Synthesis and Properties of a New Family of Chiral Mesogens Containing the 2,3-Dihydrobenzopyran Nucleus

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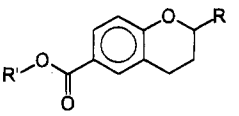
A new class of mesogens **A** with a central chiral core based on the 2,3-dihydrobenzopyran nucleus was synthesized both in the racemic and optically pure form, and the thermotropic properties were studied. The distortion from structural linearity due to the presence of the 2,3-dihydropyran ring does not inhibit the existence of mesophases, and Ch, S_A, and S_C phases were observed according to the substituents present. The conformational constrictions imposed by cyclization proved not to be very important in determining the compactness of the cholesteric helix.

Despite the large number of chiral mesogens that have been synthesized, the vast majority of these compounds have a rather conventional structure with a stereogenic element in the side chain of the molecules. This choice is dictated by the simplicity of the synthetic work and by the availability and cost of the chiral synthons used.

The synthesis of less conventional mesogens seems limited more by practical difficulties than by the researchers' creativity. Recently, some less usual chiral mesogens have been described[1] and some of them have shown interesting properties. For example, mesogens with the chiral *trans*-stilbene oxide core display extremely short cholesteric pitches.[2]

In this paper we report the synthesis and properties of a new class of chiral mesogens **A** containing the 2,3-dihydrobenzopyran nucleus. This can be considered as a conformationally frozen *p*-alkoxybenzoate or *p*-alkoxybenzoic acid (Figure 1). The free acids already give cholesteric mesophases due to the hydrogen-bonded dimer formation. Esters, instead, require the presence of extra aryl groups in order to show cholesteric and smectic mesophases.



A

Figure 1.

Results and Discussion.

Derivatives **7** in the racemic form were synthesized as described in Scheme 1 (see Table 1 for list of substituents). Esterification of *o*-hydroxyacetophenone with different acyl chlorides in pyridine afforded esters **1**. Subsequent intramolecular Claisen-type condensation in the presence of KOH gave derivatives **2**. By acidic dehydration of the corresponding hemiacetals, chromones **3** were obtained. Compound **3a** (R = C_6H_{13}) was obtained directly in a 36% yield by a one-pot procedure consisting of condensation of *o*-hydroxyacetophenone and ethyl heptanoate over metallic Na followed by acid-catalyzed dehydration and cyclization (see Experimental Section): this method proved to be unsatisfactory when the length of the aliphatic chain at position 2 was increased.

Catalytic hydrogenation of **3** over Pd in EtOH/HCl produced dihydrobenzopyrans **4**. Reduction of **3d** (R = *p*-C_6H_4–C_7H_{15}) proved to be more difficult, due to the ring opening at the benzylic C–O bond, and **4d** could only be obtained in a 22% yield. Treatment of compounds **4** with bromine (less than 1 equiv) at 0 °C in EtOH produced regiospecifically the desired 6-bromo-2,3-dihydrobenzopyrans **5**. Subsequent metal–halogen exchange with n-BuLi in ether, followed by carbonation, afforded 2,3-dihydrobenzopyran-6-carboxylic acids **6**. These were transformed into the corresponding acyl chlorides upon reaction with $SOCl_2$ and then converted into the various esters **7** by reaction with the appropriate alcohol in the presence of Et_3N in CH_3CN.

The optically pure derivatives (Scheme 2) were obtained starting from enantiomerically pure (*R*)-(−)-2-(hydroxymethyl)-2,3-dihydrobenzopyran ((*R*)-(−)-**9**), which was prepared via the kinetic resolution of (±)-ethyl 2,3-dihydrobenzopyran-2-carboxylate (**8**) with lipase (from *Pseudomonas fluorescens*) and subsequent reduction with $NaBH_4$, as described by Urban.[3] Alkylation of the corresponding triflate with hexylmagnesium bromide in the presence of catalytic CuBr·Me_2S afforded (*S*)-(−)-**4b** [optical purity was ≥95%, as determined by ^{1}H-NMR with (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol]. Bromination and metal–halogen exchange followed by carbonation gave the optically pure acid (*S*)-(−)-**6b**, which was converted into esters (*S*)-(−)-**7d** and (*S*)-(−)-**7h** by the same procedure employed for the synthesis of the corresponding racemic derivatives.

The mesogenic properties of the racemic compounds synthesized, as deduced from polarizing microscopy and differential scanning calorimetry (DSC), are reported in Table 1. The smectic phases given by derivatives **7d** and **7b** were confirmed as C and A, respectively, by X-ray diffraction.[4] A typical DSC run is reported in Figure 2. Table 2 reports the data of enantiomers with ee ≥95%.

The free acids give nematic (cholesteric) phases while their alkyl and some aryl esters (**7a**,**j**,**k**,**l**) are not mesogenic. This is connected to the hydrogen-bonded dimer

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(3) Urban, F. J.; Moore, B. S. *J. Heterocycl. Chem.* **1992**, *29*, 431.

(4) Yang, B.; Mariani, P. Private communication.

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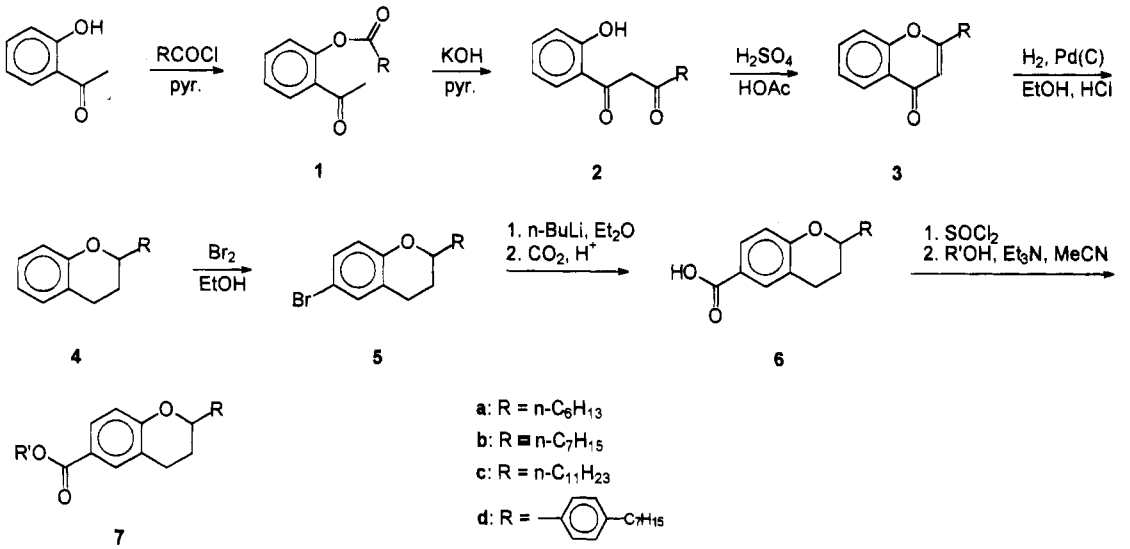
Table 1. Mesogenic Properties of Racemic Acids 6 and Esters 7

