

Design and Synthesis of New Ferroelectric Liquid Crystals.

5.¹ Properties of Some Chiral Fluorinated FLCs: A Direct Connection between Macroscopic Properties and Absolute Configuration in a Fluid Phase

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Abstract: In combination with the "bent cylinder binding site" model for the molecular origins of the ferroelectric polarization **P** in ferroelectric liquid crystals (FLCs), the observed sign and magnitude of **P** in mixtures of nonracemic guests with a low-polarization host is used to establish absolute and relative configuration of the guests. The assignments are fully confirmed by conventional methods. It is shown that fluorination with (diethylamido)sulfur trifluoride (DAST) of the benzylic epoxy alcohol 4'-(*n*-decyloxy)phenyl 4-[(*S,S*)-2,3-epoxy-(*S*)-1-hydroxynonyl]benzoate (**3**) proceeds with predominant retention of configuration, while DAST fluorination of the benzylic alcohol 4'-(decyloxy)phenyl 4-[(*S*)-1-hydroxynonyl]benzoate (**6**) proceeds with predominant inversion.

Macroscopic manifestations of molecular chirality have long been of great interest to chemists. It is, however, surprisingly rare when bulk properties resulting from molecular chirality can be related back to microscopic structure (absolute configuration) in a simple, direct way³ and rarer still that this can be done in noncrystalline media.⁴ In this paper we report results illustrating that absolute and relative configuration can be determined by measurement of the sign and magnitude of the ferroelectric polarization in ferroelectric liquid crystal (FLC) phases and that in carefully designed systems the connection between the observed macroscopic "chirality phenomenon" and the microscopic absolute configuration can be beautifully direct.

We have recently proposed a simple model for the molecular origins of the ferroelectric polarization **P** observed in chiral, layered, tilted liquid crystal phases such as the smectic C* phase.¹ This model is based upon the concept that orientation of molecules in the C* phase can be understood in terms of a novel form of molecular recognition. Specifically, the molecules are oriented with respect to conformation and rotational state (relative to the smectic C* tilt plane) by a "binding site" which takes the shape of a bent cylinder. When oriented in this binding site, alkyl tails of the LC molecules should be *less tilted* from the layer normal than the core,² and the carbon atoms of a simple alkyl tail should lie in the tilt plane.

(1) Previous papers in this series: (a) Walba, D. M.; Slater, S. C.; Thurmes, W. N.; Clark, N. A.; Handschy, M. A.; Sapon, F. *J. Am. Chem. Soc.* **1986**, *108*, 5210-5221. (b) Walba, D. M.; Vohra, R. T.; Clark, N. A.; Handschy, M. A.; Xue, J.; Parmar, D. S.; Lagerwall, S. T.; Skarp, K. *J. Am. Chem. Soc.* **1986**, *108*, 7424-7425. (c) Walba, D. M.; Clark, N. A. Model for the Molecular Origins of the Polarization in Ferroelectric Liquid Crystals. *Spatial Light Modulators and Applications II*; Efron, U., Ed.; Proc. SPIE **825**, (1988); pp 81-87. (d) A preliminary account of this work appears in paper number 4 in this series, the Proceedings of the First International Symposium on Ferroelectric Liquid Crystals, Bordeaux-Arcachon, France, September 21-23, 1987; Walba, D. M.; Clark, N. A. *Ferroelectrics*, in press.

(2) Department of Physics and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO 80309-0390.

(3) Two excellent reviews of the subject, focussing on crystals, have recently appeared: (a) Addadi, L.; Berkovitch-Yellin, Z.; Weissbuch, I.; Lahav, M.; Leiserowitz, L. *Top. Stereochem.* **1986**, *16*, 1-85. (b) Paul, I. C.; Curtin, D. Y. Gas-Solid Reactions and Polar Crystals. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987; pp 331-370.

(4) (a) Calculation of absolute configuration from optical activity measurements: Mason, S. F. *Molecular Optical Activity and Chiral Discrimination*; Cambridge University Press: Cambridge, England, 1980. (b) Determination of absolute configuration by measurement of the sign of the cholesteric helix induced upon doping an achiral nematic LC phase with a chiral dopant: Solladie, G.; Gottarelli, G. *Tetrahedron* **1987**, *43*, 1425-1437.

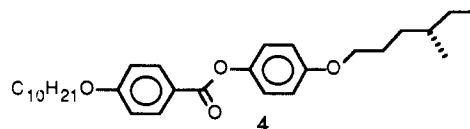
(5) Recent high-resolution X-ray scattering measurements made with the achiral smectic C phase of 4'-butoxyphenyl 4-(decyloxy)benzoate indicate that indeed the tails are less tilted than the cores in this prototypical system: Keller, E. N.; Nachaliel, E.; Davidov, D.; Böffel, C. *Phys. Rev. A* **1986**, *34*, 4363-4369.

