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CHIRAL MESOGENS CONTAINING THE 2,3-DIHYDROBENZOPYRAN NUCLEUS

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Abstract Some chiral derivatives containing the 2,3-dihydrobenzopyran unit were synthesised and their thermotropic behaviour was investigated. Noticeably, *p*-cyanobenzoates of 2-alkyl-2,3-dihydrobenzopyrans showed S_A mesophases with good stability near to room temperature.

INTRODUCTION

In the large majority of the cases, asymmetry in chiral liquid crystals is introduced as a chirality centre located in an aliphatic tail. The synthesis of calamitic liquid crystals bearing a chirality element in the core of the molecule is still a challenging task.

There is in fact a sort of internal contradiction in having a chirality element located in the typically rigid and flat central part of the molecule, as any small deviation from linearity can strongly inhibit the ability of molecules to self-assemble into mesophases. On the other hand, the restricted conformational freedom of a stereogenic centre located in the core of the molecule should markedly affect the mesophase properties: chiral core mesogens for instance have been shown to possess extremely short cholesteric pitches[1].

We have already described the synthesis of thermotropic properties of some 2-substituted 2,3-dihydrobenzopyran-6-carboxylic acids and esters[2]. Some liquid crystalline 2,3-dihydrobenzopyrans have also been reported by other groups[3a]. A few homochiral 2,3-dihydrobenzopyrans have been tested as chiral dopants[3b].

In this paper we report our further investigation on the 2,3-dihydrobenzopyran nucleus. Derivatives of type **A**, **B** and **C** (Figure 1) have been synthesised and their thermotropic properties have been studied.

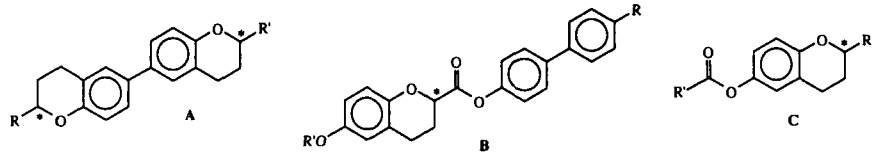


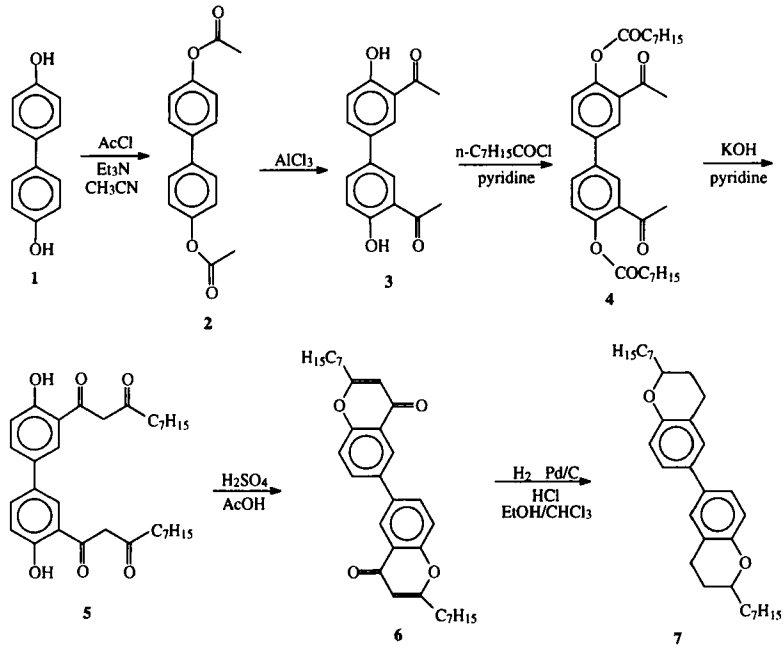
FIGURE 1

RESULTS AND DISCUSSION

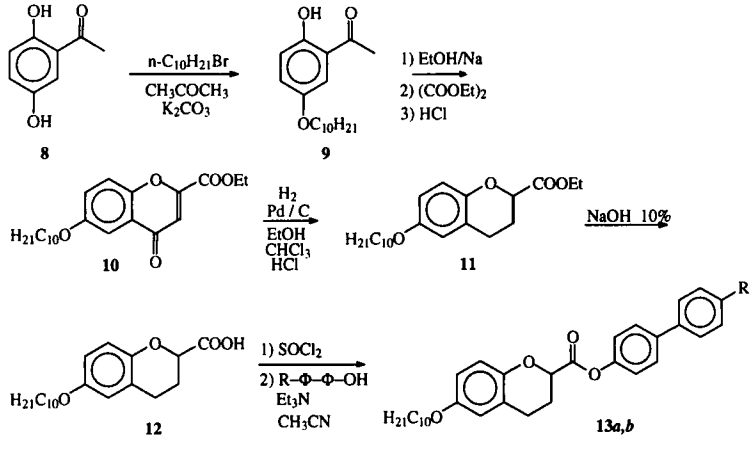
Synthesis

Derivative **A**, namely 2,2'-diheptyl-6,6'-dibenzopyran **7**, carrying a biphenyl moiety and two chirality centres, was prepared starting from 4,4'-dihydroxybiphenyl **1** (Scheme 1). Esterification with acetyl chloride in the presence of triethylamine, followed by $AlCl_3$ catalysed Fries rearrangement afforded diketone **3**. This compound was esterified with octanoyl chloride in pyridine to produce derivative **4**, which underwent a base-promoted intramolecular Claisen condensation to afford bis-diketone **5**. Acid catalysed dehydration of the corresponding hemiacetal produced 6,6'-bichromane **6**, which was catalytically reduced to the target compound **7**.

Derivatives **B** were prepared starting from 2,5-dihydroxyacetophenone **8** (Scheme 2), which was converted to its 4-n-decyl ether **9** and condensed with diethyl oxalate to produce chromen-4-one **10**. This compound was catalytically reduced with H_2 over Pd to 2,3-dihydrobenzopyran **11**. Hydrolysis of the ester function followed by conversion into the acid chloride and esterification with hydroxy biphenyls afforded derivatives **13*a*** and **13*b***.



SCHEME 1



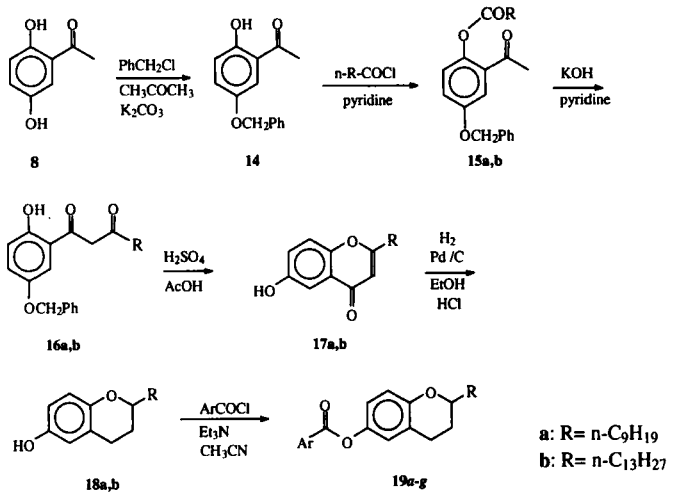
SCHEME 2

Derivatives **C** were prepared as described either in scheme 3 or 4.