derivative	R	R′	phase transitions[a] (°C)
6a	n-C_6H_{13}	H	K 128 N 142 I
6b	n-C_7H_{15}	H	K 127 N 140 I
6c	n-$C_{11}H_{23}$	H	K 115 N 121 I
6d	*p*-(C_6H_4)-C_7H_{15}	H	K 167 N 202 I
7a	n-C_6H_{13}	*p*-(C_6H_4)−OC_6H_{13}	K 96 I
7b	n-$C_{11}H_{23}$	*p*-(C_6H_4)-$OC_{12}H_{25}$	K 82 S_A 86 I
7c	n-C_6H_{13}	*p*,*p*′-(C_6H_4)$_2$-$OC_{12}H_{25}$	K 116 S_C 146 N 179 I
7d	n-C_7H_{15}	*p*,*p*′-(C_6H_4)$_2$-$OC_{12}H_{25}$	K 119 S_C 150 N 175 I
7e	n-$C_{11}H_{23}$	*p*,*p*′-(C_6H_4)$_2$-$OC_{12}H_{25}$	K 108 S_C 158 N 167 I
7f	*p*-(C_6H_4)-C_7H_{15}	*p*,*p*′-(C_6H_4)$_2$-$OC_{12}H_{25}$	K 150 S_C 218 N 220 I
7g	n-C_6H_{13}	*p*-(C_6H_4)-CN	K 81 N+I 84 I
7h	n-C_7H_{15}	*p*-(C_6H_4)-CN	K 72 N 88 I
7i	n-$C_{11}H_{23}$	*p*-(C_6H_4)-CN	K 75 S_A 84 N 88 I
7j	n-C_6H_{13}	CH_3	isotropic liquid
7k	n-C_6H_{13}	C_7H_{15}	isotropic liquid
7l	n-$C_{11}H_{23}$	$C_{10}H_{21}$	K 43 I

[a] K = crystal; S_A = smectic A; S_C = smectic C; N = nematic; I = isotropic. Data refer to heating cycles.

Scheme 1



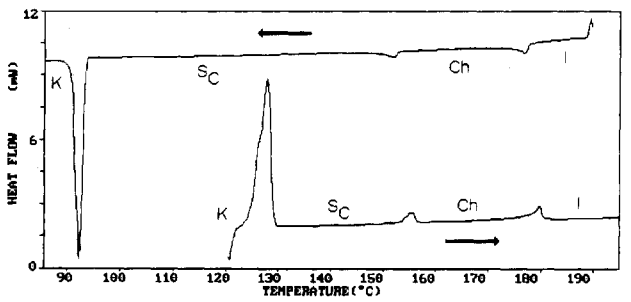


Figure 2. DSC thermograms of (*S*)-(−)-**7d**.

formation[5] (Figure 3), which doubles the molecular length of the acids. Esters, which cannot dimerize, must contain adequate groups in order to show mesomorphic properties: a simple *p*-alkoxyphenyl group is not sufficient to give mesophases. The *p*-cyanophenyl group instead is a very effective substituent also in this family of compounds: it gives rise to a nematic phase already with R = C_6H_{13}. As is often observed, when the substituent groups become longer, smectic phases appear. It is interesting to notice that derivative **7h**, in the racemic form, gives an enantiotropic nematic phase, while in the enantiomerically pure form it gives a monotropic cholesteric. This depends on the melting temperature of the pure enantiomer, which is ca. 20 °C higher than that of the racemate[6] and higher than the clearing temperature of the nematic phase. On the other hand, the clearing temperatures of the nematic and cholesteric phases, as deduced from the cooling cycle of DSC, are identical (Figure 4). The other enantiomerically pure derivatives **6b** and **7d** melt at temperatures very close to those of the corresponding racemates.

The typical reflection colors of the cholesteric phases are observed only when the ee of the sample is lowered.

Table 2. Mesogenic Properties of Optically Pure Derivatives

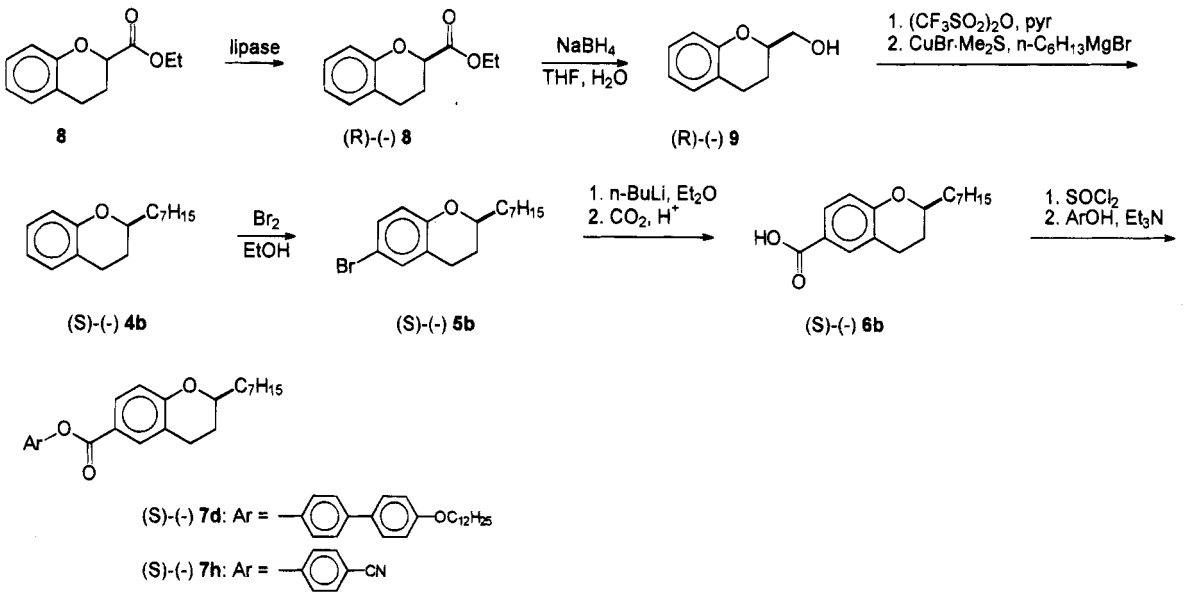
derivative	cholesteric pitch (nm)	handedness	phase transitions (°C)[a]
(*S*)-(−)-**6b**	200	P	K 129 Ch 141 I
(*S*)-(−)-**7d**	–	–	K 125 S_C 153 Ch 178 I
(*S*)-(−)-**7h**	350	P	K 91 I[b]

[a] Ch = cholesteric; for the other symbols, see Table 1. Data refer to heating cycles. All the derivatives showed a blue phase (BP) in a narrow range (~1 °C) prior to the Ch−I transition. [b] The compound shows a monotropic behavior (see text).

(5) Coates, D. in *Liquid Crystals—Applications and Uses*; Bahadur, B., Ed.; World Scientific: Singapore, 1990; Vol. 1, p 91 ff.

