Compound **3** was a needle-shaped crystals Under the examination of a polarizing microscope, the solid melted at 66 7℃ into a nematic liquid crystal with a clearing temperature of 167 9℃ These transition temperatures are very close to those reported for the corresponding racemic mixture

Table 1. Mesomorphic phases and transition temperatures of compounds **2**, **3**, **5**, **6**, **7**, **8** and **9**

Compounds	mesomorphic phases and transition temperatures	T (P_s)
2	K 74 S_H 103 1 S_G 114 6 S_F 123 4 S_C 133 S_A 141 6 CH 148 5 I	131℃
3	K 66 7 N 167 9 I	
5	K_1 96 K_2 102 S_C 112 CH 157 5 BPI 159 3 BPII 159.4 I	101-113 7℃
6	K_1 92 K_2 95 S_C 115 2 CH 157 5 BPI 157.6 BPII (<0 1) I	93-116℃
7	K_1 96 K_2 100 S_C 111 CH 157 BPI 157.5 BPII 157.6 I	101 6-113.5℃
8	K_1 89 K_2 95 5 S_C 117 CH 157 5 BPI 157 6 BPII (<0 1) I	96.1-118 5℃
9	K 127 (S_B 123) S_A 208 I	

Compounds **5-8** had similar mesomorphic phases and transition temperatures. The existence of many smectic phases was apparent. Spontaneous polarization reading was taken on cooling. All four compounds **(5-8)** have P_s ranging from 4 to 10 nC/cm^2. Taking into account the standard deviation of the apparatus (including conductivity of these compounds), these compounds have essentially the same P_s values.

Compound **9** displayed a high temperature S_A phase and a monotropic S_B phase. It did not exhibit any tilted smectic phases, therefore no spontaneous polarization and tilt angle could be measured.

As stated in the Introduction Section, our interest in the synthesis of cyclohexenyl liquid crystals is to prepare optically active compounds with a chiral center in the mesogenic core. One of the incentives in preparing the optically active cyclohexenecarboxylates was to obtain ferroelectric liquid crystals with high spontaneous polarization (P_s), which can be used in surface-stabilized ferroelectric liquid crystal displays. The reasoning for this is that the molecular segments about the chiral center in the "rigid" core would have more restricted rotation and thereby possibly larger average lateral dipole moments. The optically active compound **2** does have a S_C* phase (Table 1) The specific rotation of this compound is quite large ($[a]^{25}_D$ = -35.17°) and its tilt angle is quite normal (Fig. 3). Unfortunately, its value of P_s is extremely small, being only -0 53 nC/cm^2 when the temperature is 131°C The possible reason for this is the following. Using a tripos force field calculation,[27] it was shown that there are two preferred configurations in which the plane containing an all-*trans* chain would be normal to the best plane of the cyclohexene ring. In these two configurations, the small dipole associated with the chiral carbon is in the tilt plane and will not contribute to **P**, and the dipole moment of the carbonyl group opposite to each other. Therefore, **2** and similar cyclohexenyl carboxylates[27] have low P_s values in spite of the presence of a chiral center in the mesogenic core.

Although compound **9** does not have a S_C* phase, potentially it can be used as a chiral dopant in achiral S_C hosts It has been shown that substituted α-aryl-γ-lactones can be used as chiral dopants to prepare ferroelectric liquid crystalline (FLC) mixtures with fast response.[28,29] Similar to the γ-lactones, compound **9** has two chiral centers and a carbonyl group in the ring. Therefore, the use of **9** and its analogs as chiral dopants for FLC displays is worth further study

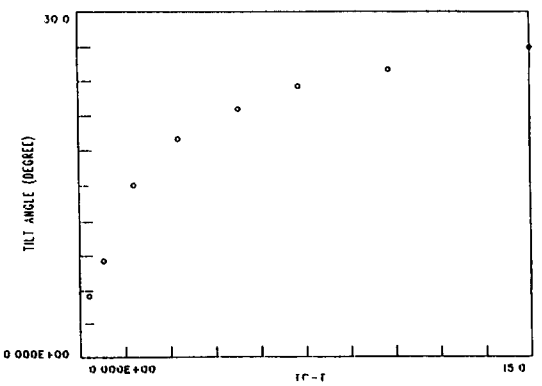


Fig 3 Tilt angle of compound **2**

Experimental Section

All reagents and solvents were reagent grade. All solvents were purified and dried by standard

methods.[30] Optical rotations were taken on a AA-1000 Polarimeter or a JASCO DIP-370 Polarimeter. NMR spectra were recorded on a Bruker Cryospec WM 250 spectrometer (250 MHz for ^1H and 62.5 MHz for ^{13}C). All NMR measurements were carried out at room temperature in chloroform solution. Chemical shifts are reported as parts per million (ppm) in δ units on the scale downfield from tetramethylsilane (TMS) or relative to the resonance of chloroform solvent (7.26 ppm in the ^1H, 77.0 ppm for the central line of the triplet in the ^{13}C modes, respectively) Mass spectral (MS) data were obtained on a VG 7070F mass spectrometer Analytical thin-layer chromatography (TLC) was carried out on commercial E. Merck 60 PF_{254} silica gel plates (Art. 5554) E Merck 230-400 mesh silica gel (Art. 9385) was used for column chromatography. Elemental analyses were performed at Shanghai Institute of Organic Chemistry, Academia Sinica, China.

(*S*)-(-)-β-Pinene Epoxide (15).[5] To a one liter three-necked flask were charged methanol (400 mL), potassium bicarbonate (10 g), benzonitrile (30.6 g, 0.3 mol), (*S*)-(-)-β-pinene **(14)** [42 g, 0.6 mol, $[\alpha]^{22}_D$ -19.0° (neat)] and finally 30% hydrogen peroxide (68 g, 0.6 mol) The mixture was stirred for 24 h in a large water bath at room temperature. The clear solution was poured into water (375 mL) and extracted with dichloromethane (3 × 100 mL) The combined extracts were washed with water (100 mL), dried over anhydrous magnesium sulfate, and concentrated under a 30 cm Vigreaux column on a steam bath to a pot temperature of 75 °C The chilled concentrate was freed of benzamide by filtration and the filtrate was further concentrated on a rotary evaporator The crude product was shown by G C. analysis to consist of unreacted (*S*)-(-)-β-pinene **(14)** and (*S*)-(-)-β-pinene epoxide **(15)** Distillation of this material through a 15 cm Vigreaux column gave (*S*)-(-)-β-pinene epoxide **(15)** (16 g, 35% based on benzonitrile), which was identical in in all aspects with a commercial sample bp 118 °C (40 mmHg) [lit[5] bp 98-99°C (25 mmHg)]

Conversion of (*R*)-(+)-α-Pinene (22) to (*R*)-(+)-β-Pinene (25).[13] To a stirred suspension of *n*-BuLi (1.4 M, 180 mL, 250 mmol) in hexane and *t*-BuOK (28g, 250 mmol) was added (*R*)-(+)-α-pinene **(22)** (27.2g, 200 mmol, $[\alpha]_D$ +39.1° (neat), Aldrich P4,568-0) slowly at -78 C under nitrogen atmosphere After the addition was completed, the reaction mixture was warmed slowly to room temperature and stirred at that temperature for 48 h The reaction mixture was then cooled to -78 C, and trimethyl borate (67g, 650mmol) in anhydrous diethyl ether (50 mL) was added slowly with efficient stirring Then the mixture was slowly warmed to room temperature and stirred for 1 h Hydrolysis was achieved by adding 10% hydrochloric acid (100 mL) and stirred for 1 h, or water (100 mL) and stirred for 3 h The organic layer was separated, and the aqueous layer was extracted with hexane (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous magnesium sulfate, and concentrated The residue was distilled under reduced pressure to furnish (*R*)-(+)-β-pinene **(25)** (17 1 g, 63%): bp 87°C (40 mmHg) [lit[13] bp 55°C (12 mmHg)], $[\alpha]_D$ +19 4° (neat, 85% ee) The ^1H NMR spectrum of synthetic (*R*)-(+)-β-pinene **(25)** was in complete agreement with the ^1H NMR spectrum of the natural (*S*)-(-)-β-pinene **(14)**

(*R*)-(+)-β-Pinene Epoxide (26). Compound **26** was generated as described for **15** from benzonitrile (30 6 g, 0 3 mol), (*R*)-(+)-β-pinene **(25)** (42 g, 0 6 mol) and 30% hydrogen peroxide (68 g, 0 6 mol) in 35% yield based on benzonitrile bp 112-114 °C (37 mmHg) [lit[5] bp 98-99°C (25 mmHg)], whose physical data are identical in all aspects with an authentic sample