To test this idea and to obtain new materials with large **P** (of great potential use in many optoelectronic device applications^{1c}), the 4'-(decyloxy)phenyl 4-[(*S,S*)-2,3-epoxy-1-fluorononyl]benzoate diastereomers **1** and **2** (Figure 1) were prepared and characterized.^{1d} The model suggests that the preferred conformation and rotational orientation for compounds **1** and **2** is as shown in Figure 1 and allows the predictions indicated in the figure regarding the ferroelectric properties of the stereoisomers: Compound **1** should possess small polarization, while compound **2** should possess large negative **P**.

Fluoro epoxides **1** and **2** were prepared by treatment of epoxy alcohol **3** (from Sharpless kinetic resolution⁶ of the racemic allylic alcohol) with (diethylamido)sulfur trifluoride (DAST)⁷ in dichloromethane. When the reaction was run at -78 °C, a clean 3:1 mixture of diastereomers was obtained, while at 0 °C, a 2:1 mixture of the same products resulted. Separation of the diastereomers by flash chromatography on silica gel gave pure samples of each (Scheme I).

The structures of the diastereomers were established by determination of the ferroelectric polarization of the materials in the C* phase. While neither pure isomer possessed any liquid crystal phases, the binding-site model states that doping of a chiral compound (the guest) into an achiral (or low-polarization) C phase (the host) will afford orientation of the guest molecules (such as shown in Figure 1) such that measurement of the properties of the mixture can establish the properties of the guest.

We have had excellent results using the FLC phenyl benzoate **4**, first prepared by Keller,⁸ as a low-polarization host.⁹ Indeed, when mixed with host **4** (10% by weight of guest), guest compounds **1** and **2** afford stable, well-behaved C* phases. Mea-



surement of the polarization of these mixtures in the surface-stabilized ferroelectric liquid crystal geometry¹ gave the results shown in the figure. The major product of the DAST reaction

(6) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237-6240.

(7) Middleton, W. J. *J. Org. Chem.* **1975**, *40*, 574.

(8) Keller, P. *Ferroelectrics* **1984**, *58*, 3-7. Compound **4**, 4'-[(*S*)-(+)-(4-methylhexyl)oxy]phenyl 4-(decyloxy)benzoate, is available from Aldrich.

(9) The ferroelectric polarization of host **4** is too small to measure directly. Indirect measurements done in our laboratories indicate that for neat compound **4** **P** is negative, and the magnitude of **P** ≈ 1 nC/cm² at 30 °C.

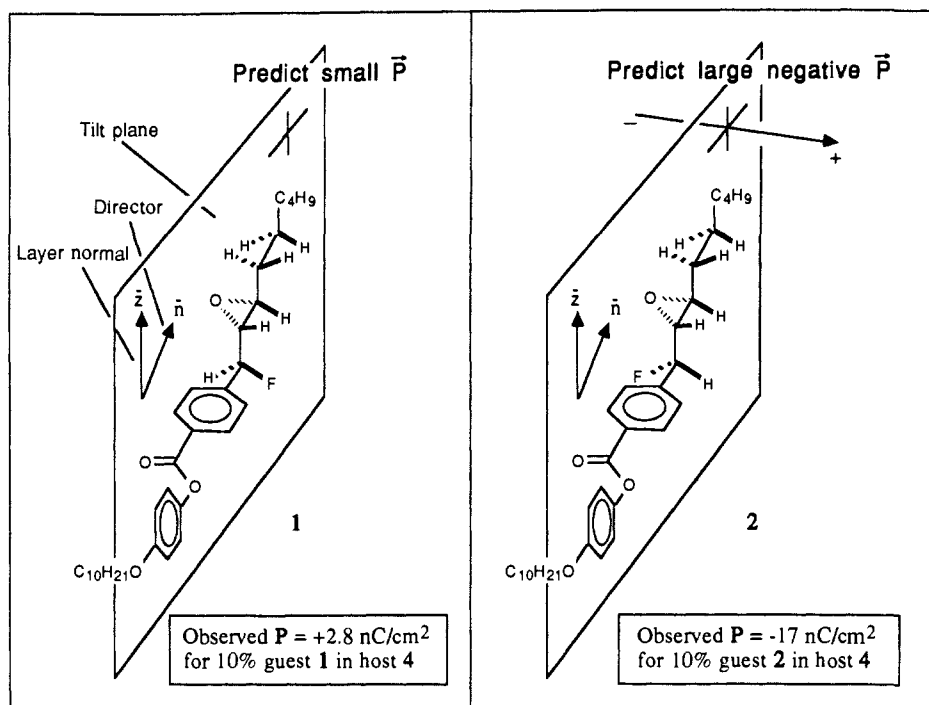
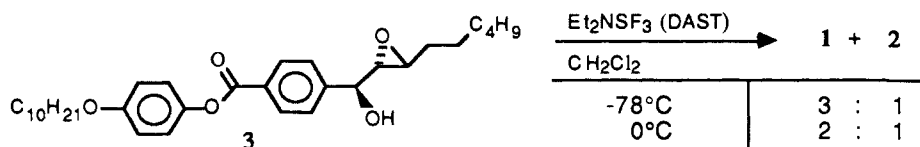