(6) This behavior is often indicative of the formation of a conglomerate; however, in the present case we do not have a conglomerate as shown by the phase diagram deduced by DSC and by the solid state IR spectra, which are not superimposable for the racemate and the enantiomerically pure compound.

Scheme 2



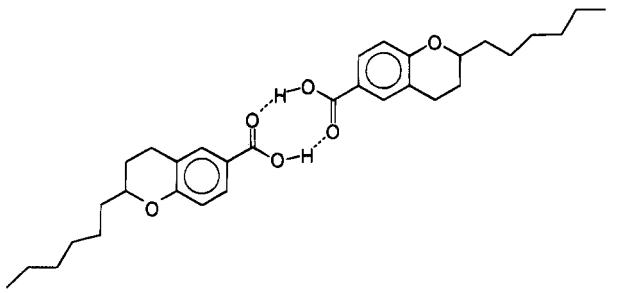


Figure 3.

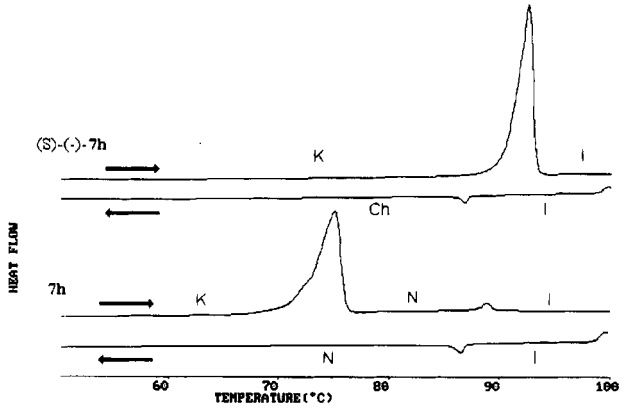


Figure 4. DSC thermograms of racemic **7h** and (*S*)-(−)-**7h**.

This fact points out that the pitch values are in the UV region in the case of cholesterics obtained from the optically pure compounds. The pitch values were determined by CD spectroscopy and the Grandjean–Cano–Heppke method, using mixtures with suitable ee by extrapolating to 100% ee, assuming a linear dependence of 1/pitch *vs* ee (see Experimental Section). The pitch values were found to be in the UV region. In addition, both methods were used to assign the cholesteric handedness and it is worth noticing that the spectroscopic and nonspectroscopic methods also in this case gave the same answer.[7]

The pitch value of the free acid is considerably shorter than that of the ester and we think that this is related to the dimer formation: it has been reported[8] that

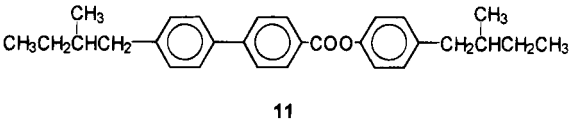


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Figure 5.

Figure 6.

derivative **11** (Figure 5), with both stereogenic centers having the same configuration, has a pitch of ca. 100 nm, while similar derivatives with a single chiral group have a pitch of ca. 230 nm. With respect to ester **7h**, the free acid **6b** therefore seems equivalent to a molecule with two stereogenic centers.

In general, our chromanes give cholesteric phases with pitch values very similar to those given by open-chain benzoates; therefore, the conformational constrictions imposed by cyclization has proved to be unimportant in determining the compactness of the cholesteric phases. This is probably connected to the very similar energy of the two possible half-chair conformers with opposite helicity. The presence of the substituent at position 2, which assumes a pseudoaxial or pseudoequatorial position in the two conformers (Figure 6), is not enough to stabilize one half-chair with respect to the other, as calculated from standard molecular mechanics routines and observed for analogous compounds.[9]

The pitch observed is therefore an average of the contributions from both conformers. In open-chain chiral benzoates the situation is more complex, and the observed pitch is an average of many contributions from all the conformers present. However, the overall cancel-

(7) (a) Grandjean, F. *Compt. Rend.* **1921**, *172*, 71. (b) Cano, R. *Bull. Soc. Fr. Mineral. Cristallogr.* **1968**, *91*, 20. (c) Heppke, G., Oestreicher, F. *Z. Naturforsh.* **1977**, *A32*, 899. (d) Gibson, H. W. In *Liquid Crystals*; Saeva, F. D., Ed.; Marcel Dekker: New York, 1979; p 99 ff.

(8) McDonnel, D. G. In *Thermotropic Liquid Crystals*; Gray, G. W., Ed.; Wiley: Chichester, 1987; p 120 ff.

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lation of opposite-handed contributions in cyclic and open-chain derivatives eventually gives a similar result.

Experimental Section

Melting points are uncorrected. Yields represent isolated compounds. ^1H and ^{13}C NMR spectra were run at 200 and 50 MHz respectively in $CDCl_3$ as solvent, and data are reported on the δ scale relative to TMS as reference.^{13}C NMR assignments were confirmed by DEPT experiments. IR spectra were recorded on an FTIR spectrometer. Optical rotations were measured with a digital polarimeter in a 1 dm cell. Mass spectra were obtained at 70 eV (EI). DSC thermograms were recorded over 5 mg samples at 5 °C/min heating rate. Cholesteric pitch values and handedness[7] were obtained by means of the Grandjean–Cano–Heppke method, using a standard microscope, and by CD spectroscopy detecting the wavelength and handedness of the cholesteric pitch band. TLC chromatography was performed on precoated silica gel IBF2 plates (Baker). Silica gel 60 (70–230 mesh) (Merck) was used for column chromatography. Preparative plates (20 × 20 cm, 1 mm thickness) were prepared from silica gel $60PF_{254}$ (Merck).

Reagents were used as purchased, without further purification. For reactions requiring anhydrous conditions, solvents were dried according to standard procedures. (*R*)-(−)-2-(Hydroxymethyl)-2,3-dihydrobenzopyran (**9**) was obtained according to the procedure described by Urban and Moore,[3] by using lipase from *P. fluorescens* (Fluka).

Typical Procedure for the Synthesis of 2-Acetylphenyl Esters (1b–d). *o*-Hydroxyacetophenone (3.01 mL, 25 mmol) and 30 mmol of the selected acid chloride in dry pyridine (5 mL) were stirred for 1 h at room temperature. The mixture was then poured into a separatory funnel containing 50 g of crushed ice and 120 mL of 1 M HCl. Ether was added and the organic layer was collected. The water layer was washed twice with ether and the combined organic layers were dried over Na_2SO_4 and evaporated in vacuo, and the residue was chromatographed on silica gel.

Octanoic acid 2-acetylphenyl ester (1b): 89% yield as a colorless oil (petroleum ether/Et_2O 15:1); ^1H NMR δ 0.90 (t, 3H), 1.25–1.55 (m, 8H), 1.77 (m, 2H), 2.54 (s, 3H), 2.61 (t, 2H), 7.05–7.85 (m, 4H); MS *m/z* (rel intensity) 262 (M^+, 3), 247 (1), 163 (2), 136 (62), 127 (61), 57 (100); IR (film) 1759, 1689 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.24; H, 8.46. Found: C, 73.03; H, 8.53.