(*S*)-(-)-Perillalcohol (16).[6] To a stirred suspension of ammonium nitrate (3 g, 0 037 mol) in nitromethane (160 mL) was added dropwise a solution of (*S*)-(-)-β-pinene epoxide **(15)** (45 6 g, 0 3 mol) in nitromethane (40 mL) in a period of 1 h at 80 °C After being stirred for a further 4 h at the same temperature, nitromethane was removed by distillation under reduced pressure leaving behind a red oily residue, which was partitioned between 2% aqueous sodium hydroxide (300 mL) and hexane (300 mL) The organic phase was separated, and the aqueous phase was extracted with hexane (3 × 100 mL) The combined organic layers were washed with brine (50 mL) and dried over anhydrous magnesium sulfate The solvent was removed and the resulting red oil was distilled in vacuo to give (*S*)-(-)-perillalcohol **(16)** (31 g, 68%) as a yellow oil· bp 152 °C (30 mmHg) [lit[6] bp 62°C (9 3 Pa)], which was identical in all aspects with an authentic sample, $[\alpha]_D$ -58 2° (*c* 1 3, CH_3OH) After further purification by column chromatography on silica gel with hexane/ethyl acetate (10 1) $[\alpha]_D$ -68 0° (*c* 1 47, CH_3OH, 88% ee), ^1H NMR δ 5 70 (br s, 2H), 4 72 (br s, 2H), 3 99 (s, 2H), 2 19-1 83 (m, 6H), 1 74 (s, 3H), 1 56-1 43 (m, 1H), MS *m/z* 152 (M^+, 11 84)

(*R*)-(+)-Perillalcohol (27). Compound **27** was generated as described for **16** from (*S*)-(-)-β-pinene epoxide **(26)** (45 6 g, 0 3 mol) in 65% yield as a yellow oil, which was identical in all aspects with an authentic sample $[\alpha]_D$ +52 0° (*c* 1 76, CH_3OH, 89% ee), ^1H NMR δ 5 71 (br s, 1H), 4 72 (br s, 2H), 4 00 (s, 2H), 2 20-1 83 (m, 6H), 1 74 (s, 3H), 1 56-1.48 (m, 1H); MS *m/z* 152 (M^+, 10 43).

(*S*)-(-)-Perillyl Pivalate (17).[7] To a stirred solution of (*S*)-(-)-perillalcohol **(16)** (38 g, 0 25 mol) and anhydrous pyridine (25 mL, 0 3 mol) in anhydrous diethyl ether (250 mL) was added dropwise

pivaloyl chloride (45.2 g, 0.38 mol) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Then the mixture was poured into ice-water (250 mL), and stirred for a further 1 h. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 250 mL). The combined organic layers were washed sequentially with saturated sodium bicarbonate (50 mL) and brine (50 mL), dried over anhydrous magnesium sulfate and evaporated. The residue was distilled in vacuo to afford (*S*)-(-)-perillyl pivalate (**17**) (54 g, 92%) as a colorless oil: bp 108 °C (3.5 mmHg), $[\alpha]_D$ -55.3° (*c* 10.0, $CHCl_3$); ^1H NMR δ 5.74-5.72 (m, 1H), 4.74-4.72 (m, 2H), 4.45 (br s, 2H), 2.20-1.83 (m, 6H), 1.74 (s, 3H), 1.54-1.44 (m, 1H), 1.21 (s, 9H); MS *m/z* 236 (M^+, 1.99) Anal. Calcd for $C_{15}H_{24}O_2$· C, 76 23; H, 10.23. Found: C, 76.91, H, 10.20

(*R*)-(+)-Perillyl Pivalate (28). Compound **28** was generated as described for **17** from (*R*)-(+)-perillalcohol **27** (38 g, 0.25 mol) The crude product was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (20.1) to afford (*R*)-(+)-perillyl pivalate (**28**) (52 7 g, 90%) as a colorless oil $[\alpha]_D$ +54 0° (*c* 7 24, $CHCl_3$); ^1H NMR δ 5.74-5 72 (m, 1H), 4.73-4.72 (m, 2H), 4.45 (br s, 2H), 2.20-1.82 (m, 6H), 1.74 (s, 3H), 1.53-1 44 (m, 1H), 1.21 (s, 9H); MS *m/z* 236 (M^+, 2.16). HRMS calcd for $C_{14}H_{24}O_2$ 236 3573, found 236.3578.

(*S*)-(-)-1-Pentyl-4-(2-propenyl)-1-cyclohexene (18).[8] The suspension of freshly recrystallized cuprous iodide (5 72 g, 30 mmol) in anhydrous diethyl ether (200 mL) was kept at 0°C under a nitrogen atmosphere, to which was added dropwise a solution of *n*-butyllithium (1.4 M, 40 mL, 55 mmol) in hexane with stirring. After 10 min, the mixture was chilled to -40°C and a solution of (*S*)-(-)-perillyl pivalate (**17**) (1.18 g, 5 mmol) in anhydrous diethyl ether (10 mL) was introduced. After being stirred at the same temperature for 2 h, the reaction mixture was quenched with 2N aqueous hydrochloric acid (100 mL) and the undissolved residue was removed by suction filtration. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel eluted with hexane afforded (*S*)-(-)-1-pentyl-4-(2-propenyl)-1-cyclohexene (**18**) (720 mg, 75%) as a colorless oil· $[\alpha]_D$ -68.8° (*c* 10 5, $CHCl_3$), ^1H NMR δ 5.40 (br s,1H), 4 70 (br s, 2H), 2 20-1.75 (m, 8H), 1 73 (s, 3H), 1.55-1 23 (m, 7H), 0.89 (br t, *J* = 6.9 Hz, 3H), MS *m/z* 192 (M^+, 10 54); HRMS calcd for $C_{14}H_{24}$ 192.1878, found 192 1874. Anal Calcd for $C_{14}H_{24}$· C, 87.42, H, 12 58 Found C, 87 38, H, 12 83

(*R*)-(+)-1-Pentyl-4-(2-propenyl)-1-cyclohexene (29). Compound **29** was generated as described for **18** from (*R*)-(+)-perillyl pivalate (**28**) (1.18 g, 5 mmol) in 78% yield as a colorless oil· $[\alpha]_D$ +55.2° (*c* 3.1, $CHCl_3$); ^1H NMR δ 5 40 (br s, 1H), 4 70 (br s, 2H), 2 20-1.76 (m, 8H), 1.73 (s, 3H), 1 54-1.22 (m, 7H), 0 89 (br t, *J* = 6.9 Hz, 3H); HRMS calcd for $C_{14}H_{24}$ 192.1878, found 192 1877. Anal Calcd for $C_{14}H_{24}$: C, 87 42, H, 12.58 Found. C, 87 32; H, 12.64.

(*S*)-(-)-1-Pentyl-4-(2-propenyl)-cyclohexane-1,2-epoxide (19).[9] To a stirred solution of (*S*)-(-)-1-pentyl-4-(2-propenyl)-1-cyclohexene (**18**) (1.92 g, 10 mmol) in chloroform (50 mL) containing a catalytic amount of methyltrioctylammonium chloride (MTOAC) was added a solution of magnesium monoperoxyphthalic acid (MMPP) (85%, 5 82 g, 10 mmol) in water (50 mL) over 1 h at 50°C The mixture was stirred for a further 4 h at the same temperature The organic layer was separated, and the aqueous layer was extracted with chloroform (3 × 50 mL). The combined organic layers were washed with aqueous sodium bicarbonate (50 mL), dried over anhydrous magnesium sulfate and evaporated. The crude oil was purified by column chromatography on neutral grade III alumina Elution with hexane afforded (*S*)-(-)-1-pentyl-4-(2-propenyl)-cyclohexane-1,2-epoxide (**19**) (1.2 g, 58%) as a colorless oil consisting of a mixture of two diastereomers which was used in the next reaction without further separation. $[\alpha]_D$ -44 7° (*c* 8 0, $CHCl_3$), ^1H NMR δ (two diastereomers) 4 72, 4 67 (br s, br s, 2H), 3.04, 2.99, 2.97 (br s, br s, br s, 1H), 1.69, 1.67 (s, s, 3H), 2 20-1.27 (m, 15H), 0 89 (br t, *J* = 6.7 Hz, 3H), MS *m/z* 208 (M^+, 2 91), HRMS calcd for $C_{14}H_{24}O$ 208.1827, found 208 1832 Anal Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80 46, H, 11 91

(*R*)-(+)-1-Pentyl-4-(2-propenyl)-cyclohexane-1,2-epoxide (30). Compound **30** was prepared as described for **19** from (*R*)-(+)-1-pentyl-4-(2-propenyl)-1-cyclohexene (**29**) (1.92 g, 10 mmol) in 60% yield as a colorless oil consisting of two diastereomers which was used in the next reaction without further separation $[\alpha]_D$ +42 3° (*c* 4 0, $CHCl_3$), ^1H NMR δ (two diastereomers) 4.72, 4 67 (br s, br s, 2H), 3 04, 299, 2 97 (br s, br s, br s, 1H), 1.69, 1 67 (s, s, 3H), 2.20-1 27 (m, 15H), 0.89 (br t, *J* = 6.8 Hz, 3H), HRMS calcd for $C_{14}H_{24}O$ 208 1827, found 208.1832 Anal Calcd for $C_{14}H_{24}O$: C, 80 71, H, 11.61.

Found: C, 80.56, H, 11.80.