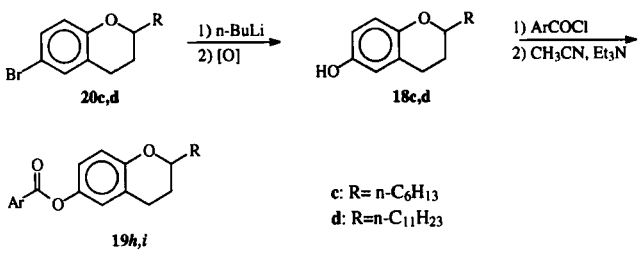
According to scheme 3, dihydroxyacetophenone **8** was protected at the 5-hydroxy function with benzyl chloride[4]. Esterification of the 2-hydroxy function with either decanoyl chloride or tetradecanoyl chloride afforded derivatives **15a** and **15b**,

respectively. Intramolecular Claisen condensation and acidic treatment of the diketones **15a** and **15b** thus obtained, produced the deprotected chromen-4-ones **17a** and **17b**, which were converted into the corresponding 2,3-dihydrobenzopyrans **18a** and **18b** by catalytic hydrogenation. Esterification of the hydroxy function with different aroyl chlorides gave rise to target esters ***19a-g***.

The alternative synthetic route started from 6-bromo-2-hexyl-2,3-dihydrobenzopyran **20c** or 6-bromo-2-undecyl-2,3-dihydrobenzopyran **20d**, prepared as described previously[2]. Metal-halogen exchange followed by oxidation with hexamethyldisilyl peroxide[5] or (1S)-(+)-(10-camphorsulphonyl)oxaziridine[6] gave phenols **18c,d**. Esterification with 4-cyanobenzoic acid chloride afforded the target derivatives ***19h,i***.

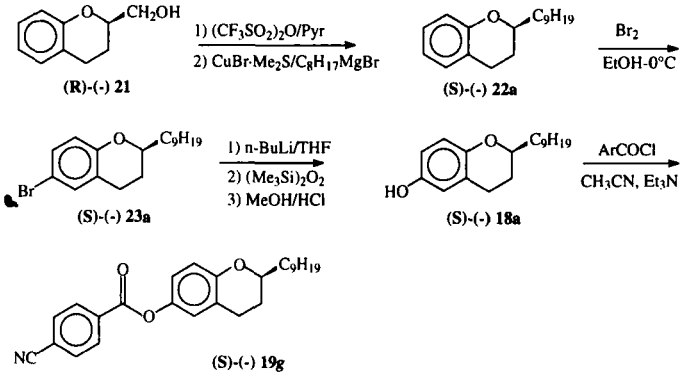


SCHEME 3



SCHEME 4

Optically pure (S)-(-)-**19*g*** was prepared from optically pure alcohol (R)-(-)-**21**[2,7] (Scheme 5). The alcohol was converted into the corresponding triflate and reacted with octylmagnesiumbromide in the presence of catalytic $CuBr{\cdot}Me_2S$ to afford (S)-(-)-2-nonyl-2,3-dihydrobenzopyran **22a**. Regiospecific bromination, metal-halogen exchange with n-BuLi and oxidation with hexamethyldisilylperoxide[5] produced phenol (S)-(-)-**18a**, which was converted into target ester (S)-(-)-**19*g*** upon treatment with 4-cyanobenzoic acid chloride.



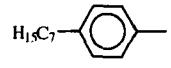
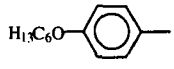
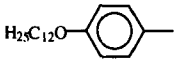
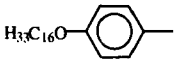
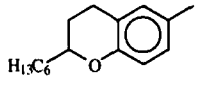
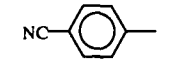
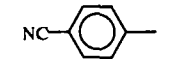
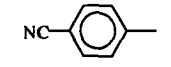
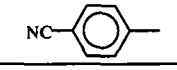
SCHEME 5

Mesomorphic properties

The mesomorphic properties of the target compounds synthesised, as obtained from polarising microscopy, differential scanning calorimetry and X-ray diffraction, are reported in table 1. Compound **7** (type **A**) had a sharp melting point, with no appearance of mesophases neither on heating nor on cooling. Also between derivatives of type **B** only **13*b*** did show a narrow monotropic nematic phase on cooling. The large majority of derivatives of type **C** possessed instead mesomorphic character. Derivative **19*a*** is the only one showing a sharp melting point. Replacement of the alkyl chain with an alkoxy chain of analogous length produced the appearance of a nematic phase (**19*b***), whose stability increased when the alkoxidic chain length was increased (**19*c***), leading eventually to the appearance of a smectic phase (**19*d***). Derivative **19*e***, obtained by esterification of **18a** with 2-hexyl-2,3-dihydrobenzopyran-6-carboxylic acid, which possesses itself liquid crystalline properties (K 128 N 142 I)[2], showed a nematic phase in a narrow range: in spite of its reduced linearity, **19*e*** did not behave differently from dimensionally similar derivative **19*b***. Among the derivatives obtained, the most interesting are the *p*-cyanobenzoates **19*f-i***, which showed almost exclusively S_A

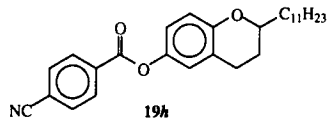
mesophases with good stability and at temperatures not too far from room temperature. Optically pure (S)-(-)-**19*g*** showed the same behaviour as racemic **19*g***.

Table 1. Mesogenic properties of target compounds.

Derivative	R	Ar	Phase transitions (°C)#
(±) **7**	-	-	**K** 106 **I**
(±) **13*a***	n-$C_{12}H_{25}O$-	-	**K** 153 **I**
(±) **13*b***	-CN	-	**K** 128 **I**§
(±) **19*a***	-C_9H_{19}		**K** 67 **I**
(±) **19*b***	-C_9H_{19}		**K** 72 **N** 76 **I**
(±) **19*c***	-C_9H_{19}		**K** 68 **N** 78 **I**
(±) **19*d***	-C_9H_{19}		**K** 67 S_A 81 **I**
(±) **19*e***	-C_9H_{19}		**K** 77 **N** 79 **I**
(±) **19*f***	-C_6H_{13}		**K** 76 **N** 88 **I**
(±) **19*g***	-C_9H_{19}		**K** 73 S_A 94 **I**
(S)-(-) **19*g***	"	"	"
(±) **19*h***	-$C_{11}H_{23}$		**K** 70 S_A 95 **I**
(±) **19*i***	-$C_{13}C_{27}$		**K** 81 S_A 107 **I**

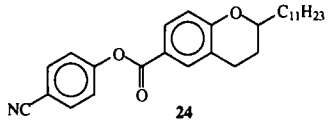
(#) **K** = crystal, S_A = smectic A, **N** = nematic, **I** = isotropic. Data refer to heating cycles.
(§) The compound shows a monotropic nematic phase between 106 and 103 °C.

It is interesting to notice how a minor change in the molecular structure can strongly affect molecular interactions responsible for mesophases stability. In figure 2 compound **19*h*** is compared with ester **24**, previously obtained by us[2]. The two derivatives possess identical geometry and length, but differ because of the inverted connectivity of the carboxylic group: this determines both a difference on the kind of mesophases and on their overall stability range.