Dodecanoic acid 2-acetylphenyl ester (1c): 91% yield as a colorless oil (petroleum ether/Et_2O 9:1); ^1H NMR δ 0.89 (t, 3H), 1.22–1.50 (m, 16H), 1.77 (m, 2H), 2.55 (s, 3H), 2.61 (t, 2H), 7.06–7.82 (m, 4H); MS *m/z* (rel intensity) 318 (M^+, 1), 183 (75), 136 (100), 121 (31); IR (CCl_4) 1760, 1688 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.24; H, 8.46. Found: C, 73.03; H, 8.53.

4-Heptylbenzoic acid 2-acetylphenyl ester (1d): 79% yield as a yellow oil (CH_2Cl_2/petroleum ether 1:1); ^1H NMR δ 0.89 (t, 3H), 1.20–1.43 (m, 8H), 1.65 (m, 2H), 2.51 (s, 3H), 2.70 (t, 2H), 7.10–8.20 (m, 8H); MS *m/z* (rel intensity) 338 (M^+, 1), 203 (100), 118 (3), 91 (10). Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.06; H, 7.75. Found: C, 78.28; H, 7.65.

Typical Procedure for the Synthesis of 1-(2-Hydroxyphenyl)-1,3-diones (2b–d). Ester **1** (10 mmol) was dissolved in 10 mL of dry pyridine and the solution was heated at 50 °C. KOH (0.90 g, 16 mmol) was quickly powdered and added in one portion to the solution. The mixture was stirred at 50 °C for 1.5 h and allowed to cool down to room temperature. A 10% solution of acetic acid (15 mL) was then added.

1-(2-Hydroxyphenyl)decane-1,3-dione (2b). The mixture was extracted three times with ether and the solution dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (CH_2Cl_2) giving the product in a 71% yield as a waxy solid: mp 27–29 °C; ^1H NMR δ 0.90 (t, 3H), 1.20–1.48 (m, 8H), 1.68 (m, 2H), 2.37 (t, 2H), 4.08 and 6.16 (s, s, 2H), 6.80–7.74 (m, 4H), 12.11 (s, 1H); MS *m/z* (rel intensity) 262 (M^+, 10), 245 (2), 178 (11), 163 (100), 136 (20), 121 (76), 57 (47); IR ($CHCl_3$) 1719, 1639 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.24; H, 8.46. Found: C, 73.37; H, 8.40.

1-(2-Hydroxyphenyl)tetradecane-1,3-dione (2c). The same procedure was followed as described above, and yellow crystals were formed after addition of acetic acid and cooling in an ice bath. Crystals were washed with water and dried in vacuo at 50 °C: yield 68%; mp 41–43 °C; ^1H NMR δ 0.88 (t, 3H), 1.15–1.47 (m, 16H), 1.67 (m, 2H), 2.35 (t, 2H), 4.09 and 6.17 (s, s, 2H), 6.82–7.70 (m, 4H), 12.11 (s, 1H); MS *m/z* (rel intensity) 318 (M^+, 40), 300 (14), 178 (37), 163 (100), 136 (32), 121 (73); IR ($CHCl_3$) 1711, 1635 cm^{-1}. Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.42; H, 9.50. Found: C, 75.20; H, 9.60.

1-(4-Heptylphenyl)-3-(2-hydroxyphenyl)propane-1,3-dione (2d). The same procedure was followed as described above for **2c**, and the title compound was obtained as yellow crystals: yield 78%; mp 69–71 °C; ^1H NMR δ 0.85 (t, 3H), 1.16–1.41 (m, 8H), 1.61 (m, 2H), 2.66 (t, 2H), 4.60 and 6.80 (s, s, 2H), 6.85–8.04 (m, 8H), 12.17 (s, 1H); MS *m/z* (rel intensity) 338 (M^+, 31), 321 (4), 203 (100), 163 (2), 121 (10), 91 (10); IR ($CHCl_3$) 1606, 1582 cm^{-1}. Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.06; H, 7.75. Found: C, 78.18; H, 7.60.

Typical Procedure for the Synthesis of Chromen-4-ones (3b–d). Dione **2** (7.5 mmol) was dissolved in 10 mL of glacial acetic acid. To the solution were added 0.4 mL of concd H_2SO_4 and the mixture was heated at 90 °C for 1.5 h. The hot solution was then poured onto 50 g of crushed ice. Stirring was continued until complete melting of the ice.

2-Heptylchromen-4-one (3b). The mixture was extracted several times with ether and the organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude compound was purified by column chromatography on silica gel (CH_2Cl_2 then Et_2O). Fractions containing the product were dried in vacuo at 40 °C for 2 h in order to remove traces of acetic acid. The product was obtained in a 83% yield as pale yellow crystals: mp 32–34 °C; ^1H NMR δ 0.89 (t, 3H), 1.20–1.50 (m, 8H), 1.75 (m, 2H), 2.62 (t, 2H), 6.18 (s, 1H), 7.32–8.23 (m, 4H); ^{13}C NMR δ 14.45 (CH_3), 23.02 (CH_2), 27.25 (CH_2), 29.38 (CH_2), 29.40 (CH_2), 32.10 (CH_2), 34.77 (CH_2), 110.26 (CH), 118.28 (CH), 124.25 (C), 125.30 (CH), 126.13 (CH), 133.80 (CH), 157.00 (C), 170.25 (C), 178.77 (C); MS *m/z* (rel intensity) 244 (M^+, 37), 173 (53), 160 (100), 121 (92); IR (KBr) 1654 cm^{-1}. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.64; H, 8.26. Found: C, 78.91; H, 8.19.

2-Undecylchromen-4-one (3c). The crystals, which separate from water, were filtered and washed with water until washings were no longer acidic. The product was dried in vacuo at 40 °C. Off-white crystals were obtained in a 93% yield: mp 34–36 °C; ^1H NMR δ 0.88 (t, 3H), 1.12–1.49 (m, 18H), 1.72 (m, 2H), 2.61 (t, 2H), 6.19 (s, 1H), 7.32–8.22 (m, 4H); MS *m/z* (rel intensity) 300 (M^+, 30), 173 (100), 160 (46), 121 (34); IR (KBr) 1655 cm^{-1}. Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.94; H, 9.40. Found: C, 79.78; H, 9.44.

2-(4-Heptylphenyl)chromen-4-one (3d). The procedure described for **3c** was followed and off-white crystals were obtained in 95% yield: mp 45–47 °C; ^1H NMR δ 0.89 (t, 3H), 1.16–1.48 (m, 8H), 1.66 (m, 2H), 2.69 (t, 2H), 6.81 (s, 1H), 7.28–8.30 (m, 8H); MS *m/z* (rel intensity) 320 (M^+, 100), 235 (49), 207 (17); IR ($CHCl_3$) 1633 cm^{-1}. Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.45; H, 7.55. Found: C, 82.69; H, 7.47.