(*S*)-(-)-1-Pentyl-4-acetyl-1-cyclohexene (20).[10,11] A solution of (*S*)-(-)-1-pentyl-4-(2-propenyl)-cyclohexane-1,2-epoxide **(19)** (1.04 g, 5.0 mmol) in dichloromethane (50 mL) was cooled to -78°C while ozone was passed through the solution via a gas dispersion tube until the solution became blue in color. After that, nitrogen was passed through the solution for 15 min. Then the solution was added to a suspension of zinc dust (1.86 g, 28.6 mmol), sodium acetate (0.43 g, 5 2 mmol) and sodium iodide (1 27 g, 8.5 mmol) in glacial acetic acid (3 mL) at 0°C, and the mixture was allowed to warm slowly to room temperature and stirred overnight at that temperature. The zinc dust was removed by filtration and washed with dichloromethane (50 mL) The combined filtrates were washed successively with aqueous sodium bicarbonate (20 mL), brine (10 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a colorless oil which was purified by column chromatography with hexane/ethyl acetate (50 1) to furnish (*S*)-(-)-1-pentyl-4-acetyl-cyclohexene **(20)** (600 mg, 62%): $[\alpha]_D$ -66.0° (*c* 11 0, $CHCl_3$), ^1H NMR δ 5 39 (br s , 1H), 259-2.49 (m, 1H), 2 20-2 10 (m, 2H), 2.05-1.90 (m, 5H), 2 17 (s, 3H), 1 66-1 49 (m, 1H), 1 44-1 19 (m, 6H), 0 88 (br t, *J* = 6.9 Hz, 3H), ^{13}C NMR δ 210 40, 137.01, 117 78, 46.63, 36.49, 30 61, 26.92, 26.80, 26.42, 26 17, 24.12, 21.54, 12 96; MS *m/z* 194 (M^+, 23 89) Anal. Calcd for $C_{13}H_{22}O$ C, 80.35; H, 11.41. Found: C, 80 42; H, 11.56.

(*R*)-(+)-1-Pentyl-4-acetyl-cyclohexene (31). Compound **31** was prepared as described for **20** from (*R*)-(+)-1-pentyl-4-(2-propenyl)-cyclohexane-1,2-epoxide **(30)** (1 04 g, 5 0 mmol) in 65% yield as a colorless oil $[\alpha]_D$ +66 5° (*c* 11.5, $CHCl_3$), ^1H NMR δ 5 39 (br s, 1H), 2 59-2 49 (m, 1H), 2 20-2.10 (m, 2H), 2.17 (s, 3H), 2 05-1.90 (m, 5H), 1.66-1.49 (m, 1H), 1 44-1 19 (m, 6H), 0 88 (br t, *J* = 6 9Hz, 3H), ^{13}C NMR δ 210 80, 137 57, 118.53, 47.25, 37.22, 31 33, 27 62, 27 42, 27 11, 26.86, 24 82, 22 26, 13 68, MS *m/z* 194 (M^+, 29 58) Anal Calcd for $C_{13}H_{22}O$ C, 80.35, H, 11 41 Found: C, 80 02, H, 11 62.

(*S*)-(-)-4-Pentyl-3-cyclohexene-1-carboxylic Acid (21).[11] To a vigorously stirred solution of (*S*)-(-)-1-pentyl-4-acetylcyclohexene **(20)** (1 94 g, 10 mmol) in dioxane (40 mL) and 10% aqueous sodium hydroxide (10 mL) was added dropwise a solution of iodine-potassium iodide-water (1 2.1) at room temperature until the color of iodine persisted The mixture was stirred for an additional 1 h at room temperature, then warmed to 60 °C and stirred for a further 1 h at that temperature. After that, the reaction mixture was cooled to room temperature and quenched by addition of aqueous $Na_2S_2O_5$, and then acidified with hydrochloric acid and extracted with diethyl ether (3 × 50 mL) The organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate Upon evaporation of the solvent, the remaining oil was chromatographed on silica gel with hexane/ethyl acetate (4 1) to afford (*S*)-(-)-4-pentyl-3-cyclohexene-1-carboxylic acid **(21)** as a viscous oil (1 27 g, 65%) The optical purity was found to be 77% ee by conversion to the corresponding alcohol **33** and analysis by ^1H NMR spectra with $Eu(hfc)_3$ $[\alpha]_D$ -56 7° (*c* 4 2, $CHCl_3$), ^1H NMR δ 5 38 (br s, 1H), 2 60-2 49 (m, 1H), 2 30-2 20 (m, 2H), 2 10-1.90 (m, 5H), 1 79-1 61 (m, 1H), 1 44-1 16 (m, 6H), 0 88 (br t, *J* = 6.9 Hz, 3H), ^{13}C NMR δ 181 97, 137 92, 118 53, 39 35, 37 50, 31 58, 27 53 (2), 27 36, 25 41, 22 53, 13 96, MS *m/z* 196 (M^+, 32 65), HRMS calcd for $C_{12}H_{20}O_2$ 196 1463, found 196 1463 Anal Calcd for $C_{12}H_{20}O_2$ C, 73 43, H, 10 27. Found C, 73 51, H, 9 96

(*R*)-(+)-4-Pentyl-3-cyclohexene-1-carboxylic Acid (32). Compound **32** was prepared as described for **21** from (*R*)-(+)-1-pentyl-4-acetylcyclohexene **(31)** (1 94 g, 10 mmol) in 67% yield The optical purity was found to be 83% ee by conversion to the corresponding alcohol **(34)** and analysis by ^1H NMR spectra with $Eu(hfc)_3$ mp 65-66°C, $[\alpha]_D$ +52 1° (*c* 8 2, $CHCl_3$), ^1H NMR δ 5.38 (br s, 1H), 2 60-2 48 (m, 1H), 2 30-2 20 (m, 2H), 2 10-1 90 (m, 5H), 1 79-1 61 (m, 1H), 1 44-1 16 (m, 6H), 0 88 (br t, *J* = 6 9 Hz, 3H), ^{13}C NMR δ 182.24, 137 57, 118 35, 39 21, 37 33, 31 42, 27 30 (2), 27.16, 25 16, 22 39, 13 80, HRMS calcd for $C_{12}H_{20}O_2$ 196 1463, found 196 1457 Anal Calcd for $C_{12}H_{20}O_2$ C, 73 43, H, 10 27 Found C, 72 97, H, 10 09

(*S*)-(-)-4'-(4''-cyanobiphenyl) 4-Pentyl-3-cyclohexene-1-carboxylate (1). A solution of (*S*)-(-)-4-pentyl-3-cyclohexene-1-carboxylic acid **(21)** (196 mg, 1 0 mmol), 4-hydroxy-4'-cyanobiphenyl **(11)** (195 mg, 1 0 mmol), *N*,*N*'-dicyclohexylcarbodiimide (DCC) (206 mg, 1 0 mmol) in dry dichloromethane (20 mL) containing 4-dimethylaminopyridine (DMAP) (12 2 mg, 0 1 mmol) was stirred at room temperature overnight The reaction mixture was filtered and the filtrate was evaporated in vacuo The residue was chromatographed on silica gel with hexane/ethyl acetate (10 1) as an eluent and was further purified by recrystallization from hexane to afford (*S*)-(-)-4'-(4''-cyanobiphenyl) 4-pentyl-3-cyclohexene-1-carboxylate **(1)** (213 mg, 57%) mp 65-66°C, $[\alpha]^{22}_D$ -42.8° (*c* 2 72, $CHCl_3$), ^1H NMR δ 7 72, 7 66 (AB q, *J* = 8 5 Hz, 4H), 7 59, 7 20 (AB q, *J* = 8 6 Hz, 4H), 5 44 (br s, 1H), 2 81-2 74 (m, 1H), 2 50-2 40 (m,

2H), 2 22-2.09 (m, 3H), 2.00-1 81 (m, 3H), 1 47-1.23 (m, 6H), 0 90 (br t, J = 6.8 Hz, 3H); ^{13}C NMR δ 174 23 (C), 151.57 (C), 144.90 (C), 138.02 (C), 136 73 (C), 132.62 (CH), 128.25 (CH), 127.68 (CH), 122.29 (CH), 118.72 (C), 118.41 (CH), 111.22 (C), 39.72 (CH), 37.50 (CH_2), 31.58 (CH_2), 27.69 (CH_2), 27.51 (CH_2), 27.38 (CH_2), 25.56 (CH_2), 22.54 (CH_2), 13.99 (CH_3); MS *m/z* 373 (M^+, 1.53) Anal Calcd for $C_{25}H_{27}O_2N$: C, 80.40, H, 7.30, N, 3.75 Found: C, 80 20; H, 7.22; N, 3.63

(*S*)-(-)-4'-(4''-Octoxybiphenyl) 4-Pentyl-3-cyclohexene-1-carboxylate (2). A solution of (*S*)-(-)-4-pentyl-3-cyclohexene-1-carboxylic acid (**21**) (418 mg, 2.13 mmol), 4-hydroxy-4'-octoxybiphenyl (**13**) (686 mg, 2.3 mmol), *N*,*N*'-dicyclohexylcarbodiimide (DCC) (433 mg, 2.13 mmol) and 4-pyrrolidinopyridine (31 mg, 0.21 mmol) in diethyl ether (20 mL) was stirred at room temperature overnight. The resulting *N*,*N*'-dicyclohexylurea was filtered and the filtrate was washed with water (3 × 10 mL), 5% acetic acid solution (3 × 10 mL), again with water (3 × 10 mL), and dried over anhydrous magnesium sulfate The solvent was evaporated to give the crude product (*S*)-(-)-4'-(4''-octoxybiphenyl) 4-pentyl-3-cyclohexene-1-carboxylate (**2**) was obtained by flash column chromatography on silica gel eluted with toluene/hexane (2·3) (620 mg, 63%)· mp 148 °C (*n*-hexane); $[\alpha]^{23}_D$ -35 2° (*c* 2, $CHCl_3$); ^{1}H NMR δ 8 94, 8 44 (AB q, J = 8 42 Hz, 4H), 8 88, 8.26 (AB q, J = 8 74 Hz, 4H), 5 35 (br s, 1H), 3.92 (t, J = 6 62 Hz, 2H), 2 8-2 6 (m, 1H), 2.4-2.3 (m, 2H), 2.05-2.15 (m, 1H), 2 00-2.05 (m, 2H), 1 95-1 85 (m, 2H), 1 85-1 65 (m, 3H), 1.45-1 10 (m, 9H), 0 82 (br t, J = 6.6 Hz, 3H), ^{13}C NMR δ 174.52, 158.78, 149.82, 138 52, 137 89, 132 77, 128.05, 127 50, 121.69, 118 44, 114 82, 68 13, 39.63, 37 50, 31.81, 31 55, 29.36, 29 30, 29 23, 27.66, 27.49, 27.33, 26 06, 25 53, 22 64, 22.56, 14.06, 14.05; MS *m/z* 477 (M^++1, 4 2), 476 (M^+, 13.7), 298 (100), HRMS calcd for $C_{32}H_{44}O_3$ 476 3290, found 476 3326 Anal. Calcd for $C_{32}H_{44}O_3$ C, 80 63; H, 9.30 Found· C, 80 55, H, 9.33.