19*h*

K 70 S_A 95 I



24

K 75 S_A 84 N 88 I

FIGURE 2

X-RAY DIFFRACTION EXPERIMENTS

Figure 3 presents four X-ray diffraction spectra (a-d) of (±)**19*g*** obtained at different temperatures during the first thermal cycle: there are many sharp peaks appearing on both spectra (a, 20°C) and (b, 65°C) which indicate that the sample forms two different crystalline phases on heating. The two crystalline phases are metastable, since they appear only during the first heating run. Spectrum (c) was recorded at 85°C during the first heating cycle and is characterised by a sharp low angle peak and a diffuse wide angle halo, which clearly demonstrates the formation of a disordered smectic phase with layer spacing of 41.3 Å. The smectic phase is stable up to 95°C and was also observed in the cooling cycle from 90°C to 60°C. Below this temperature, a crystalline phase forms: the diffraction pattern of spectrum (d, 20°C) indicates that this stable phase, which forms after the first heating and cooling cycle, is different from those observed during the heating process.

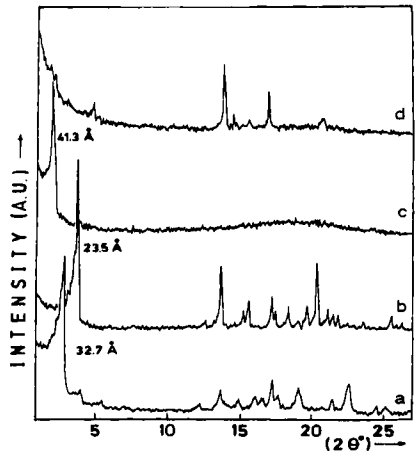


FIGURE 3

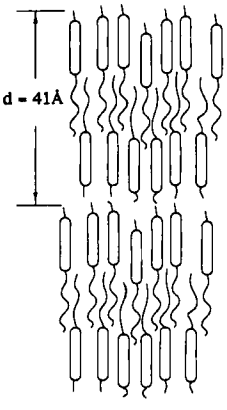


FIGURE 4

The phases sequence for (±)**19*i*** is very similar to the one observed for (±)**19*g***. Also in this case, two metastable crystalline phases, one disordered smectic phase and a stable crystalline phase after the first heating and cooling cycle have been detected. For this sample, the layer spacing of the smectic phase is 46.5 Å.

To conclude, the two samples have very similar structure and thermal behaviour.

In order to gain information about the structural properties of the smectic phase, several models of packing were examined, on the basis of molecular length and d-spacing. The fully extended molecular length of (±)**19*g*** and (±)**19*i*** are ca. 25.8 Å and 23.3 Å, respectively: the best results show that molecules pack "head-to-head" with -CH_2- chains interdigitated each other. Smectic bilayers with the thickness of 41 Å and 46 Å for (±)**19*g*** and (±)**19*i*** respectively are present, in agreement with observed d-spacings (figure 4). According to this model, the smectic phase can be described as a smectic A phase.

EXPERIMENTAL

Melting points are uncorrected. Yields represent isolated compounds. ^1H and ^{13}C NMR spectra were run at 200 or 300 MHz in $CDCl_3$ as solvent, and data are reported on the δ scale relative to TMS as reference. Coupling constants are reported in Hz. ^{13}C NMR assignments were confirmed by DEPT experiments. FTIR were recorded on a FTIR spectrometer. Optical rotations were measured with a digital polarimeter in a 1 dm cell. Mass spectra were obatined at 70 eV (EI). DSC thermograms were recorded over 5 mg samples at 5 °C/min heating rate. TLC chromatography was performed on precoated silica gel IBF2 plates (Baker). Silica gel 60 (70-230 mesh) (Merk) was used for column chromatography. Preparative plates (20×20 cm, 1 mm thickness) were prepared from silica gel 60PF254 (Merk).

Reagents were used as purchased, without further purification. For reactions requiring anhydrous conditions, solvents and reagents were dried according to standard procedures. (R)-(-)-2-(Hydroxymethyl)-2,3-dihydrobenzopyran (R)-(-) **21** was obtained according to the procedure described by Urban and Moore[7], by using lipase from Pseudomonas fluorescens (Fluka).

4,4'-Diacetoxybiphenyl **2**. To a solution of 5.0 g (27 mmol) of 4,4'-dihydroxybiphenyl in 50 mL of acetonitrile were added 8.5 mL (59 mmol) of triethylamine and 4.2 mL (59 mmol) of acetyl chloride. The mixture was stirred at room temperature for 4 h, then poured on 10% $NaHCO_3$ (20 mL) and extracted with Et_2O (2×30 mL). The combined organic fractions were dried over Na_2SO_4 and solvents were removed under reduced pressure. Crystallization (EtOH) of the crude reaction mixture afforded **2** in a 96% yield as white crystals. mp 158°-160°C; ^1H-NMR: δ 2.31 (s, 6H), 7.12-7.56 (AB quartet, 8H) ppm; MS: *m/z* 270 (M^+), 228, 186, 43; IR: ($CHCl_3$) 1760 cm^{-1}.

3,3'-Diacetyl-4,4'-dihydroxybiphenyl **3**. Finely powdered 4,4'-diacetoxybiphenyl **2** (1.0 g, 3.7 mmol) and dry $AlCl_3$ (1.6 g, 12 mmol) were mixed in a flask connected to a NaOH trap via a $CaCl_2$ guard tube. The mixture was progressively heated to 170°C and allowed to react for 3 h. After cooling, crushed ice (7 g) was carefully added, followed by conc. HCl (0.5 mL). The resulting yellow-green solid was filtered and washed with water. Chromatography ($CHCl_3$) of the residue afforded **3** as a yellow solid in a 57% yield. m.p.: 212-214° C; ^{1}H-NMR: δ 2.68 (s, 6H), 7.08 (d, *J*=7.4, 2H), 7.64 (dd, *J*=7.4 and 1.5, 2H), 7,81 (d, *J*=1.5, 2H) 8.15 (s, 2H); MS: *m/z* 270 (M^+), 255, 120, 43; IR: (CCl_4) 3400, 1660 cm^{-1}.

3,3'-Diacetyl-4,4'-dioctanoyloxybiphenyl **4**. A solution of 3,3'-diacetyl-4,4'-dihydroxybiphenyl **3** (0.80 g, 3.0 mmol) and n-octanoyl chloride (1.3 mL, 7.7 mmol) in 2.5 mL of pyridine was stirred at room temperature under inert atmosphere for 22 h. The reaction mixture was then poured onto 15 g of crushed ice and 30 mL of HCl 1N and extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was chromatographed on silica (CH_2Cl_2 / MeOH 100:1). The product was obtained in a 77% yield as a white solid. mp 79°-81° C; ^{1}H-NMR: δ 0.90 (t, 6H), 1.25-1.50 (m, 16H), 1.80 (quint., 4H), 2.6 (s, 6H), 2.65 (t, 4H,), 7.21 (d, *J*=8.7, 2H), 7.72 (dd, *J*=8.7 and 2.4, 2H), 7.95 (d, *J*=2.4, 2H); MS: *m/z* 522 (M^+), 396, 270, 255, 127, 57, 43; IR: (CCl_4) 1770, 1695 cm^{-1}.

1-[4,4'-Dihydroxy-3'-(3-oxo-decanoyl)-biphenyl-3-yl]-decane-1,3-dione **5**. Powdered KOH (0.40 g 7.0 mmol) was added under inert atmosphere and with stirring to a solution of **4** (1.2 g, 2.3 mmol) in pyridine (5 mL). The mixture was heated at 50°C for 1h, then cooled to room temperature. A 10% solution of acetic acid (5 mL) was then added and the resulting deep red oil was stirred for a few minutes, diluted with 5 mL of water and extracted twice with $CHCl_3$ (2×15 mL). The collected organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude was chromatographed on silica (CH_2Cl_2 as the eluent) and the title compound was obtained in a 45% yield as yellow glass (80% purity). ^{1}H-NMR: δ 0.85 (t, 6H), 1.28 (m, 16H), 1.65 (quint, 4H), 2.38 (t, 4H), 4.18 and 6.22 (2s, 4H), 7.05 (d, *J*=8.5, 2H), 7.58 (dd *J*=8.5 and 2.4, 2H), 7.70 (d, *J*=2.4, 2H), 12.10 (s, 2H); MS: *m/z* 522 (M^+), 396, 270, 57, 43.