2-Hexylchromen-4-one (3a). Powdered sodium was obtained from 2.41 g (150 mmol) of oxide-free sodium and 22 mL of dry xylene. After cooling to room temperature, the xylene was decanted and the sodium was washed with dry ethyl ether. The flask was cooled to 5 °C and a mixture of *o*-hydroxyacetophenone (5.3 mL, 44 mmol) and ethyl heptanoate (22 mL, 120 mmol) was added dropwise during 2.5 h. The mixture was then heated to 90 °C and left under stirring for an additional 2.5 h. After cooling, the yellow solid was carefully transferred while stirring into a flask containing 30 g of crushed ice. Volumes of 30 mL of water and 10 mL of glacial acetic acid were then added and the mixture stirred for 30 min. The phases were then separated and the water layer extracted twice with 20 mL portions of ethyl ether. The combined organic portions were concentrated and 15 mL of glacial acetic acid and 1 mL of concentrated hydrochloric acid added. The solution was refluxed for 45 min and concentrated.

The oily residue was chromatographed on silica gel with CH_2Cl_2 until the elution of unreacted *o*-hydroxyacetophenone and then with $CHCl_3$. The title compound was obtained as a pale yellow oil (3.63 g, 36% yield): ^1H NMR δ 0.91 (t, 3H), 1.20–1.49 (m, 6H), 1.76 (m, 2H), 2.63 (t, 2H), 6.20 (s, 1H), 7.32–8.24 (m, 4H); MS *m/z* (rel intensity) 230 (M^+, 29), 173 (33), 160 (97), 121 (100); IR (film) 1656 cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.22; H, 7.88. Found: C, 78.01; H, 7.91.

General Procedure for the Synthesis of Racemic 2,3-Dihydrobenzopyrans 4a–c. Ketone **3** (7.5 mmol) was dissolved in 14 mL of ethanol and 4 mL of concd HCl. To this solution was added 0.50 g of Pd 10% on carbon and the suspension was left under H_2 pressure (2 bar) in a Parr apparatus for 60 h. The crude reaction mixture was then filtered through Celite. Solvents were removed under reduced pressure and the residue purified by chromatography on silica gel ($CHCl_3$).

2-Hexyl-2,3-dihydrobenzopyran (4a): 63% of colorless oil; ^1H NMR δ 0.90 (t, 3H), 1.11–2.02 (m, 12H), 2.63–2.95 (m, 2H), 3.90–4.02 (m, 1H), 6.74–7.12 (m, 4H); MS *m/z* (rel intensity): 218 (M^+, 33), 133 (26), 120 (21), 107 (100). Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.28; H, 10.21.

2-Heptyl-2,3-dihydrobenzopyran (4b): 95% of colorless oil; ^1H NMR δ 0.89 (t, 3H), 1.19–2.06 (m, 14H), 2.64–2.94 (m, 2H), 3.89–4.03 (m, 1H), 6.75–7.12 (m, 4H); ^{13}C NMR δ 14.52 (CH_3), 23.13 (CH_2), 25.30 (CH_2), 25.80 (CH_2), 27.92 (CH_2), 29.74 (CH_2), 30.09 (CH_2), 32.33 (CH_2), 35.91 (CH_2), 76.41 (CH), 117.23 (CH), 120.31 (CH), 122.55 (C), 127.76 (CH), 129.93 (CH), 155.88 (C); MS *m/z* (rel intensity) 232 (M^+, 41), 133 (29), 120 (20), 107 (100). Anal. Calcd for $C_{16}H_{24}O$: C, 82.69; H, 10.42. Found: C, 82.47; H, 10.51.

2-Undecyl-2,3-dihydrobenzopyran (4c): 97% of colorless oil; ^1H NMR δ 0.89 (t, 3H), 1.12–2.09 (m, 22H), 2.65–2.94 (m, 2H), 3.90–4.04 (m, 1H), 6.76–7.13 (m, 4H); MS *m/z* (rel intensity) 288 (M^+, 43), 133 (22), 120 (19), 107 (100). Anal. Calcd for $C_{20}H_{32}O$: C, 83.26; H, 11.19. Found: C, 83.35; H, 11.10.

2-(4-Heptylphenyl)-2,3-dihydrobenzopyran (4d). A mixture of 1.85 g (5.8 mmol) of **3d**, 10 mL of glacial acetic acid, 3 mL of concd HCl, and 0.40 g of Pd 10% on carbon was prepared in an autoclave. The system was heated at 50 °C and left under hydrogen pressure (5 bar) and vigorous magnetic stirring for 48 h. The crude product was then filtered through Celite, diluted with ether, and washed with water. The ethereal phase was dried over Na_2SO_4 and the solvent removed in vacuo. The residue was chromatographed on silica ($CHCl_3$ and then $CHCl_3$/EtOH 95:5). The product was obtained in a 23% yield as a colorless oil: ^1H NMR δ 0.88 (t, 3H), 1.13–1.41 (m, 8H), 1.50–1.71 (m, 2H), 1.97–2.26 (m, 2H), 2.60 (t, 2H), 2.70–3.08 (m, 2H), 5.01 (dd,1H), 6.78–7.37 (m, 8H); MS *m/z* (rel intensity) 308 (M^+, 62), 223 (14), 209 (100), 133 (6), 117 (49). Anal. Calcd for $C_{22}H_{28}O$: C, 85.65; H, 9.16. Found: C, 85.41; H, 9.21.

General Procedure for the Synthesis of Racemic 6-Bromo-2,3-dihydrobenzopyrans (5a–d). 2,3-Dihydrobenzopyran **4** (9.8 mmol) was dissolved in 15 mL of ethanol and the solution was cooled in an ice bath. Bromine (0.50 mL, 9.7 mmol) dissolved in 12 mL of ethanol was added dropwise with stirring over 2 h. The reaction was followed by TLC on silica gel (double elution with petroleum ether). The mixture was concentrated in vacuo and the residue purified by column chromatography on silica gel (CH_2Cl_2).

6-Bromo-2-hexyl-2,3-dihydrobenzopyran (5a): 89% as a pale yellow oil; ^1H NMR δ 0.89 (t, 3H), 1.15–2.06 (m, 12H), 2.59–2.92 (m, 2H), 3.86–4.00 (m, 1H), 6.67 (d, 1H, J = 9.4 Hz), 7.12–7.19 (m, 2H); MS *m/z* (rel intensity) 296 (M^+, 96), 211 (20), 198 (39), 185 (100), 132 (38), 107 (19). Anal. Calcd for $C_{15}H_{21}BrO$: C, 60.79; H, 7.15. Found: C, 60.91; H, 7.10.