(*R*)-(+)-4'-(4''-cyanobiphenyl) 4-Pentyl-3-cyclohexene-1-carboxylate (3). Compound **3** was prepared as described for **1** from (*R*)-(+)-4-pentyl-3-cyclohexene-1-carboxylic acid (**32**) (196 mg, 1 0 mmol) in 74% yield $[\alpha]^{22}_D$ +41.3° (*c* 2 0, $CHCl_3$), ^{1}H NMR δ 7.71, 7 65 (AB q, J = 8.5 Hz, 4H), 7 58, 7 19 (AB q, J = 8 6 Hz, 4H), 5 44 (br s, 1H), 2 81-2.73 (m, 1H), 2.50-2.40 (m, 2H), 2 22-2.09 (m, 3H), 2 00-1 78 (m, 3H), 1 47-1 18 (m, 6H), 0.90 (br t, J = 6 8 Hz, 3H), ^{13}C NMR δ 174 13 (C), 151 53 (C), 144 80 (C), 137 95 (C), 136 63 (C), 132 54 (CH), 128 18 (CH), 127.61 (CH), 122 22 (CH), 118.64 (C), 118.36 (CH), 111 15 (C), 39 66 (CH), 37 44 (CH), 31 52 (CH_2), 27 63 (CH_2), 27 45 (CH_2), 27 32 (CH_2), 25 50 (CH_2), 22 47 (CH_2), 13.92 (CH_3), MS *m/z* 373 (M^+, 3.50). Anal Calcd for $C_{25}H_{27}O_2N$· C, 80 40, H, 7 30, N, 3 75. Found. C, 80 20; H, 7.28; N, 3.71

(*S*)-(-)-1-Pentyl-4-hydroxymethyl-1-cyclohexene (33). To a stirred suspension of lithium aluminum hydride (34 mg, 0.9 mmol, 80% excess) in anhydrous diethyl ether (5 mL) was added dropwise a solution of (*S*)-(-)-4-pentyl-3-cyclohexene-1-carboxylic acid (**21**) (98 mg, 0 5 mmol) in anhydrous diethyl ether (5 mL) at room temperature The mixture was stirred for 1 h, then the excess lithium aluminum hydride was destroyed by the addition of water and dilute hydrochloric acid The ether layer was washed with dilute sodium bicarbonate (5 mL), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure Column chromatography on silica gel with hexane/ethyl acetate (10·1) gave (*S*)-(-)-1-pentyl-4-hydroxymethyl-1-cyclohexene (**33**) as an oil in quantitative yield $[\alpha]^{24}_D$ -59 8° (*c* 1 0, $CHCl_3$, 77% ee); ^{1}H NMR δ 5 37 (br s, 1H), 3 53 (br s, 2H), 1 98-1 22 (m, 15H), 0 88 (br t, J = 6 9 Hz), 3H), MS *m/z* 182 (M^+, 9 01) Anal Calcd for $C_{12}H_{22}O$ C, 79 06, H, 12 16 Found C, 79 31, H, 11 80.

(*R*)-(+)-1-Pentyl-4-hydroxymethyl-1-cyclohexene (34). Compound **34** was prepared as described for **33** from (*R*)-(+)-4-pentyl-3-cyclohexene carboxylic acid (**32**) (98 mg, 0.5 mmol) as an oil in quantitative yield $[\alpha]^{24}_D$ +46 6° (*c*, 0 74, $CHCl_3$, 83% ee), ^{1}H NMR δ 5 37 (br s, 1H), 3 54 (br s, 2H), 1 96-1 22 (m, 15H), 0 88 (br t, J = 6 9 Hz, 3H); MS *m/z* 182 (M^+, 16 63) Anal Calcd for $C_{12}H_{22}O$ C, 79 06, H, 12 16 Found C, 79 45, H, 11 56

(4*S*)-(-)-Perillyl Butyl Ether (35).[14] To a stirred slurry of sodium hydride (4.4 g, 100 mmol, 85% dispersion in oil) in dry tetrahydrofuran (60 mL) at 45-50°C under nitrogen atmosphere was added a solution of *n*-butyl bromide (16 4 g, 13 mL, 120 mmol) in anhydrous tetrahydrofuran (20 mL), followed by the dropwise addition of a solution of (*S*)-(-)-perillalcohol (**16**) (12 2 g, 80 mmol) in anhydrous tetrahydrofuran (20 mL). After refluxing for a further 10 h, the reaction mixture was cooled and hydrolyzed by dropwise addition of sufficient water to dissolve any precipitate The aqueous layer was separated and extracted with diethyl ether (3 × 250 mL) The combined organic extracts were washed with brine (50 mL), dried over anhydrous magnesium sulfate, and evaporated The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (50 1) to give pure (*S*)-(-)-perillyl butyl ether (**35**)

(15.0 g, 90%) as a colorless oil: $[\alpha]^{22}_D$ -57 9 °(*c* 1.33, $CHCl_3$), ^{1}H NMR δ 5.70 (br s, 1H), 4.72 (br s, 2H), 3 83 (s, 2H), 3.37 (t, *J* = 6 6 Hz, 2H), 2.17-1.81 (m, 6H), 1.74 (s, 3H), 1 59-1.33 (m, 5H), 0.92 (br t, *J* = 7 3 Hz, 3H); ^{13}C NMR δ 149 83 (C), 135.16 (C), 123.73 (CH), 108.54 (CH_2), 75.11 (CH_2), 69.77 (CH_2), 41 26 (CH), 31 92 (CH_2), 30.56 (CH_2), 27 61 (CH_2), 26.45 (CH_2), 20.68 (CH_3), 19.40 (CH_2), 13.82 (CH_3), MS *m/z* 208 (M^+, 13.29) Anal Calcd for $C_{14}H_{24}O$ C, 80.71; H, 11.61 Found: C, 80 17; H, 11 62.

(*S*)-(-)-1-Butoxymethyl-4-(2-propenyl)-cyclohexane-1,2-epoxide (36). Compound **36** was prepared as described for **19** from (*S*)-(-)-1-perillyl butyl ether (**35**) (2 08 g, 10 mmol) in 55% yield as a colorless oil consisting of a mixture of two diastereomers which was used in the next reaction without further separation: $[\alpha]_D$ -40 4° (*c* 3.16, $CHCl_3$); ^{1}H NMR δ 4 72, 4 68 (br s, br s, 2H), 3 49-3.41 (m, 4H), 3.18, 3 13, 3 11 (br s, br s, br s, 1H), 2.17-1 26 (m, 14H), 0 92 (br t, *J* = 7.3 Hz, 3H), ^{13}C NMR δ 148.97 (C), 109 05 (CH_2), 74 91 (CH_2) 74 65 (CH_2), 71.30 (CH_2), 59.09 (C), 58 72 (C), 57 71 (CH), 56.25 (CH), 40 91 (CH), 36 84 (CH), 31.83 (CH_2), 30 61 (CH_2), 29 62 (CH_2), 26 31 (CH_2), 26.16 (CH_2), 24 76 (CH_2), 23.94 (CH_2), 20 87 (CH), 20 17 (CH), 19 30 (CH_2), 13 81 (CH_3), MS *m/z* 224 (M^+, 1 24) Anal Calcd for $C_{14}H_{24}O_2$· C, 74.95; H, 10 78 Found C, 74 99; H, 10 96

(*S*)-(-)-1-Butoxymethyl-4-acetyl-1-cyclohexene (37). Compound **37** was prepared as described for **20** from (*S*)-(-)-1-butoxymethyl-4-(2-propenyl)-cyclohexane-1,2-epoxide (**36**) (1 12 g, 5 0 mmol) in 30% yield as a colorless oil $[\alpha]_D$ -67 8° (*c* 3 76, $CHCl_3$), ^{1}H NMR δ 5.69 (br s, 1H), 3.83 (br s, 2H), 3 37 (t, *J* = 6.5 Hz, 2H), 2 60-2 57 (m, 1H), 2 23-1.99 (m, 5H), 2.18 (s, 3H), 1 68-1 50 (m, 3H), 1 45-1 30 (m, 2H), 0 92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR δ 210 96, 135 20, 122.26, 74.79, 69 82, 47.33, 31 82, 27 73, 26.67, 25 44, 24 66, 19 33, 13 76, MS *m/z* 169 (M-57, 1.17), 153 (M-73, 10 62). Anal Calcd for $C_{13}H_{22}O_2$ C, 74 24, H, 10 54 Found: C, 74 24; H, 10 16