2,2'-Diheptyl-[6,6']-bichromenyl-4,4'-dione **6**. Glacial acetic acid (2 mL) was added to compound **5** (0.69 g, 80% purity, 1 mmol) and the mixture was heated at 50°C until complete dissolution. After cooling to room temperature, 0.2 mL of conc. H_2SO_4 were added, the solution was heated to 90°C and left under stirring for 1.5 h. After cooling, the reaction mixture was poured onto 15 g of crushed ice and extracted with $CHCl_3$ (2×20 mL). The combined organic fractions were dried (Na_2SO_4) and solvents were removed under reduced pressure. Chromatography on silica afforded the title compound as sticky solid (72% purity, 69% yield). ^{1}H-NMR: δ 0.9 (t, 6H), 1.33 (m, 16H), 1.75 (quint, 4H), 2.68 (t, 4H), 6.24 (s, 2H), 7.55 (d, *J*=8.5, 2H), 8.00 (dd, *J*=8.5 and 2.4, 2H), 8.46 (d, *J*=2.4, 2H); MS: *m/z* 486 $(M)^+$, 415, 402, 378, 363; IR: (CCl_4) 1660-1615 cm^{-1}.

(±) 2,2'-Diheptyl-2,3,2',3'-tetrahydro-[6,6'] dibenzopyran **7**. Ketone **6** (0.50 g, 72% purity, 0.69 mmol) was dissolved in 1.0 mL of $CHCl_3$ and 2.0 mL of absolute ethanol. To this solution were added 0.12 g of Pd 10% on carbon and 0.6 mL of conc. HCl and the resulting suspension was left under H_2 pressure (2 bar) in a Parr apparatus for 4 days. The crude reaction mixture was then filtered through Celite and the filter was washed with $CHCl_3$ (2×10 mL). The filtrate was washed with water (2×10 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica (CH_2Cl_2) affording a pale yellow solid wich was further purified on preparative plates (petroleum ether/CH_2Cl_2 2:1). The title compound was obtained in a 26% yield as a white solid. m.p.: 106° C; ^{1}H-NMR: δ 0.90 (t, 6H), 1.20-1.90 (m, 28H), 2.70-3.00 (m, 4H), 3.90-4.10 (m, 2H), 6.75 (d, *J*=8.8, 2H), 7.22-7.36 (m, 4H); MS: *m/z* 462 (M^+), 363, 337, 213.

5-Decyloxy-2-hydroxyacetophenone **9**. 2,5-Dihydroxyacetophenone (5.0 g, 33 mmol) was dissolved in hot dry acetone (60 mL) under inert atmosphere. To the solution cooled to room temperature were added K_2CO_3 (4.6 g, 34 mmol) and n-decylbromide (9.0 mL, 43 mmol). The dark-green suspension was refluxed for 8 h then the solvent was removed under reduced pressure, the residue was poured onto ice (50 g) and acidified by addition of 2N H_2SO_4. The mixture was extracted with $CHCl_3$ and the aqueous phase was washed again with $CHCl_3$ (2×30 mL). The collected organic fractions were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The brown residue was purified by column chromatography on silica (CH_2Cl_2) and product **9** was obtained in a 36% yield as a yellow wax. m.p.: 20°-22°C; ^{1}H-NMR: δ 0.88 (t, 3H), 1.30 (m, 14H), 1.75 (quint, 2H), 2.61 (s, 3H), 3.90 (t, 2H), 6.90 (d, *J*=8.6, 1H), 7.1(dd, *J*=8.6 and 2.9, 1H), 7.17 (d, *J*=2.9, 1H), 11.83 (s, 1H); MS: *m/z* 292 (M^+), 152, 137, 91, 55, 43; IR: (CCl_4) 1650-1620 cm^{-1}.

2-Carbethoxy-6-decyloxychromen-4-one **10**. Metallic Na was carefully dissolved in 6 mL of absolute etanol under inert atmosphere. When evolution of gas had subsided, a mixture of **9** (3.5 g, 12 mmol) and freshly distilled diethyloxalate (2.4 mL, 18 mmol) was added dropwise with stirring. The resulting solution was refluxed for 3 h and cooled to room temperature. Conc. HCl (1.7 mL) was then carefully added and the mixture was refluxed for 30' and cooled again to room temperature. A 5N solution of HCl (14 mL) was added and the resulting mixture was refluxed for additional 5 h, cooled to room temperature and extracted with $CHCl_3$ (4×20 mL). The combined organic fractions were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was chromatographed on silica (CH_2Cl_2) and the product thus obtained was crystallized from MeOH (60 mL) affording pure **10** as white solid in a 36% yield. m.p.: 49°-51° C; ^{1}H-NMR: δ 0.90 (t, 3H), 1.30 (m, 14H), 1.44 (t, 3H), 1.83 (quint, 2H), 4.04 (t, 2H), 4.47 (q, 2H), 7.12 (s, 1H), 7.34 (dd, *J*=8.8 and 2.7, 1H), 7.53 (d, *J*=2.7, 1H), 7.56 (d, *J*=8.8, 1H); MS: *m/z* 374 $(M)^+$, 234, 55, 43; IR: (CCl_4), 1750, 1660-1618 cm^{-1}.

(±)-2-Carbethoxy-6-decyloxy-2,3-dihydrobenzopyran **11**. In a Parr apparatus were loaded 0.75 g (2.0 mmol) of **10** dissolved in 4 mL of ethanol and 2 mL of $CHCl_3$, 0.13 g of Pd 10% on carbon and 0.5 mL of conc. HCl. The resulting suspension was stirred at room temperature under H_2 pressure (2 bar) for 7 days. The crude reaction

mixture was then filtered trough Celite and the precipitate was washed with $CHCl_3$. The filtrate was then concentrated in vacuo, dissolved in $CHCl_3$ (10 mL) and washed with water (10 mL). The organic layer was then dried over Na_2SO_4 and the solvent was removed under reduced pressure. The yellow residue was then purified by chromatography (CH_2Cl_2) affording the title compound as a yellow oil in a 42% yield. ^{1}H-NMR: δ 0.85 (t, 3H), 1.29 (t, 3H), 1.30 (m, 14H), 1.72 (quint, 2H), 2.20-2.32 (m, 2H), 2.60-2.90 (m, 2H), 3.85 (t, 2H), 4.24 (q, 2H), 4.64 (q, 1H), 6.55 (d, *J*=2.3, 1H), 6.66 (dd, *J*=9.3 and 2.3, 1H), 6.83 (d, *J*=9.3, 1H); MS: *m/z* 362 (M^+), 289, 222, 149; IR: (CCl_4) 1740 cm^{-1}.