6-Bromo-2-heptyl-2,3-dihydrobenzopyran (5b): 90% as a pale yellow oil; ^1H NMR δ 0.89 (t, 3H), 1.18–2.08 (m, 14H), 2.61–2.91 (m, 2H), 3.88–4.04 (m, 1H), 6.66 (d, 1H, J = 9.6 Hz), 7.10–7.22 (m, 2H); MS *m/z* (rel intensity) 310 (M^+, 100), 211 (17), 198 (31), 185 (83), 132 (31), 107 (16). Anal. Calcd for $C_{16}H_{23}BrO$: C, 61.92; H, 7.48. Found: C, 61.73; H, 7.55

6-Bromo-2-undecyl-2,3-dihydrobenzopyran (5c): 74% as a pale yellow oil; ^1H NMR δ 0.88 (t, 3H), 1.12–2.05 (m, 22H), 2.61–2.90 (m, 2H), 3.87–4.01 (m, 1H), 6.67 (d, 1H, J = 9.5 Hz), 7.12–7.20 (m, 2H); MS *m/z* (rel intensity) 366 (M^+, 96), 211 (12), 198 (24), 185 (47), 132 (16), 107 (12). Anal. Calcd for $C_{20}H_{31}BrO$: C, 65.55; H, 8.53. Found: C, 65.82; H, 8.47.

6-Bromo-2-(4-heptylphenyl)-2,3-dihydrobenzopyran (5d): 96% as a pale yellow oil; ^1H NMR δ 0.89 (t, 3H), 1.14–1.46 (m, 8H), 1.60 (m, 2H), 1.94–2.28 (m, 2H), 2.62 and 2.55–3.10 (t, m,4H), 5.02 (dd, 1H), 6.77 (d, 1H, J = 9.7), 7.13–7.34 (m, 6H); MS *m/z* (rel intensity) 386 (M^+, 54), 307 (19), 287 (39), 117 (100). Anal. Calcd for $C_{22}H_{27}BrO$: C, 68.37; H, 7.05. Found: C, 68.26, H, 7.09.

General Procedure for the Synthesis of Racemic 2,3-Dihydrobenzopyran-6-carboxylic Acids (6a–d). To a solution of **5** (2.73 mmol) in 12 mL of ethyl ether was added 3.5 mL of n-butyllithium 1.6 M in ether. The mixture was stirred at room temperature for 45 min and then transferred into a flask containing powdered dry ice. The mixture was allowed to warm to room temperature with stirring. An 18% solution of HCl (14 mL) was then added and the organic layer was collected. The aqueous phase was extracted three times with ether and the combined ethereal solutions dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue chromatographed on silica ($CHCl_3$ and then $CHCl_3$/MeOH 100:5). Fractions containing the product were dried in vacuo at 50 °C and crystallized.

2-Hexyl-2,3-dihydrobenzopyran-6-carboxylic Acid (6a). The compound was obtained in a 39% yield as white crystals (petroleum ether): mp 128 (N), 142 (I) °C; ^1H NMR δ 0.91 (t, 3H), 1.25–2.15 (m, 12H), 2.72–2.99 (m, 2H), 4.00–4.16 (m, 1H), 6.82 (d, 1H, J = 9.2 Hz), 7.79–7.90 (m, 2H); MS *m/z* (rel intensity) 262 (M^+, 76), 245 (2), 177 (26), 164 (60), 151 (100), 107 (9); IR (KBr) 2546, 1680 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.24; H, 8.46. Found: C, 73.41; H, 8.40.

2-Heptyl-2,3-dihydrobenzopyran-6-carboxylic Acid (6b). The compound was obtained in a 35% yield as white crystals (toluene): mp 127 (N), 140 (I) °C; ^1H NMR δ 0.89 (t, 3H), 1.22–2.14 (m, 14H), 2.71–2.98 (m, 2H), 4.00–4.17 (m, 1H), 6.83 (d, 1H, J = 9 Hz), 7.80–7.93 (m, 2H); ^{13}C NMR δ 14.29 (CH_3), 22.97 (CH_2), 25.01 (CH_2), 25.64 (CH_2), 27.50 (CH_2), 29.56 (CH_2), 29.93 (CH_2), 32.19 (CH_2), 35.67 (CH_2) 77.33 (CH), 117.30 (CH), 121.32 (C), 122.38 (C), 130.26 (CH), 132.71 (CH), 160.48 (C), 171.69 (C); MS *m/z* (rel intensity) 276 (M^+, 87), 259 (2), 177 (28), 164 (66), 151 (100), 133 (10), 107 (11); HREIMS 276.172354 calcd for $C_{17}H_{24}O_3$ 276.172545; IR (KBr) 2543, 1676 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.87; H, 8.76. Found: C, 73.80; H, 8.75.

2-Undecyl-2,3-dihydrobenzopyran-6-carboxylic Acid (6c). The compound was obtained in a 52% yield as white crystals (toluene). mp 115 (N), 121 (I) °C; ^1H NMR δ 0.89 (t, 3H), 1.18–2.11 (m, 22H), 2.72–2.96 (m, 2H), 3.99–4.13 (m, 1H), 6.82 (d, 1H, J = 9.3 Hz), 7.80–7.92 (m, 2H); MS *m/z* (rel intensity) 332 (M^+, 100), 315 (2), 177 (19), 164 (41), 151 (61), 133 (4), 107 (6); IR (KBr) 2545, 1664 cm^{-1}. Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.85; H, 9.71. Found: C, 75.60; H, 9.80.

2-(4-Heptylphenyl)-2,3-dihydrobenzopyran-6-carboxylic Acid (6d). The compound was obtained in a 36% yield as white crystals (toluene): mp 167 (N), 202 (I) °C; ^1H NMR δ 0.89 (t, 3H, J = 6 Hz), 1.11–1.47 (m, 8H), 1.50–1.72 (m, 2H), 1.98–2.35 (m, 2H), 2.61 (t, 2H, J = 7.5 Hz), 2.78–3.13 (m, 2H), 5.12 (d, d, 1H, J = 10 Hz, J = 3 Hz), 6.96 (d, 1H, J = 9.5 Hz), 7.17–7.42 (m, 4H), 7.85–8.01 (m, 2H); MS *m/z* (rel intensity) 352 (M^+, 86), 335 (3), 307 (6), 267 (22), 253 (100), 177 (8); HREIMS 352.204132 calcd for $C_{23}H_{28}O_3$ 352.203845; IR ($CHCl_3$) 2550, 1684 cm^{-1}. Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.36; H, 8.01. Found: C, 78.05; H, 8.12.

General Procedure for the Synthesis of Racemic Esters 7a–i. To acid **6** (1 mmol) was added thionyl chloride (0.5 mL, 7 mmol) and the mixture refluxed for 1 h. Excess thionyl chloride was distilled off. Ether (2 mL) was added to the residue and distillation was resumed to remove the last traces of thionyl chloride. To the pink oily residue was added CH_3CN (5 mL), 0.28 mL (2 mmol) of Et_3N, and 1.3 mmol of the appropriate alcohol. The mixture was stirred overnight under inert atmosphere. Chloroform was added and the

mixture washed with saturated $NaHCO_3$ and water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue purified by chromatography on silica gel.

2-Hexyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4-(Hexyloxy)phenyl Ester (7a). The product was obtained in a 39% yield (CH_2Cl_2) as a white solid: mp 96 °C; ^1H NMR δ 0.90 (t, 6H), 1.25–2.12 (m, 20H), 2.80–2.92 (m, 2H), 3.97 (t, 2H), 4.0–4.16 (m, 1H), 6.82–7.14 (m, 5H), 7.88–7.99 (m, 2H); MS m/z (rel intensity) 438 (M^+, 17), 353 (1), 245 (100), 133 (15); IR (KBr) 1721 cm^{-1}. Anal. Calcd for $C_{28}H_{38}O_4$: C, 76.66; H, 8.74. Found: C, 76.55; H, 8.79.