(*S*)-(-)-4-Butoxymethyl-3-cyclohexene-1-carboxylic Acid (38). Compound **38** was prepared as described for **21** from (*S*)-(-)-1-butoxymethyl-4-acetyl-1-cyclohexene (**37**) (452 mg, 2 0 mmol) in 67% yield as a viscous oil $[\alpha]_D$ -60.0° (*c* 2 26, $CHCl_3$), ^{1}H NMR δ 10 2 (br, 1H), 5 68 (br, 1H), 3 84 (s, 2H), 3 38 (t, *J* = 6 6 Hz, 2H), 2 60-2 53(m, 1H), 2 32(m, 2H), 2 11-2.06(m, 3H), 1 77-1 71 (m, 1H), 1 59-1 50 (m, 2H), 1 44-1 30 (m, 2H), 0 91 (t, *J* = 7 3 Hz, 3H), ^{13}C NMR δ 181 30 (C), 135.01 (C), 122 14 (CH), 74 72 (CH_2), 69 72 (CH_2), 39 09 (CH), 31 70 (CH_2), 27 10 (CH_2), 25.01 (CH_2), 24 89 (CH_2), 19 28 (CH_2), 13 74 (CH_3), MS *m/z* 224 (M^+, 4 32) Anal Calcd for $C_{12}H_{20}O_3$· C, 67 89, H, 9 50 Found C, 67 72, H, 9 75.

(*S*)-(-)-4'-(4''-cyanobiphenyl) 4-Butoxymethyl-3-cyclohexene-1-carboxylate (4). Compound **4** was prepared as described for **1** from (*S*)-(-)-4-butoxymethyl-3-cyclohexene-1-carboxylic acid (**38**) (196 mg, 1 0 mmol) in 73% yield as colorless prisms $[\alpha]^{22}_D$ -44 7° (*c* 3 28, $CHCl_3$), ^{1}H NMR δ 7 65, 7 58 (AB q, *J* = 8 3 Hz, 4H), 7 54, 7 17 (AB q, *J* = 8 6 Hz, 4H), 5 72 (br s, 1H), 3.85 (s, 2H), 3 38 (t, *J* = 6 5 Hz, 2H), 2.87-2 76 (m, 1H), 2 50-2 40 (m, 2H), 2 24-2 12 (m, 3H), 1.93-1 81 (m, 1H), 1 62-1 51 (m, 2H), 1 45-1 31 (m, 2H), 0 92 (t, *J* = 7 3 Hz, 3H), ^{13}C NMR δ 173 45 (C), 151.12 (C), 144 21 (C), 136 18 (C), 135 01 (C), 132 20 (2CH), 127 81 (2CH), 127 21 (2CH), 121 89 (2CH), 121.36 (CH), 118 31 (C), 110 73 (C), 74 41 (CH_2), 69 50 (CH_2), 39 15 (CH), 31 54 (CH_2), 26 97 (CH_2), 24 77 ($2CH_2$), 19 07 (CH_2), 13 55 (CH_3), MS *m/z* 389 (M^+, 8 53) Anal Calcd for $C_{25}H_{27}NO_3$ C, 77 09, H, 6 99, N, 3 60 Found C, 76 59, H, 6.81, N, 3 46

(*S*)-(-)-Perillaldehyde (39). To a well stirred suspension of manganese dioxide (17.4 g, 0 2 mol) was added (*S*)-(-)-perillalcohol (**16**) (15 2 g, 10 mmol) at 0 °C. After absence of the starting alcohol, as determined by TLC, the residue of manganese dioxide was removed by suction filtration, and washed sufficiently with hexane The filtrate and the washings were combined and the solvent was removed under reduced pressure to afford (*S*)-(-)-perillaldehyde (**39**) as a colorless oil (1 2 g, 80%) The aldehyde was identical in all aspects with an authentic sample and shown to be more than 90% pure by ^{1}H-NMR analysis, which was used for the preparation of **40** without further purification ^{1}H NMR δ 9 44 (s, 1H), 6 84-6.82 (m, 1H), 4 78-4 77 (m, 1H), 4 74 (br s, 1H), 2 48-2 42 (m, 2H), 2 29-2 13 (m, 3H), 1.95-1.88 (m, 1H), 1 77 (s, 3H), 1 55-1 35 (m, 1H)

(*S*)-(-)-4-(2-Propenyl)-1-cyclohexene-1-carboxylic Acid (40).[15] Silver oxide was prepared by adding an aqueous solution of silver nitrate (1 7 g, 10 mmol) to an aqueous solution of sodium hydroxide (0 40 g, 10 mmol) Stirring during the addition ensured complete reaction and resulted in a brown semisolid mixture The silver oxide was collected and washed extensively free of nitrate with several portions of distilled water The wet oxide was covered with water (20 mL) and treated with sodium hydroxide pellets

(1.94 g, 48 5 mmol) with vigorous stirring, the temperature was adjusted to 55-60 °C, and the unpurified (*S*)-(-)-perillaldehyde (**39**) [freshly prepared from 1.52 g (10 mmol) of (*S*)-(-)-perillalcohol (**16**)] was added. After stirring for 20 minutes, the black silver suspension was removed by suction filtration and washed with several portions of hot distilled water. The cold combined filtrate and washings were acidified with dilute hydrochloric acid and extracted with dichloromethane (3 × 100 mL), dried over anhydrous magnesium sulfate. Column Chromatography on silica gel eluted with hexane/ethyl acetate (4:1) afforded (*S*)-(-)-4-(2-propenyl)-1-cyclohexene-1-carboxylic acid (**40**) [1.25 g, 75% overall from (*S*)-(-)-perillalcohol (**16**)], which was recrystallized from hexane to provide colorless prisms mp 130-132 °C, $[\alpha]^{25}_D$ -111 85 ° (*c* 1.94, $CHCl_3$), ^1H NMR δ 7.15-7 13 (m, 1H), 4.78-4.76 (m, 1H), 4.73 (br s, 1H), 2.55-2.12 (m, 5H), 1.94-1.87 (m, 1H), 1.75 (s, 3H), 1.60-1.40 (m, 1H), ^{13}C NMR δ 171.69 (C), 148.66 (C), 141 57 (CH), 129.56 (C), 109.31 (CH_2), 40.12 (CH), 31.36 (CH_2), 27.13 (CH_2), 24 32 (CH_2), 20.65 (CH_3); MS *m/z* 166 (M^+, 6.69). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26, H, 8.49. Found: C, 72.15; H, 8 47.

(*S*)-(-)-4'-(4''-Heptoxybiphenyl) 4-(2-Propenyl)-1-cyclohexene-1-carboxylate (5). Compound **5** was prepared as described for **1** from (*S*)-(-)-4-(2-propenyl)-1-cyclohexene-1-carboxylic acid (**40**) (166 mg, 1 0 mmol) in 62% yield as colorless prisms mp 102 °C, $[\alpha]^{26}_D$ -47.68° (*c* 2 51, $CHCl_3$); ^1H NMR δ 7.53, 7.14 (AB q, *J* = 8.6 Hz, 4H), 7.48, 6.95 (AB q, *J* = 8.8 Hz, 4H), 7 29-7 26 (m, 1H), 4.79 (br s, 1H), 4.76 (br s, 1H), 3.98 (t, *J* = 6.6 Hz, 2H), 2.65-2 58 (m, 1H), 2.41-2.35 (m, 2H), 2 24-2.17 (m, 2H), 1.99-1.92 (m, 1H), 1 83-1.74 (m, 2H), 1.78 (s, 3H), 1.58-1.28 (m, 10H), 0.90 (br t, *J* = 6 6 Hz, 3H); ^{13}C NMR δ 165.77 (C), 159.01 (C), 150.27 (C), 148 71 (C), 141.12 (CH), 138.56 (C), 133.08 (C), 129.98 (C), 128.15 (CH), 127.66 (CH), 121.91 (CH), 115.10 (CH), 109.44 (CH_2), 68.37 (CH_2), 40.26 (CH), 31 87 (CH_2), 31 49 (CH_2), 29 45 (CH_2), 29.12 (CH_2), 27 28 (CH_2), 26.14 (CH_2), 24.83 (CH_2), 22 64 (CH_2), 20 72 (CH_3), 14 03 (CH_3), MS *m/z* 432 (M^+, 47.16). Anal Calcd for $C_{29}H_{36}O_3$· C, 80.52, H, 8.39. Found: C, 80.66, H, 8.48.