(±)-6-Decyloxy-2,3-dihydrobenzopyran-2-carboxylic acid **12**. A 10% solution of NaOH (4.5 mL) and ester **11** (0.80 mmol) were allowed to react for 5 h at 100°C. The mixture was then cooled to room temperature and a 10% solution of HCl (10 mL) was added. Stirring was continued for 30' then the mixture was extracted with $CHCl_3$ (2×10 mL) and the collected organic fractions were washed with water (5 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was crystallized from absolute ethanol (5 mL), affording the acid in a 53% yield as a white solid. m.p.: 140°-141° C; ^{1}H-NMR: δ 0.85 (t, 3H), 1.25 (m, 14H), 1.73 (quint, 2H), 2.00-2.25 (m, 2H), 2.78 (m, 2H), 3.85 (t, 2H), 4.58-4.70 (q, 1H), 6.57 (d, *J*=2.0, 1H), 6.68 (dd, *J*=9.0 and 2.0, 1H), 8.3 (d, *J*=2.0, 1H); MS: *m/z* 334 (M^+), 288, 194, 149, 122, 55, 41.

(±)-6-Decyloxy-2,3-dihydrobenzopyran-2-carboxylic acid 4'-dodecyloxy-biphenyl ester **13*a***. Thionyl chloride (0.50 mL, 6.9 mmol) was added to acid **12** and the mixture was stirred at 60°C under inert atmosphere for 1.5 h. Excess thionyl chloride was distilled off. Ether (2 mL) was added and distillation was resumed to remove the last traces of thionyl chloride. The residue was dissolved in a mixture of CH_3CN (3 mL), ether (0.5 mL) and $CHCl_3$ (0.5 mL). Dry triethylamine (0.08 mL, 0.60 mmol) and 4-dodeciloxy-4'-hydroxy-biphenyl (0.14 g, 0.40 mmol) were then added and the resulting solution was stirred at room temperature for 15 h. The precipitate thus obtained was filtered, washed with CH_3CN, water and chromatographed (CH_2Cl_2), affording pure ester **13*a*** as white solid in a 43% yield. ^{1}H-NMR: δ 0.86 (t, 6H),1.28 (m, 32H) 1.75 (m, 4H), 2.37 (m, 2H), 2.86 (m, 2H), 3.90 (double t, 4H), 4.94 (q, 1H), 6.60 (d, *J*=2.8, 1H), 6.7 (dd, *J*=8.8 and 2.8, 1H), 6.89 (d, *J*=8.8, 1H), 6.94-7.14 (q AB, 4H), 7.46-7.54 (q AB 4H); MS: *m/z* 670 (M^+), 354, 289, 186, 149, 57, 43; IR: (CCl_4) 1775 cm^{-1}.

(±)-6-Decyloxy-2,3-dihydrobenzopyran-2-carboxylic acid 4'-cyano-biphenyl ester **13*b***. The acyl chloride was prepared as described above for **13*a***, starting from **12** (0.080 g, 0.24 mmol) and thionyl chloride (0.40 mL, 5.5 mmol). After removal of excess thionyl chloride, the residue was dissoved in CH_3CN (2.5 mL) and $CHCl_3$ (0.5 mL). Triethylamine (0.07 mL, 0.49 mmol) and 4-cyano-4'-hydroxy-biphenyl (0.062 g, 0.32 mmol) were added and the mixture was stirred overnight at room temperature. Chloroform (10 mL) was added and the crude reaction mixture was extracted with 10% $NaHCO_3$ (2×10 mL) and water (10 mL).The organic fraction was then dried over Na_2SO_4 and concentrated under reduced pressure. The solid residue was chromatographed on preparative plates (CH_2Cl_2) and pure **13*b*** was obtained in a 32% yield as a white solid. m.p.: 127°-128°C; ^{1}H-NMR: δ 0.86 (t, 3H), 2.28 (m, 14H), 1.72

(quint, 2H), 2.36 (m, 2H), 2.85 (m, 2H), 3.86 (t, 2H), 4.93 (q, 1H), 6.60 (d, *J*=1.8, 1H), 6.70 (dd, *J*=8.6 and 1.8, 1H), 6.89 (d, *J*=8.6, 1H), 7.20-7.58 (q AB, 4H), 7.64-7.72 (q AB, 4H); MS: *m/z* 511 (M^+), 289, 195, 149, 121, 57, 43; IR:($CHCl_3$) 2235, 1775 cm^{-1}.

(2-Acetyl-4-benzyloxyphenyl)decanoate **15a**. Decanoyl chloride (4.3 mL, 21 mmol) and 2-hydroxy-5-benzyloxyacetophenone[4] (4.2 g, 17 mmol) were allowed to react at room temperature for 15 h in the presence of pyridine (5.5 mL). Methanol was added and the reaction mixture was poured onto crushed ice (30 g). To the slurry were added 1N HCl (70 mL) and Et_2O (100 mL). The two phases thus formed were separated and the aqueous layer was extracted with Et_2O (2×80 mL). The collected organic fractions were dried over Na_2SO_4 and concentrated in vacuo. The oily residue was chromatographed on silica (gradient from CH_2Cl_2/petroleum ether 2:1 to pure CH_2Cl_2) affording **15a** in a 82% yield as a off-white solid. m.p.: 34-36°C; ^{1}H-NMR: δ 0.86 (t, 3H), 1.27 (m, 12H), 1.74 (quint, 2H), 2.50 (s, 3H), 2.57 (t, 2H), 5.06 (s, 2H), 6.98 (d, *J*=9.1, 1H), 7.10 (dd, *J*=9.1 and 2.5, 1H), 7.30-7.46 (m, 6H); MS: *m/z* 396 (M^+), 242, 91, 71, 57, 43; IR: (CCl_4) 1765, 1690 cm^{-1}.

(2-Acetyl-4-benzyloxyphenyl)tetradecanoate **15b**. By following the same procedure as described above for **15a**, starting from tetradecanoic acid chloride, after chromatography ($CHCl_3$), compound **15b** was obtained in a 83% yield as pale yellow solid. m.p.:51°-54°C; ^{1}H-NMR: δ 0.86 (t, 3H), 1.27 (m, 20H), 1.74 (quint, 2H), 2.50 (s, 3H), 2.55 (t, 2H), 5.07 (s, 2H), 6.98 (d, *J*=9.5, 1H), 7.10 (dd, *J*=9.5 and 2.5, 1H), 7.30-7.45 (m, 6H); MS: *m/z* 452 (M^+), 242, 91, 71, 57, 43; IR: (CCl_4) 1770, 1700 cm^{-1}.

1-(5-Benzyloxy-2-hydroxyphenyl)dodecan-1,3-dione **16a**. A solution of **15a** (5.6 g, 14 mmol) in pyridine (25 mL) was heated to 50°C in an oil bath under inert atmosphere. Quickly powdered KOH (1.5g, 27 mmol) was added and the mixture was left to react for 15 h. After cooling in an ice bath, 10% acetic acid was added and the mixture was extracted with ether (50 mL). The organic phase was concentrated as much as possible in vacuo, ether (50 mL) was added and the resulting solution was extracted with 1N HCl (2×40 mL). The ethereal solution was then dried over Na_2SO_4 and concentrated under reduced pressure, affording a brown solid (4.1 g) which was difficult to purify and was used in the subsequent step as it was. ^{1}H-NMR: δ 0.88 (t, 3H), 1.28 (m, 12H), 1.65 (quint, 2H), 2.35 (t, 2H), 4.00, 6.05 and 15.0 (3s, 2H), 5.02 (s, 2H), 6.84-7.46 (m, 8H), 11.67 (s, 1H).