2-Undecyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4-(Dodecyloxy)phenyl Ester (7b). The product was obtained in a 58% yield ($CHCl_3$) as a white solid: mp 82 (S), 86 (I) °C; ^1H NMR δ 0.89 (t, 6H), 1.19–2.12 (m, 42H), 2.81–2.91 (m, 2H), 3.96 (t, 2H), 4.0–4.15 (m, 1H), 6.82–7.12 (m, 5H), 7.88–7.97 (m, 2H); MS m/z (rel intensity) 592 (M^+, 3), 315 (100); IR (KBr) 1720 cm^{-1}. Anal. Calcd for $C_{39}H_{60}O_4$: C, 78.99; H, 10.21. Found: C, 78.61; H, 10.30.

2-Hexyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4'-(Dodecyloxy)biphenyl-4-yl Ester (7c). The product was obtained in a 50% yield (CH_2Cl_2/petroleum ether 1:1) as a white solid: mp 116 (S), 146 (N), 179 (I) °C; ^1H NMR δ 0.80–0.98 (m, 6H), 1.10–2.13 (m, 32H), 2.82–2.93 (m, 2H), 4.00 (t, 2H), 4.0–4.17 (m, 1H), 6.83–7.01 (m, 3H), 7.20–7.25 (m, 2H), 7.48–7.63 (m, 4H), 7.90–7.99 (m, 2H); MS m/z (rel intensity) 598 (M^+, 6), 354 (3), 245 (100); IR (KBr) 1720 cm^{-1}. Anal. Calcd for $C_{40}H_{54}O_4$: C, 80.21; H, 9.09. Found: C, 80.02; H, 9.12.

2-Heptyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4'-(Dodecyloxy)biphenyl-4-yl Ester (7d). The product was obtained in a 68% yield (CH_2Cl_2) as a white solid: mp 119 (S), 150 (N), 175 (I) °C; ^1H NMR δ 0.81–0.98 (m, 6H), 1.20–2.13 (m, 34H), 2.78–2.99 (m, 2H), 4.00 (t, 2H), 4.0–4.16 (m, 1H), 6.83–7.01 (m, 3H), 7.18–7.29 (m, 2H), 7.45–7.63 (m, 4H), 7.90–7.99 (m, 2H); MS m/z (rel intensity) 612 (M^+, 8), 354 (5), 259 (100); HREIMS 612.418217, calcd for $C_{41}H_{56}O_4$ 612.417861; IR (KBr) 1719 cm^{-1}. Anal. Calcd for $C_{41}H_{56}O_4$: C, 80.34; H, 9.22. Found: C, 80.61; H, 9.19.

2-Undecyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4'-(Dodecyloxy)biphenyl-4-yl Ester (7e). The product was obtained in a 56% yield ($CHCl_3$/petroleum ether 1:1, double elution on preparative plates) as a white solid: mp 108 (S), 158 (N), 167 (I) °C; ^1H NMR δ 0.89 (t, 6H), 1.22–2.13 (m, 42H), 2.81–2.95 (m, 2H), 4.00 (t, 2H), 4.0–4.17 (m, 1H), 6.84–7.02 (m, 13H), 7.18–7.25 (d, 2H), 7.46–7.63 (m, 4H), 7.91–8.00 (m, 2H); MS m/z (rel intensity) 668 (M^+, 5), 354 (4), 315 (100); IR (KBr) 1719 cm^{-1}. Anal. Calcd for $C_{45}H_{64}O_4$: C, 80.78; H, 9.65. Found: C, 80.70; H, 9.67.

2-(4-Heptylphenyl)-2,3-dihydrobenzopyran-6-carboxylic Acid 4'-(Dodecyloxy)biphenyl-4-yl Ester (7f). The compound was obtained in a 35% yield ($CHCl_3$) as white crystals: mp 150 (S), 218 (N), 220 (I) °C; ^1H NMR δ 0.90 (m, 6H), 1.15–1.71 (m, 28H), 1.71–1.90 (m, 2H), 2.03–2.39 (m, 2H), 2.63 (t, 2H), 2.80–3.11 (m, 2H), 4.01 (t, 2H), 5.15 (dd, 1H), 6.92–7.07 (m, 3H), 7.19–7.40 (m, 6H), 7.48–7.63 (m, 4H), 7.96–8.06 (m, 2H); MS m/z (rel intensity) 688 (M^+, 5), 354 (28), 335 (100); IR (KBr) 1717 cm^{-1}. Anal. Calcd for $C_{47}H_{60}O_4$: C, 81.92; H, 8.78. Found: C, 81.72; H, 8.89.

2-Hexyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4-Cyanophenyl Ester (7g). The product was obtained in a 73% yield (CH_2Cl_2) as a white solid: mp 81 (N + I), 84 (I) °C; ^1H NMR δ 0.91 (t, 3H), 1.22–2.13 (m, 12H), 2.75–3.0 (m, 2H), 4.01–4.17 (m, 1H), 6.88 (d, 1H, J = 9.7 Hz), 7.29–7.78 (m, 4H), 7.86–7.97 (m, 2H); MS m/z (rel intensity) 363 (M^+, 1), 278 (1), 245 (100), 133 (8); IR (KBr) 2222, 1720 cm^{-1}. Anal. Calcd for $C_{23}H_{25}NO_3$: C, 75.99; H, 6.94; N, 3.86. Found: C, 75.85; H, 6.98; N, 3.91.

2-Heptyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4-Cyanophenyl Ester (7h). The product was obtained in a 89% yield (CH_2Cl_2) as a white solid: mp 72 (N), 88 (I) °C; ^1H NMR δ 0.90 (t, 3H), 1.19–2.14 (m, 14H), 2.74–3.00 (m, 2H), 4.01–4.18 (m, 1H), 6.88 (d, 1H, J = 9.5 Hz), 7.30–7.78 (m, 4H), 7.87–7.96 (m, 2H); ^{13}C NMR δ 14.48 (CH_3), 23.09 (CH_2), 25.10 (CH_2), 25.68 (CH_2), 27.37 (CH_2), 29.66 (CH_2), 29.98 (CH_2), 32.26 (CH_2), 35.68 (CH_2) 77.50 (CH), 109.97 (C), 117.64 (CH), 118.77 (C), 120.38 (C), 122.82 (C), 123.42 (CH), 130.38 (CH), 132.93 (CH), 134.06 (CH), 155.07 (C), 160.88 (C), 164.66 (C); MS m/z (rel intensity) 377 (M^+, 1), 278 (1), 259 (100); IR (KBr) 2226, 1732 cm^{-1}. Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.35; H, 7.21; N, 3.71. Found: C, 76.53; H, 7.18; N, 3.67.