(*S*)-(-)-4'-(4''-Octoxybiphenyl) 4-(2-Propenyl)-1-cyclohexene-1-carboxylate (6). Compound **6** was prepared as described for **1** from (*S*)-(-)-4-(2-propenyl)-1-cyclohexene-1-carboxylic acid (**40**) (166 mg, 1.0 mmol) in 58% yield as colorless prisms: mp 96 °C, $[\alpha]^{26}_D$ -41.08° (*c* 5.24, $CHCl_3$), ^1H NMR δ 7.46, 7.07 (AB q, *J* = 8 6 Hz, 4H), 7.41, 6.88 (AB q, *J* = 8.8 Hz, 4H), 7.29-7 26 (m, 1H), 4 72 (br s, 1H), 4.69 (br s, 1H), 3.91 (t, *J* = 6.6 Hz, 2H), 2.58-2.50 (m, 1H), 2.38-2.33 (m, 2H), 2.23-2.11 (m, 2H), 1.92-1.86 (m, 1H), 1 76-1 67 (m, 2H), 1 71 (s, 3H), 1 50-1 22 (m, 12H), 0 82 (br t, *J* = 6 9 Hz, 3H), ^{13}C NMR δ 165.72 (C), 158.98 (C), 150 25 (C), 148.67 (C), 141.09 (CH), 138.52 (C), 133.04 (C), 129 94 (C), 128 12 (CH), 127.63 (CH), 121 89 (CH), 115 07 (CH), 109 42 (CH_2), 68.34 (CH_2), 40.25 (CH), 31.87 (CH_2), 31.47 (CH_2), 29.43 ($2CH_2$), 29 27 (CH_2), 27.26 (CH_2), 26 17 (CH_2), 24.82 (CH_2), 22 67 (CH_2), 20.71 (CH_3), 14 03 (CH_3), MS *m/z* 446 (M^+, 29.94). Anal Calcd for $C_{30}H_{38}O_3$ C, 80 68; H, 8 58 Found· C, 80 68; H, 8 50

(*R*)-(+)-Perillaldehyde (41). Compound **41** was prepared as described for **39** from (*R*)-(+)-perillalcohol (**27**) (15.2 g, 10 mmol) in 80% yield as a colorless oil. The aldehyde was identical in all aspects with an authentic sample and shown to be more than 90% pure by ^1H NMR analysis, which was used for the preparation of **42** without further purification.. ^1H NMR δ 9 44 (s, 1H), 6.83-6 81 (m, 1H), 4.78-4 77 (m, 1H), 4 73 (br s, 1H), 2.49-2.41 (m, 2H), 2 28-2 11 (m, 3H), 1 94-1 87 (m, 1H), 1 75 (s, 3H), 1.55-1 35 (m, 1H)

(*R*)-(+)-4-(2-Propenyl)-1-cyclohexene-1-carboxylic Acid (42). Compound **42** was prepared as described for **40** from the unpurified (*R*)-(+)-perillaldehyde (**41**) [freshly prepared from 1.52 g (10 mmol) of (*R*)-(+)-perillalcohol (**27**)] as colorless prisms in 77% yield overall from (*R*)-(+)-perillalcohol (**27**): mp 130-132 °C, $[\alpha]^{26}_D$ +98.84 ° (*c* 0.86, $CHCl_3$); ^1H NMR δ 7 15-7 13 (m, 1H), 4.78-4 76 (m, 1H), 4.73 (br s, 1H), 2.55-2 12 (m, 5H), 1.95-1 87 (m, 1H), 1.76 (s, 3H), 1 60-1 40 (m, 1H); ^{13}C NMR δ 172 51 (C), 148 63 (C), 141 62 (CH), 129 65 (C), 109 28 (CH_2), 40.09 (CH), 31 33 (CH_2), 27 09 (CH_2), 24 25 (CH_2), 20.62 (CH_3), MS *m/z* 166 (M^+, 14 72). Anal Calcd for $C_{10}H_{14}O_2$. C, 72 26, H, 8 49 Found C, 71.91, H, 8 48

(*R*)-(+)-4'-(4''-Heptoxybiphenyl) 4-(2-Propenyl)-1-cyclohexene-1-carboxylate (7). Compound **7** was prepared as described for **1** from (*R*)-(+)-4-(2-propenyl)-1-cyclohexene-1-carboxylic acid (**42**) (166 mg, 1 0 mmol) in 62% yield as colorless prisms. mp 102 °C, $[\alpha]^{26}_D$ +39.13° (*c* 2 30, $CHCl_3$), ^1H NMR δ 7 54, 7 15 (AB q, *J* = 8 6 Hz, 4H), 7 48, 6.96 (AB q, *J* = 8 8 Hz, 4H), 7 29-7 26 (m, 1H), 4.80 (br s, 1H), 4 76 (br s, 1H), 3 99 (t, *J* = 6 6 Hz, 2H), 2 65-2 57 (m, 1H), 2 40-2 30 (m, 2H), 2.25-2 18 (m, 2H), 1 99-1 94 (m, 1H), 1 86-1 78 (m, 2H), 1 81 (s, 3H), 1 51-1 25 (m, 10H), 0 90 (br t, *J* = 6 6 Hz,

3H), ^{13}C NMR δ 165.77 (C), 159.00 (C), 150.27 (C), 148.71 (C), 141.12 (CH), 138.56 (C), 133.08 (C), 129.98 (C), 128.15 (CH), 127.66 (CH), 121 91 (CH), 115.10 (CH), 109.44 (CH_2), 68.38 (CH_2), 40 27 (CH), 31.87 (CH_2), 31.50 (CH_2), 29.46 (CH_2), 29.12 (CH_2), 27.29 (CH_2), 26.14 (CH_2), 24.83 (CH_2), 22.64 (CH_2), 20.73 (CH_3), 14.03 (CH_3); MS *m/z* 432 (M^+, 40.67) Anal. Calcd for $C_{29}H_{36}O_3$: C, 80 52, H, 8.39 Found: C, 80.38; H, 8.38.

(*R*)-(+)-4'-(4''-Octoxybiphenyl) 4-(2-Propenyl)-1-cyclohexene-1-carboxylate (8). Compound **8** was prepared as described for **1** from (*R*)-(+)-4-(2-propenyl)-1-cyclohexene-1-carboxylic acid (**42**) (166 mg, 1.0 mmol) in 56% yield as colorless prisms: mp 96 °C, $[\alpha]^{25}_D$ +41.41° (*c* 1.92, $CHCl_3$), ^{1}H NMR δ 7.54, 7.15 (AB q, *J* = 8 6 Hz, 4H), 7.49, 6 96 (AB q, *J* = 8.7 Hz, 4H), 7.29-7.26 (m, 1H), 4 80 (br s, 1H), 4.77 (br s, 1H), 3 99 (t, *J* = 6.6 Hz, 2H), 2 65-2.58 (m, 1H), 2.45-2 31 (m ,2H), 2.25-2 18 (m, 2H), 2 00-1 94 (m, 1H), 1.86-1.75 (m, 2H), 1 79 (s, 3H), 1.56-1 29 (m, 12H), 0.89 (br t, *J* = 6.7 Hz, 3H), ^{13}C NMR δ 165 78 (C), 159 00 (C), 150.26 (C), 148 71 (C), 141 12 (CH), 138.56 (C), 133 08 (C), 129 97 (C), 128 14 (CH), 127.66 (CH), 121.90 (CH), 115.10 (CH), 109.13 (CH_2), 68 37 (CH_2), 40.26 (CH), 31.89 (CH_2), 31.49 (CH_2), 29 43 (2CH_2), 29 29 (CH_2), 27 27 (CH_2), 26 17 (CH_2), 24.83 (CH_2), 22 69 (CH_2), 20.72 (CH_3), 14 03 (CH_3); MS *m/z* 446 (M^+, 32 82) Anal Calcd for $C_{30}H_{38}O_3$ C, 80 68, H, 8 58 Found· C, 80 38; H, 8 57

(5*S*)-2-Methylene-5-(2-propenyl)-1-cyclohexanol (44).[16] A solution of *n*-butyllithium (1 4 M, 85 5 mL, 0 12 mol) in hexane was added to diisopropylamine (11 1 g, 15 4 mL, 0 11 mol) in anhydrous diethyl ether (300 mL) at 0 °C under a nitrogen atmosphere After being stirred for 10 minutes, (*S*)-(-)-limonene oxide (**43**) [15 2 g, 16 4 mL, 0 10 mol, purchased from Aldrich Chem. Co (Aldrich 21,833-2) as a mixture of *cis* and *trans* isomers, $[\alpha]_D$ 69° (neat)] in anhydrous diethyl ether (60 mL) was added dropwise over a 30-minute period. The resulting mixture was warmed to room temperature and stirred for 12 h After the clear homogeneous mixture was cooled in an ice bath, water (300 mL) was added. The ether phase was separated and washed successively with 100 mL portions of 2N hydrochloric acid, water, saturated aqueous sodium bicarbonate, and brine. The aqueous phase and each washing was extracted twice with 50 mL portions of diethyl ether, and the ethereal extracts were combined, dried over anhydrous magnesium sulfate, distilled through a short distillation head and further purified by column chromatography on silica gel with hexane/ethyl acetate (20/1) to yield (5*S*)-(-)-2-methylene-5-(2-propenyl)-1-cyclohexanol (**44**) (89%) and a small amount of (3*S*)-6-Hydroxy-6-methyl-3-(2-propenyl)-1-cyclohexene (**45**) (2.7%) as a light yellow oil

(5*S*)-(-)-2-methylene-5-(2-propenyl)-1-cyclohexanol (**44**)· $[\alpha]^{22}_D$ -30 2° (*c* 5 30, $CHCl_3$); ^{1}H NMR δ 4 96-4 70 (m, 4H), 4.36-4 34 (m, 0.38 H), 4 09-4 06 (m, 0 62 H), 2 79 (br s, 1H), 2 49-1.17 (m, 7H), 1 71, 1 71 (s, s, 3H); ^{13}C NMR δ 151.06 (C), 149 97 (C), 149 25 (C), 148.49 (C), 109 36 (CH_2), 108 95 (CH_2), 108 75 (CH_2), 103 86 (CH_2), 72 20 (CH), 72 00 (CH), 44 14 (CH), 42 13 (CH_2), 39 17 (CH_2), 38 09 (CH), 33 73 (CH_2), 32 68 (CH_2), 32 59 (CH_2), 29 92 (CH_2), 20 78 (CH_3), 20 55 (CH_3), MS *m/z* 152 (M^+, 5 12) Anal. Calcd for $C_{10}H_{16}O$ C, 78 90, H, 10 59 Found C, 78.52; H, 10 64 ^{1}H NMR analysis showed the peak areas of the signals of the carbon-2 protons corresponding to 1 1 65 ratio of the two diastereomers.