1-(5-Benzyloxy-2-hydroxyphenyl)hexadecan-1,3-dione **16b**. The product was prepared as described above for **16a**, starting from **15b** (7.7 g, 17 mmol). Attempts of purification of the product, carried out on silica over a small portion of crude, afforded 6-benzyloxy-2-tridecylchromen-4-one in a 25% yield. m.p.: 60-62°C; ^{1}H-NMR: δ 0.85 (t, 3H), 1.22 (m, 20H), 1.70 (m, 2H), 2.57 (t, 2H), 5.10 (s, 2H), 6.13 (s, H) 7.22-7.46 (m, 7H), 7.63 (d, *J*=2.5, 1H); MS: *m/z* 434(M^+), 406, 343, 329, 279, 266, 189, 176, 91, 65, 55, 41; IR (KBr): 1660, 1620 cm^{-1}; ^{13}C-NMR: δ 14.06 (CH_3), 22.63, 26.78, 28.93, 29.22 ($2CH_2$), 29.40 ($2CH_2$), 29.57 ($3CH_2$), 31.85, 34.20 (CH_2), 70.49 (CH_2), 106.01 (CH), 109.00, 119.15, 123.77 (CH), 124.21 (C), 127.57 (2CH), 128.08 (CH), 128.54

(2CH), 136.26, 151.37, 155.76, 169.53, 178.12 (C) ppm), and therefore the product was used in the subsequent step without purification.

6-Hydroxy-2-nonylchromen-4-one **17a**.
Crude diketone **16a** and glacial acetic acid (15 mL) were warmed at 50°C with stirring. Concentrated H_2SO_4 (0.9 mL) was added dropwise, the temperature was raised to 90°C and stirring was continued for 3 h. After cooling the mixture was poured onto crushed ice (40 g) and extracted with ether (2×70 mL). The combined organic layers were concentrated under reduced pressure, the residue was dissolved in ether (70 mL), and washed with 10% $NaHCO_3$ (2×70 mL). The organic fraction was dried over Na_2SO_4 and .concentrated in vacuo. Chromatography of the crude (petroleum ether/ethyl acetate 5:2) afforded **17a** as a white solid in a 39% yield (based on **15a**). m.p.: 105°-108°C; ^{1}H-NMR: 0.87 (t, 3H), 1.26 (m, 12H), 1.73 (quint, 2H), 2.63 (t, 2H), 6.23 (s, 1H), 7.20-7.42 (m, 2H), 7.99 (d, *J*=2.0, 1H), 9.63 (s, 1H); MS: *m/z* 288 (M^+), 189, 176, 137, 55, 41; IR: (KBr) 3370, 1640, 1600 cm^{-1}.

6-Hydroxy-2-tridecylchromen-4-one **17b**. Starting from crude **16b** (10g, purity ~20%) and following the procedure described above for **17a**, the title compound was obtained as a white solid (yield 75%) after chromatography (CH_2Cl_2 then ethyl acetate/petroleum ether 1:2). m.p.: 101-102°C; ^{1}H-NMR: 0.87 (t, 3H), 1.24 (m, 20H), 1.72 (quint, 2H), 2.60 (t, 2H) ,3.99 (m, 1H), 6.20 (s, 1H), 7.24 (d, *J*=10.0 and *J*=2.0, 1H), 7.37 (d, *J*=10.0, 1H) 7.84 (d, *J*=2.0, 1H); MS: *m/z* 344 (M^+), 189, 176, 137, 55, 41; IR: (CCl_4) 3370, 1640-1600 cm^{-1}.

(±) 6-Hydroxy-2-nonyl-2,3-dihydrobenzopyran **18a**. Chromone **17a** (1.4 g, 5.0 mmol) was dissolved in ethanol (20 mL). Concentrated HCl (2.3 mL) and Pd 10% on carbon (2.0 g) were added and the resulting suspension was left under H_2 pressure (3 bar) for 20 h. The crude reaction mixture was worked-up as described for **7**. Chromatography (petroleum ether/ethyl acetate 5:2) afforded pure **18a** as white solid in a 60% yield. m.p.:59°-60°C; ^{1}H-NMR: δ 0.88 (t, 3H), 1.30 (m, 12H), 1.47-2.05 (m, 6H), 2.60-2.90 (m, 2H), 3.87 (m, 1H), 4.37 (s, 1H), 6.54 (d, *J*=2.0, 1H), 6.57 (dd, *J*=9.9 and 2.0, 1H), 6.68 (d, *J*=9.9, 1H); MS: *m/z* 276 (M^+), 149, 136, 123, 55, 41; IR: (CCl_4) 3610 cm^{-1}.

(±) 6-Hydroxy-2-tridecyl-2,3-dihydrobenzopyran **18b**. Chromone **17b** (1.1 g, 3.1 mmol) was dissolved in glacial acetic acid (25 mL). Concentrated HCl (1.5 mL) and Pd 10% on carbon (1.2 g) were added and the resulting suspension was left under H_2 pressure (5.5 bar) for 24 h. The crude reaction mixture was worked-up as described for **7**. Chromatography (petroleum ether/ethyl acetate 5:1) afforded pure **18b** as white solid in a 40% yield. m.p.: 71°-72°C; ^{1}H-NMR: δ 0.87 (t, 3H), 1.27 (m, 20H), 1.47-2.05 (m, 6H), 2.60-2.90 (m, 2H), 3.89 (m, 1H), 4.75 (s, 1H), 6.50 (d, *J*=2.0, 1H), 6.54 (dd, *J*=9.9 and 2.0, 1H), 6.66 (d, *J*=9.9, 1H); MS: *m/z* 332 (M^+), 149, 136, 123, 55, 41; IR: (CCl_4) 3610 cm^{-1}.

(±) 2-Hexyl-6-hydroxy-2,3-dihydrobenzopyran **18c**. To a solution of 6-bromo-2-hexyl-2,3-dihydrobenzopyran **20c**[2] (0.68 mmol) in ether (3 mL) was added a 1.6M solution of n-butyllithium (1.1 mL, 1.8 mmol). The mixture was stirred at room

temperature for 1.5 h then cooled to -78°C. A solution of hexamethyl-disilylperoxide (0.43g, *title* 41%)[5] was added slowly *via* a syringe and the mixture was allowed to warm to room temperature. Stirring was continued for 20 h, diluted with pentane (5 mL) and concentrated in vacuo. The residue was dissolved in ether (10 mL) and washed with sat. NH_4Cl (10 mL). The organic layer was concentrated in vacuo, affording a brown oil which was dissolved in CH_3OH/HCl 20:1 (5 mL) and left under stirring for 8 h. Water (10 mL) was added and the resulting solution was extracted with ether (2×10 mL). The combined organic fractions were dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on preparative plates ($CHCl_3$) affording **18c** as a white solid in a 18% yield. ^{1}H-NMR: δ 0.85 (t, 3H), 1.28 (m, 8H), 1.38-2.05 (m, 4H), 2.60-2.85 (m, 2H), 3.87 (m, 1H), 4.37 (s, 1H), 6.50 (d, *J*=2.4, 1H), 6.53 (dd, *J*=8.0 and 2.4, 1H), 6.65 (d, *J*=8.0, 1H); MS: *m/z* 234 (M^+), 149, 136, 123, 55, 41; IR: (CCl_4) 3610 cm^{-1}.