2-Undecyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4-Cyanophenyl Ester (7i). The product was obtained in a 67% yield ($CHCl_3$) as a white solid: mp 75 (S), 84 (N), 88 (I) °C; ^1H NMR δ 0.89 (t, 3H), 1.18–2.13 (m, 22H), 2.80–2.96 (m, 2H), 4.02–4.18 (m, 1H), 6.88 (d, 1H, J = 9.6 Hz), 7.30–7.77 (m, 4H), 7.87–7.98 (m, 2H); MS m/z (rel intensity) 433 (M^+, 3), 315 (100); IR (KBr) 2234, 1732 cm^{-1}. Anal. Calcd for $C_{28}H_{35}NO_3$: C, 77.55; H, 8.14; N, 3.23. Found: C, 77.46; H, 8.19; N, 3.29.

2-Undecyl-2,3-dihydrobenzopyran-6-carboxylic Acid Decyl Ester (7l). The product was obtained in a 49% yield as a white solid after chromatography on preparative plates ($CHCl_3$) and crystallization (ethanol): mp 43 °C; ^1H NMR δ 0.88 (t, 6H), 1.15–2.10 (m, 38H), 2.72–2.96 (m, 2H), 3.97–4.10 (m, 1H), 4.26 (t, 2H), 6.80 (d, 1H, J = 9.4 Hz), 7.72–7.80 (m, 2H); MS m/z (rel intensity) 472 (M^+, 100), 332 (27), 315 (17); IR (KBr) 1705 cm^{-1}. Anal. Calcd for $C_{31}H_{52}O_3$: C, 78.75; H, 11.09. Found: C, 78.60; H, 11.19.

2-Hexyl-2,3-dihydrobenzopyran-6-carboxylic Acid Methyl Ester (7j). To a solution of **6a** (0.27 g, 1.03 mmol) in MeOH (10 mL) was added concd H_2SO_4 (0.5 mL) and the mixture refluxed overnight. After cooling, the solvent was removed under reduced pressure. The residue was diluted with Et_2O (15 mL), washed with saturated $NaHCO_3$ (3 × 4 mL) and water (5 mL), and dried (Na_2SO_4). The excess alcohol was removed under reduced pressure and the residue purified by column chromatography (CH_2Cl_2). The product was obtained in a 98% yield as a colorless oil: ^1H NMR δ 0.90 (t, 3H), 1.21–2.10 (m, 12H), 2.71–2.96 (m, 2H), 3.86 (s, 3H), 3.97–4.11 (m, 1H), 6.80 (d, 1H, J = 9.6 Hz), 7.73–7.81 (m, 2H); MS m/z (rel intensity) 276 (M^+, 86), 245 (11), 217 (1), 191 (21), 178 (34), 165 (100); IR (film) 1720 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.87; H, 8.76. Found: C, 74.00; H, 8.70.

2-Hexyl-2,3-dihydrobenzopyran-6-carboxylic Acid Heptyl Ester (7k). The procedure given above for derivative **7j** was followed, and the title compound was obtained in a 71% yield as a colorless oil: ^1H NMR δ 0.90 (m, 6H), 1.20–2.11 (m, 22H), 2.71–2.95 (m, 2H), 3.97–4.11 (m, 1H), 4.27 (t, 2H), 6.80 (d, 1H, J = 9.7 Hz), 7.72–7.85 (m, 2H); MS m/z (rel intensity) 360 (M^+, 100), 275 (25), 245 (57); IR (film) 1720 cm^{-1}. Anal. Calcd for $C_{23}H_{36}O_3$: C, 76.61; H, 10.07. Found: C, 76.58; H, 10.09.

(*S*)-(−)-2-Heptyl-2,3-dihydrobenzopyran, (*S*)-(−)-4b. A solution of hexylmagnesium bromide, prepared from 0.62 g (25.5 mmol) of Mg and 3.47 mL (24.7 mmol) of 1-hexyl bromide in Et_2O (15 mL), was added over 40 min to a solution of (*R*)-(−)-2-[[(trifluoromethanesulfonyl)oxy]methyl]-2,3-dihydrobenzopyran ($[\alpha]_D$ −61.9°, *c* 1.50 in MeOH) (lit.[3] $[\alpha]_D$ −65.1, *c* 1 in MeOH) (2.32 g, 7.84 mmol) and cuprous bromide dimethyl sulfide complex (0.28 g 1.36 mmol) in 30 mL of tetrahydrofuran at −5 °C under argon. After stirring for 2 h at 0 °C, the solution was poured into a stirred mixture of water (80 mL), NH_4Cl (9.6 g), and CH_2Cl_2 (40 mL). The phases were separated and the aqueous layer extracted twice with CH_2Cl_2. The combined organic fractions were washed with saturated NH_4Cl and water and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue purified by chromatography, giving the product as a colorless liquid in a 87% yield. Spectral data were identical with those reported above for the corresponding racemic compound; $[\alpha]_D$ −79.6° (*c* 1.36 in MeOH). Anal. Calcd for $C_{16}H_{24}O$: C, 82.69; H, 10.42. Found: C, 82.40; H, 10.51.

(*S*)-(−)-6-Bromo-2-heptyl-2,3-dihydrobenzopyran, (*S*)-(−)-5b. The compound was obtained as a pale yellow oil in an 87% yield by following the procedure described above for the preparation of racemic **5b**. Spectral data were identical with those reported above for the racemic compound, $[\alpha]_D$ −80.7° (*c* 0.84 in MeOH). Anal. Calcd for $C_{16}H_{23}BrO$: C, 61.92; H, 7.48. Found: C, 61.72; H, 7.55.

(*S*)-(−)-2-Heptyl-2,3-dihydrobenzopyran-6-carboxylic Acid, (*S*)-(−)-6b. The compound was obtained as white

crystals (toluene) in a 48% yield by following the procedure described above for the preparation of racemic **6b**. Spectral data were identical with those reported above for the racemic compound: mp 129 (Ch), 141 (I) °C; $[\alpha]_D$ −125.2° (*c* 1.18 in MeOH). Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.87; H, 8.76. Found: C, 74.10; H, 8.70.

(*S*)-(−)-2-Heptyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4′-(Dodecyloxy)biphenyl-4-yl Ester, (*S*)-(−)-7d. The compound was obtained as white crystals in a 66% yield by following the procedure described above for the preparation of racemic **7d**. Spectral data were identical with those reported above for the racemic compound: mp 125 (S_C), 153 (Ch), 178 (I) °C; $[\alpha]_D$ −62.9° (*c* 0.95 in $CHCl_3$). Anal. Calcd for $C_{41}H_{56}O_4$: C, 80.34; H, 9.22. Found: C, 80.01; H, 9.27.

(*S*)-(−)-2-Heptyl-2,3-dihydrobenzopyran-6-carboxylic Acid 4-Cyanophenyl Ester, (*S*)-(−)-7h. The compound was obtained as white crystals in a 92% yield by following the procedure described above for the preparation of racemic **7h**. Spectral data were identical with those reported above for the racemic compound: mp 91 °C; $[\alpha]_D$ −98.6° (*c* 1.19 in MeOH). Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.35; H, 7.21; N, 3.71. Found: C, 76.49; H, 7.16; N, 3.65.

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