(3*S*)-6-Hydroxy-6-methyl-3-(2-propenyl)-1-cyclohexene (**45**) ^{1}H NMR δ 5.72-5.59 (m, 2H), 4 78-4 77 (m, 1H), 4.67-4.66 (m, 1H), 2 80-2 70 (m, 1H), 2 17 (s, 1H), 1 73 (s, 3H), 2 00-1 40 (m, 4H), 1 28 (s, 3H), ^{13}C NMR δ 147 16(C), 134 55 (CH), 130 39 (CH), 110 69 (CH_2), 68 44 (C), 42 48 (CH), 36 11 (CH_2), 28 82 (CH_3), 25 03 (CH_2), 20 92 (CH_3), MS *m/z* 152 (M^+, 2.58). Anal Calcd for $C_{10}H_{16}O$ C, 78 90, H, 10 59 Found C, 78 29, H, 10.60

The ratio of (5*S*)-2-methylene-5-(2-propenyl)-1-cyclohexanol (**44**) and (3*S*)-6-hydroxy-6-methyl-3-(2-propenyl)-1-cyclohexene (**45**) was about 33 1

(5*S*)-2-Methylene-5-(2-propenyl)-1-cyclohexanone (46).[17] A solution of (5*S*)-2-methylene-5-(2-propenyl)-1-cyclohexanol (**44**) (1 52 g, 10 mmol) in dry dichloromethane (10 mL) was added to a solution of Dess-Martin periodinane (5 51 g, 13 mmol) in dry dichloromethane (100 mL) with stirring After 2 h, the homogeneous reaction mixture was diluted with diethyl ether (250 mL), and 5% sodium hydroxide (100 mL) was added to the resulting suspension of iodinane to hydrolyze the iodinane to the water-soluble 2-iodosobenzoate After the mixture was stirred for 10 minutes, the ether layer was separated and washed with 5% sodium hydroxide (100 mL), and water (100 mL), dried over anhydrous magnesium sulfate for 1 h Removal of the solvent under reduced pressure at below 30 °C yielded (5*S*)-2-methylene-5-(2-propenyl)-1-cyclohexanone (**46**) as a sensitive oil which polymerized upon prolonged standing at room temperature [Caution the solvent should not be removed completely to prevent the sensitive enone from polymerization] The crude enone was distilled azeotropically with benzene and used in the next reaction

without further purification. ^{1}H NMR δ 5.86 (br s, 1H), 5 17-5.16 (m, 1H), 4 81-4 79 (m, 1H), 4.73-4 72 (m, 1H), 2 80-1.50 (m, 7H), 1.76 (s, 3H)

(2*S*,5*S*)-2-Pentyl-5-(2-propenyl)-1-cyclohexanone (47). To a suspension of freshly recrystallized cuprous iodide (11.44 g, 60 mmol) in anhydrous diethyl ether (200 mL) was added a solution of *n*-butyllithium (1 4 M, 79 mL, 110 mmol) in hexane with stirring at 0℃ under a nitrogen atmosphere. After 10 min, the mixture was chilled to -78℃ and (5*S*)-(-)-methylene-5-(2-propenyl)-1-cyclohexanone (**46**) [freshly prepared by Dess-Martin oxidation of (5*S*)-2-methylene-5-(2-propenyl)-1-cyclohexanol (**44**) (10 mmol) and dried by azeotropic distillation with benzene at room temperature under vacuum] was introduced and the reaction mixture was stirred for 1 h at that temperature. The reaction was quenched with 2N aqueous hydrochloric acid (100 mL) followed by filtering. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous magnesium sulfate and concentrated. The crude product was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (50/1) to afford (2*S*, 5*S*)-(-)-2-pentyl-5-(2-propenyl)-1-cyclohexanone (**47a**) and (2*R*, 5*S*)-(-)-2-pentyl-5-(2-propenyl)-1-cyclohexanone (**47b**) [1 31g, 63% overall from (5*S*)-(-)-methylene-5-(2-propenyl)-1-cyclohexanone (**44**) (10 mmol)].

(2*S*, 5*S*)-(-)-2-Pentyl-5-(2-propenyl)-1-cyclohexanone (**47a**) $[\alpha]^{24}_D$ -4.2° (*c* 6.0, $CHCl_3$), ^{1}H NMR δ 4 75-4 72 (m, 2H), 2.44-2.13 (m, 5H), 1.98-1.91 (m, 1H), 1 72-1.64 (m, 2H), 1.72 (s, 3H), 1.34-1 23 (m, 8H), 0 87 (br t, *J* = 6 7 Hz, 3H), ^{13}C NMR δ 211.30 (C), 147 34 (C), 109.35 (CH_2), 49 86 (CH), 46 99 (CH_2), 46 99 (CH), 32 61 (CH_2), 31 82 (CH_2), 30.63 (CH_2), 28 75 (CH_2), 26.64 (CH_2), 22 31 (CH_2), 20 14 (CH_3), 13.73 (CH_3), MS *m/z* 209 (M+1, 8.17), 208 (M^+, 4 26), 209 (M+1, 8.17)18 Anal Calcd for $C_{14}H_{24}O$ C, 80 71; H, 11.61 Found: C, 80.35, H, 11.93

(2*R*, 5*R*)-(-)-2-Pentyl-5-(2-propenyl)-1-cyclohexanone (**47b**) ^{1}H NMR δ 4.81-4.80 (m, 1H), 4 71 (br s, 1H), 2 65-2 10 (m, 4H), 2.00-1 60 (m, 7H), 1.34-1 23 (m, 8H), 0 87 (br t, *J* = 6.7 Hz, 3H).

(2*S*,5*S*)-(-)-2-Pentyl-5-(2-propenyl)-1-cyclohexanone Ethylene Acetal (48).[18,19] A solution of (2*S*,5*S*)-(-)-2-pentyl-5-(2-propenyl)-1-cyclohexanone (**47**) (2 08 g, 10 mmol), ethylene glycol (3 10 g, 50 mmol) and pyridinium tosylate (750 mg, 3 mmol) in dry benzene (100 mL) was stirred vigorously and refluxed with water separation by a Dean-Stark trap with Drierite in the side arm to aid in water removal until the starting ketone was completely consumed (about 1 day). The mixture was cooled and washed with saturated aqueous sodium bicarbonate (20 mL), brine (10 mL), and dried over anhydrous magnesium sulfate The solvent was removed under reduced pressure to give the sufficiently pure ketal **48**, which was further purified by column chromatography on silica gel with hexane/ethyl acetate (50 1) (222 mg, 88%)· ^{1}H NMR δ 4 68 (br s, 2H), 3 96-3 93 (m, 4H), 2.35-1 00 (m, 19H), 0 88 (br t, *J* = 6 3 Hz, 3H), ^{13}C NMR δ 149 61, 111.18, 108 43, 65 05, 64.80, 44.86, 42 77, 40.50, 32.33, 31 13, 29 20, 27.95, 27 18, 22 65, 20 74, 14 01, MS *m/z* 252 (M^+, 5 2) Anal Calcd for $C_{16}H_{28}O_2$· C, 76 14, H, 11 18. Found C,75.72; H, 11 22

(2*S*,5*S*)-2-Pentyl-5-acetyl-1-cyclohexanone Ethylene Acetal (49). A solution of (2*S*,5*S*)-(-)-2-pentyl-5-(2-propenyl)-cyclohexanone ethylene acetal (**48**) [prepared from (5*S*)-(-)-2-pentyl-5-(2-propenyl)-1-cyclohexanone (**47**) (208 mg, 10 mmol)] in dichloromethane (20 mL) and methanol (20 mL) was saturated with ozone at -78℃ until the appearance of a persistent blue color The reaction mixture was flushed with oxygen for 10 minutes longer The ozonide was reduced by the addition of an excess of dimethyl sulfide at -78℃ and the mixture was allowed to warm to room temperature and stirred overnight. The excess of dimethyl sulfide and the solvent was removed under reduced pressure The residue was diluted with dichloromethane (50 mL), washed with brine (10 mL), and dried over anhydrous magnesium sulfate Solvent removal and column chromatography on silica gel with hexane/ethyl acetate (10/1) afforded (2*S*,5*S*)-(2-pentyl-5-acetyl-1-cyclohexanone ethylene acetal (**49**) [203 mg, 80% overall from (5*S*)-(-)-2-pentyl-5-(2-propenyl)-1-cyclohexanone (**47**)] as an oil $[\alpha]^{24}_D$ +28° (*c* 10, $CHCl_3$), ^{1}H NMR δ 4 02-3 90 (m, 4H), 2 63-2 62 (m 1H), 1.53 (s, 3H), 1 92-1 23 (m, 15H), 0 88 (t, *J* = 6 9 Hz, 3H), ^{13}C NMR δ 210 32 (C), 110 37 (C), 64 96 (CH_2), 64 80 (CH_2), 49 18 (CH), 44 45 (CH), 36 82 (CH_2), 32.13 (CH_2), 28 50 (CH_2), 27 69 (CH_3), 27 40 ($2CH_2$), 26 95 (CH_2), 22.48 (CH_2), 13.87 (CH_3), MS *m/z* 254 (M^+, 3.48), 211 (M-43, 100) Anal Calcd for $C_{15}H_{26}O_3$ C, 70 83, H, 10 30 Found C, 70.96, H, 10 53