(±) 6-Hydroxy-2-undecyl-2,3-dihydrobenzopyran **18d**. To a solution of 6-bromo-2-undecyl-2,3-dihydrobenzopyran **20d**[2] (0.15g, 0.41 mmol) in THF (1.5 mL) was added a 1.6M solution of n-butyllithium (0.28 mL, 0.46 mmol). The mixture was stirred at room temperature for 1.5 h then transferred *via* a cannula into a cold (-78°C) THF solution (2 mL) containing (1S)-(+)-(10-camphorsufonyl) oxaziridine (0.13 g, 0.54 mmol). The mixture was stirred at -78°C for 17 h then warmed to 0°C. Sat. NH_4Cl (1.8 mL) was added and the mixture was allowed to reach room temperature. The two phases were separated and the aqueous layer was washed twice with ether. The collected organic fractions were dried over Na_2SO_4 and solvents were removed under reduced pressure. Chromatography on preparative plates afforded **18d** in a 10% yield. ^{1}H-NMR: δ 0.85 (t, 3H), 1.28 (m, 18H), 1.38-2.05 (m, 4H), 2.60-2.85 (m, 2H), 3.90 (m, 1H), 4.37 (m, 1H), 6.54 (d, *J*=2.4, 1H), 6.56 (dd, *J*=8.0 and 2.4, 1H), 6.67 (d, *J*=8.0, 1H); IR: (CCl_4) 3610 cm^{-1}.

General procedure for the synthesis of racemic esters **19**. To the appropriate benzoic acid (0.20 mmol) was added thionyl chloride (0.40 mL, 5.5 mmol) and the mixture was refluxed for 1.5 h. Excess thionyl chloride was distilled off. Ether (2 mL) was added and the distillation resumed to remove the last traces of thionyl chloride. To the residue were added CH_3CN (2 mL), 6-hydroxy-2,3-dihydrobenzopyran **18** (0.25 mmol) and Et_3N (0.050 mL, 0.40 mmol). The mixture was stirred overnight at room temperature under inert atmosphere. Solvents were removed under reduced pressure and the residue was purified by chromatography.

(±) 4-Heptylbenzoic acid 2-nonyl-2,3-dihydrobenzopyran-6-yl ester **19*a***. The product was obtained in a 75% yield as white solid after chromatography (petroleum ether / ethyl acetate 20:1) and crystallisation (abs. EtOH).m.p.: 67°C; ^{1}H-NMR: δ 0.88 (t, 6H), 1.26 (m, 22H), 1.45-2.00 (m, 6H) 2.70 (m, 4H), 3.95 (m, 1H), 6.75-6.90 (m, 3H), 7.28-8.08 (q AB, 4H); MS: *m/z* 478 (M^+), 276, 203, 123, 91, 43; IR: (CCl_4) 1730 cm^{-1}.

(±) 4-Hexyloxybenzoic acid 2-nonyl-2,3-dihydrobenzopyran-6-yl ester **19*b***. The product was obtained in a 90% yield as white solid after double chromatography (petroleum ether / ethyl acetate 4:1 then CH_2Cl_2). m.p.: K 72 N 76 I (°C); ^{1}H-NMR: δ

0.88-0.91 (double t, 6H), 1.26-2.04 (m, 26H), 2.79 (m, 2H), 3.97 (m, 1H), 4.03 (t, 2H), 6.74-6.87 (m, 3H), 6.95-8.12 (q AB, 4H); MS: *m/z* 480 (M^+), 276, 205, 121, 43; IR: (CCl_4) 1725 cm^{-1}; ^{13}C-NMR: δ 14.54, 14.64 (CH_3), 23.10, 23.20, 25.42, 25.82, 26.17, 27.61, 29.58, 29.85, 30.11 ($2CH_2$), 30.14, 32.06, 32,42, 35.86 (CH_2), 68.78 (CH_2-O), 76.56 (CH-O), 114.70 (2CH), 117.79, 120.82 (CH), 122.27 (C), 122.68 (CH), 123.26 (C), 132.67 (2CH), 144.23, 153.25, 163.88, 165.95 (C).

(±) 4-Dodecyloxybenzoic acid 2-nonyl-2,3-dihydrobenzopyran-6-yl ester **19*c***. The product was obtained in a 80% yield as white solid after double chromatography (petroleum ether / ethyl acetate 5:1 then CH_2Cl_2). m.p.: K 68 N 78 I (°C); ^{1}H-NMR: δ 0.87 (t, 6H), 1.29-1.46 (m, 32H), 1.69-2.02 (m, 6H), 2.70-2.92 (m, 2H), 3.97 (m, 1H), 4.20 (t, 2H), 6.80-6.90 (m, 3H), 6.95-8.12 (q AB, 4H); MS: *m/z* 564 (M^+), 289, 276, 121, 43; IR: (CCl_4) 1725 cm^{-1}.

(±) 4-Hexadecyloxybenzoic acid 2-nonyl-2,3-dihydrobenzopyran-6-yl ester **19*d***. The product was obtained in a 75% yield as white solid after chromatography (petroleum ether / ethyl acetate 4:1) and crystallisation (abs. EtOH). m.p.: K 67 S_A 81 I (°C); ^{1}H-NMR: δ 0.88 (t, 6H), 1.28 (m, 40H), 1.45-2.00 (m, 6H) 2.80 (m, 2H), 3.97 (m, 1H), 4.09 (t, 2H), 6.84-6.87 (m, 3H), 6.95-8.12 (q AB 4H); MS: *m/z* 620 (M^+), 345, 276, 149, 121, 69, 55, 43; IR: (CCl_4) 1730 cm^{-1}.

(±) 2-Hexyl-2,3-dihydrobenzopyran-6-carboxilic acid 2-nonyl-2,3-dihydrobenzopyran-6-yl ester **19*e***. The product was obtained in a 95% yield as white solid after chromatography (petroleum ether / ethyl acetate 4:1). m.p.: K 77 N 79 I (° C); ^{1}H-NMR: δ 0.88-0.90 (dt, 6H), 1.28 (m, 22H), 1.50-2.00 (m, 8H), 2.78 (m, 4H), 3.95 (m, 2H), 6.80-6.90 (m, 4H), 7.89-7.94 (m, 2H); MS: *m/z* 520 (M^+), 276, 245, 123; IR: (CCl_4) 1720 cm^{-1}; ^{13}C-NMR: δ 14.61 ($2CH_3$), 23.12, 23.19, 25.16, 25.41, 25.70, 25.71, 25.80, 27.47, 27.49, 27.59, 29.76, 29.83, 30.11, 32.28, 32.40, 35.77, 35.84 (CH_2), 76.55, 77.33 (CH), 117.35, 117.77, 120.83 (CH), 121.56, 122.51 (C), 122.67, 123.25 130.15, 132.70 (CH), 144.26, 153.20, 160.20, 166.15 (C).

(±) 4-Cyanobenzoic acid 2-hexyl-2,3-dihydrobenzopyran-6-yl ester **19*f***. The product was obtained in a 43% yield as white solid after chromatography ($CHCl_3$). m.p.: K 76 N 88 I (°C); ^{1}H-NMR: δ 0.90 (t, 3H), 1.33 (m, 8H), 1.52-2.10 (m, 4H), 2.80 (m, 2H), 4.00 (m, 1H), 6.80-6.95 (m, 3H), 7.80-8.28 (q AB, 4H); MS: *m/z* 363 (M^+), 278, 252, 163, 149, 130, 102, 55, 41; IR: (CCl_4) 2240, 1740 cm^{-1}; ^{13}C-NMR: δ 14.59 (CH_3), 23.11, 25.40, 25.73, 27.48, 29.77, 32.28, 35.78 (CH_2), 76.65 (CH-O), 117.30 (C), 118.00 (CH), 118.40 (C), 120.40, 122.29 (CH), 123.53 (C), 131.06 (2CH), 132.81 (2CH), 134.12, 143.66, 153.70, 164.55 (C).