(2*S*,5*S*)-2-Pentyl-5-hydroxycarbonyl-1-cyclohexanone Ethylene Acetal (50). To a well stirred solution of (2*S*,5*S*)-(-)-2-pentyl-5-(2-propenyl)-1-cyclohexanone) (**49**) (254 mg, 1 0 mmol) in dioxane (40 mL) and 10% aqueous sodium hydroxide (10 mL) was added dropwise a solution of iodine-potassium iodide in water (1.2 1) at room temperature until the color of iodine persisted. The mixture was stirred for an additional 1 h at room temperature, then warmed to 60 ℃ and stirred continuously for 1 h at that temperature After cooling to 0℃ in an ice-bath, the solution of the crude acid salt was treated with saturated

aqueous $Na_2S_2O_5$ and then acidified to pH 5 by dropwise addition of 6N hydrochloric acid and extracted with diethyl ether (5 × 50 mL) The organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. Upon evaporation of the solvent an oil remained which was chromatographed on silica gel with ethyl acetate to afford (2*S*,5*S*)-2-pentyl-5-hydroxycarbonyl-1-cyclohexanone ethylene acetal (**50**) (145 mg, 57%) $[\alpha]^{23}_D$ +26 5° (*c* 7 1, EtOAc), ^{1}H NMR δ 3.96-3.84 (m, 4H), 2 58-2.48 (m, 1H), 2 02-1 82 (m, 3H), 1 78-0.90 (m, 12H), 0 81 (br t, *J* = 6 7 Hz, 3H); ^{13}C NMR δ 181 41 (C), 110 04 (C), 65 00 (CH_2), 64 92 (CH_2), 44 34 (CH), 40 97 (CH), 37 25 (CH_2), 32 22 (CH_2), 28 23 (CH_2), 27 85 (CH_2), 27.61 (CH_2), 27 01 (CH_2), 22.60 (CH_2), 14 02 (CH_3); MS *m/z* 256 (M^+, 29 82). HRMS calcd for $C_{14}H_{24}O_4$ 256 1674, found 256 1670.

(1*S*,4*S*)-4-Pentyl-3-cyclohexanone-1-carboxylic Acid (51). (2*S*,5*S*)-2-Pentyl-5-hydroxycarbonyl-1-cyclohexanone ethylene acetal (**50**) (256 mg, 1 0 mmol) was dissolved in acetone (5 mL) and treated with a catalytic amount of 6 N hydrochloric acid at room temperature. The reaction was quenched after 3 h by addition of saturated sodium bicarbonate (50 mL) The mixture was extracted with dichloromethane (3 × 20 mL). The organic layer was washed with brine (10 mL), dried over anhydrous magnesium sulfate Upon evaporation of the solvent an oil remained which was purified by column chromatography on silica gel eluted with ethyl acetate to afford (1*S*,4*S*)-4-pentyl-3-cyclohexanone-1-carboxylic acid (**51**) (180 mg, 85%) $[\alpha]^{22}_D$ +8 5° (*c* 2 0, EtOAc), ^{1}H NMR δ 10.1 (br, 1H), 2 82-2 52 (m, 3H), 2 28-2 18 (m, 3H), 1 90-1 78 (m, 2H), 1 42-1 26 (m, 8H), 0 88 (br t, *J* = 6.7 Hz, 3H), ^{13}C NMR δ 210 11, 179.07, 49 95, 44 13, 43 30, 31.89, 31 84, 28 82, 28.06, 26 68, 22 46, 13.90; MS *m/z* 212 (M^+, 1 34) Anal Calcd of the methyl ester of **45** for $C_{13}H_{22}O_3$ C, 68 99, H, 9.79 Found C, 69.52; H, 9 62

(1*S*,4*S*)-4'-(4''-Heptoxybiphenyl) 4-Pentyl-3-cyclohexanone-1-carboxylate (9). Compound **9** was prepared as described for **1** from (1*S*,4*S*)-4-pentyl-3-cyclohexanone-1-carboxylic acid (**51**) (106 mg, 0 5 mmol) This material can be further recrystallized from hexane to afford (1*S*,4*S*))-4'-(4''-heptoxybiphenyl) 4-pentyl-3-cyclohexanone-1-carboxylate (**9**) (180 mg, 75%). ^{1}H NMR δ 7.54, 7 11 (AB q, *J* = 8 6 Hz, 4H), 7 48, 6 96 (AB q, *J* = 8 8 Hz, 4H), 3 99 (t, J = 6 6 Hz, 2H), 2 90-3 05 (m, 1H), 2.82-2 65 (m, 2H), 2 45-2 30 (m, 3H), 2 03-1.75 (m, 5 H), 1 45-1 10 (m, 15H), 0.92-0 87 (m, 6H), ^{13}C NMR δ 209 70 (C), 172 09 (C), 158 95 (C), 149 55 (C), 138 93 (C), 132 65 (C), 128 06 (2CH), 127 67 (2CH), 121 46 (2CH), 114 95 (2CH), 68 21 (CH_2), 50 03 (CH), 44 57 (CH), 43 61 (CH_2), 31.95 ($2CH_2$), 31 78 (CH_2), 29 33 (CH_2), 29 04 (CH_2), 28 89 (CH_2), 28 31 (CH_2), 26 75 (CH_2), 26 03 (CH_2), 22 57 (CH_2), 22 57 (CH_2), 13 98 ($2CH_3$), MS *m/z* 478 (M^+, 14 29) Anal Calcd for $C_{31}H_{42}O_4$· C, 77 79; H, 8 84 Found C, 77 23, H, 8 75

(2*S*,5*S*)-2-Pentyl-5-hydroxymethyl-1-cyclohexanone Ethylene Acetal (52). To a stirred suspension of lithium aluminum hydride (34 mg, 0 9 mmol, 80% excess) in anhydrous diethyl ether (5 mL) was added dropwise a solution of (2*S*,5*S*)-2-pentyl-5-hydroxycarbonyl-1-cyclohexanone ethylene acetal (**50**) (128 mg, 0 5 mmol) in anhydrous diethyl ether (5 mL) at room temperature The mixture was allowed to stir for 1 h, then the excess lithium aluminum hydride was destroyed by the addition of ethyl acetate and water The organic layer was separated, and the aqueous layer was extracted with diethyl ether The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure Column chromatography on silica gel with hexane/ethyl acetate (10·1) gave (2*S*,5*S*)-2-pentyl-5-hydroxymethyl-1-cyclohexanone ethylene acetal (**52**) as an oil in quantitative yield $[\alpha]^{23}_D$ +12 3° (*c* 6 0, *n*-C_6H_{14}), ^{1}H NMR δ 3 96-3 89 (m, 4H), 3 44-3 41 (m, 2H), 1 90-0 95 (m, 15H), 0.85 (br t, *J* = 6 8 Hz), 3H), ^{13}C NMR δ 110 93 (C), 67 90 (CH_2), 64.99 (CH_2), 64.78 (CH_2), 45 02 (CH), 38 44(CH_2), 38 40 (CH), 32 28 (CH_2), 28 46 ($2CH_2$), 27 87 (CH_2), 27.15 (CH_2), 22 61 (CH_2), 13.99 (CH_3), MS *m/z* 242 (M^+, 11 74) HRMS calcd for $C_{14}H_{26}O_3$ 242 1882, found 242 1919

(2*S*,5*S*)-2-Pentyl-5-hydroxymethyl-1-cyclohexanone (53). (2*S*,5*S*)-2-Pentyl-5-hydroxymethyl-1-cyclohexanone ethylene acetal (**52**) (121 mg, 0 5 mmol) was dissolved in acetone (5 mL) and treated with a catalytic amount of 6 N hydrochloric acid at room temperature The reaction was quenched after 3 h by addition of saturated sodium bicarbonate (50 mL) The mixture was extracted with dichloromethane (3 × 20 mL) The organic layer was washed with brine (10 mL), dried over anhydrous magnesium sulfate Upon evaporation of the solvent an oil remained which was purified by column chromatography on silica gel eluted with hexane/ethyl acetate (4·1) to afford (2*S*,5*S*)-2-pentyl-5-hydroxymethyl-1-cyclohexanone (**53**) (89 mg, 90%) $[\alpha]^{23}_D$ -2.7° (*c* 4 0, $CHCl_3$), ^{1}H NMR δ 3 57 (br s, 1H), 3 55 (br s, 1H), 2 40-1 10 (m, 16H), 0 87 (br t, *J* = 6 8 Hz, 3H), MS *m/z* 198 (M^+, 3 74) HRMS

calcd for $C_{12}H_{22}O_2$ 198.1620, found 198 1679

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