(±) 4-Cyanobenzoic acid 2-nonyl-2,3-dihydrobenzopyran-6-yl ester **19*g***. The product was obtained in a 94% yield as white solid after chromatography (petroleum ether / ethyl acetate 5:2). m.p.: K 73 S_A 94 I (°C); ^{1}H-NMR: δ 0.88 (t, 3H), 1.29 (m, 14H), 1.50-2.06 (m, 4H), 2.79 (m, 2H), 3.98 (m, 1H), 6.80-6.92 (m, 3H), 7.80-8.30 (q AB, 4H); MS: *m/z* 405 (M^+), 279, 252, 167, 149, 130, 71, 57, 43; IR: (CCl_4) 2240, 1740 cm^{-1}; ^{13}C-NMR: δ 14.10 (CH_3), 22.67, 24.90, 25.26, 26.98, 29.31, 29.58 ($3CH_2$), 31.88, 35.29 (CH_2), 76.14 (CH-O), 116.80 (C), 117.48 (CH), 117.86 (C),

119.91, 121.79 (CH), 123.00 (C), 130.53 (2CH), 132.31 (2CH), 133.80, 143.15, 153.20, 164.00 (C).

(±) 4-Cyanobenzoic acid 2-undecyl-2,3-dihydrobenzopyran-6-yl ester **19*h***. The product was obtained in a 48% yield as white solid after chromatography ($CHCl_3$). m.p.: K 70 S_A 95 I (°C); ^{1}H-NMR: δ 0.88 (t, 3H), 1.25 (m, 18H), 1.45-2.06 (m, 4H), 2.80 (m, 2H), 3.90 (m, 1H), 6.80-6.92 (m, 3H), 7.80-8.28 (q AB, 4H); MS: *m/z* 433 (M^+), 278, 252, 163, 149, 130, 102, 55, 43; IR: (CCl_4) 2250, 1750 cm^{-1}; ^{13}C-NMR: δ 14.63 (CH_3), 23.20, 25.43, 25.79, 27.50, 29.86, 30.12 ($2CH_2$), 30.19($2CH_2$), 32.42, 35.81 (CH_2), 76.68 (CH-O), 112.79, 117.22 (C), 118.01 (CH), 118.36 (C), 120.42, 122.30 (CH), 123.55 (C), 131.07 (2CH), 132.84 (2CH), 143.20, 153.09, 164.42 (C).

(±) 4-Cyanobenzoic acid 2-tridecyl-2,3-dihydrobenzopyran-6-yl ester **19*i***. The product was obtained in a 87% yield as white solid after chromatography (petroleum ether / ethyl acetate 5:1). m.p.: K 81 S_A 107 I (°C); ^{1}H-NMR: δ 0.88 (t, 3H), 1.30 (m, 22H),1.45-2.06 (m, 4H) 2.79 (m, 2H), 3.98 (m, 1H), 6.80-6.92 (m, 3H), 7.80-8.30 (q AB, 4H); MS: *m/z* 461 (M^+), 279, 252, 130, 81, 69, 55, 43; IR: (CCl_4) 2250, 1750 cm^{-1}; ^{13}C-NMR: δ 14.10 (CH_3), 22.68, 24.91, 24.92, 25.27, 25.32, 26.99, 27.00, 29.35, 29.64 ($4CH_2$), 31.91 , 35.30 (CH_2), 76.16 (CH-O), 116.70 (C), 117.50 (CH), 117.90 (C), 119.91, 121.79 (CH), 123.03 (C), 130.56 (2CH), 132.33 (2CH), 132.99, 142.82, 152.82, 163.71 (C).

(S)-(-)-2-Nonyl-2,3-dihydrobenzopyran **22a**. A solution of octylmagnesium bromide, obtained from 0.13 g (5.5 mmol) of Mg and 0.92 mL (5.3 mmol) of n-octyl bromide in 5 mL of ether, was added over 40' to a solution of (R)-(-)-2-[[(trifluoromethanesulfonyl)oxy]methyl]-2,3-dihydrobenzopyran (0.45 g, 1.5 mmol) ($[\alpha]_D$-61.3°, c 1.5 in MeOH) (lit.[7] $[\alpha]_D$-65.1, c 1 in MeOH) and cuprous bromide dimethyl sulfide complex (0.060 g, 0.29 mmol) in 8 mL of THF at -5°C under argon. After stirring for 2 h at 0°C the solution was poured into a stirred mixture of 2.2 M NH_4Cl (17 mL) and CH_2Cl_2 (8 mL) and left for 2 h.The phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic fractions were washed with sat. NH_4Cl, water and dried over Na_2SO_4. Solvents were removed under reduced pressure and the residue purified by chromatography ($CHCl_3$), affording the product as a colorless oil in a 60% yield. ^{1}H-NMR: δ 0.95 (t, 3H), 1.35-2.10 (m, 18H), 2.82 (m, 2H), 4.00 (m, 1H), 6.80-6.90 (m, 2H), 7.04-7.14 (m, 2H); MS: *m/z* 260 (M^+), 147, 133, 120, 107; $[\alpha]_D$ = -70.0° (c 0.33 in MeOH).

(S)-(-)-6-Bromo-2-nonyl-2,3-dihydrobenzopyran **23a**. Derivative (S)-(-) **22a** (0.21 g, 0.81 mmol) was dissolved in ethanol (2 mL) and the solution was cooled in an ice bath. Bromine (0.040 mL, 0.78 mmol) dissolved in ethanol (1.5 mL) was added dropwise over 1 h. The mixture was stirred at 0°C for 30' then allowed to warm to r.t. and stirred for 12 h. The crude was concentrated in vacuo and the resulting oil was purified by chromatography ($CHCl_3$), giving the title compound as a pale yellow oil in a 73% yield. ^{1}H-NMR: δ 0.92 (t, 3H), 1.31-2.10 (m, 18H), 2.80 (m, 2H), 3.95 (m, 1H), 6.65-8.00 (m, 1H), 7.13-7.20 (m, 2H); MS: *m/z* 338, 211, 198, 185, 132, 55, 41; $[\alpha]_D$ = -70.7° (c 1.09 in MeOH).

(S)-(-)-6-Hydroxy-2-nonyl-2,3-dihydrobenzopyran **18a**. The procedure described for **18c** was followed, starting from (S)-(-) **23a** (0.43 mmol). Chromatography ($CHCl_3$) afforded pure (S)-(-) **18a** as a white solid in a 18% yield. Spectral data were identical with those reported above for the corresponding racemic compound. $[\alpha]_D$ = -60.3° (c 0.38 in MeOH).

(S)-(-)-4-Cyanobenzoic acid 2-nonyl-2,3-dihydrobenzopyran-6-yl ester **19g**. The general procedure described above for the synthesis of racemic esters was followed. The product was obtained in a 52% yield after chromatography on preparative plates ($CHCl_3$).Spectral data were identical with those reported above for the corresponding racemic compound. $[\alpha]_D$ = -85.4° (c 0.27 in CH_2Cl_2).

X-ray diffraction experiments were performed by using a rotating anode generator "RIGAKU DENKI RU300" (40kV and 200mA). Ni-filtered Cu-K_α radiation (λ=1,54Å) was used. X-ray diffraction spectra of powder samples were recorded in transmission geometry by using a conventional powder diffractometer. The sample was sealed in a glass capillary (ϕ=1mm) put into a home made sample holder containing two electrical resistors. Temperature was controlled with a precision of ±0.1°C from 0°C up to 200°C by a BT 300/301 control system supplied by SMC (Grenoble, France). X-ray diffraction patterns were recorded for each sample at different temperatures during the first heating and cooling cycles from 25°C to 150°C.

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