Figure 1. Proposed preferred conformation and orientation relative to the tilt plane for diastereomeric 4-(decyloxy)phenyl 4-[(*S,S*)-2,3-epoxy-1-fluorononyl]benzoates in the C^* binding site. Predicted and observed polarizations are indicated in the figure.

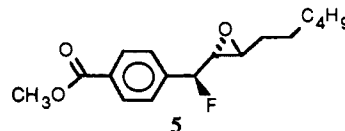
Scheme 1



induces small, positive polarization and may therefore be assigned structure **1**, while the minor product, affording large, negative polarization, may be assigned structure **2** according to the model. It should be noted that the extrapolated polarization of compound **2** (-130 nC/cm^2 , or about -0.4 D/molecule) is comparable to the measured values of typical "high polarization" materials.¹⁰

Thus, in this system the DAST fluorination apparently proceeds with predominant *retention* of configuration! This somewhat surprising result¹¹ was proven unequivocally by single-crystal X-ray analysis of the methyl ester **5** deriving from the major product of the DAST reaction (phenyl benzoate **1**) by hydrolysis (LiOH,

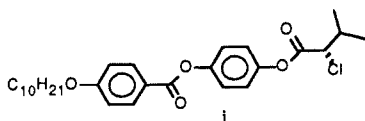
MeOH, reflux) followed by esterification (DCC, DMAP, MeOH, CH_2Cl_2).



In this work, the relative configuration of fluoro epoxides **1** and **2** was in fact first established by measurement of the ferroelectric polarization of C^* mixtures containing the two compounds as guests and application of the binding-site model as shown in Figure 1. The *absolute configuration* of both fluoro epoxides was set in a Sharpless epoxidation, though the observed sign of P for compound **2** is also indicative of absolute configuration.

Occasion to apply this approach for a priori assignment of absolute configuration quickly arose in our laboratories. Thus, a synthesis of the (decyloxy)phenyl (1-fluorononyl)benzoate **7** was achieved by treatment of benzylic alcohol **6** (from reduction of a phenyl propargyl ketone with *R*-Alpine-Borane according to Midland¹²) with DAST. Measurement of the optical rotation of samples of compound **7** prepared at -78°C and at 0°C showed that, at least at the higher temperature, considerable racemization was occurring. Which was the major enantiomer, **7(R)** or **7(S)**, was not known, since the process could occur with predominant inversion or retention.

Measurement of the properties of a mixture of compound **7** with host **4** showed that the material formed in the fluorination had a moderately large positive polarization ($P_{\text{obs}} = +21 \text{ nC/cm}^2$ in a 1:1 mixture by weight with host **4**), in agreement with that

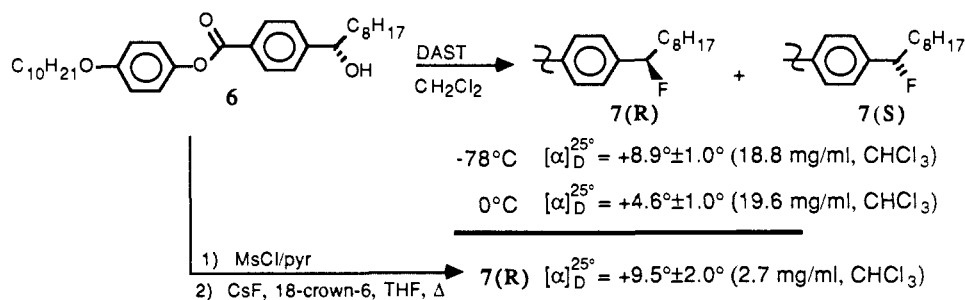


polarization of neat chloro ester **i** is -125 nC/cm^2 , and the observed polarization of a mixture containing 11% by weight of guest **i** in host **4** is -11 nC/cm^2 .

(11) We know of only one other example in the literature where DAST fluorination proceeds with retention in the absence of standard neighboring group participation: (a) Bird, T. G. C.; Felsky, G.; Fredericks, P. M.; Jones, E. R. H.; Meakins, G. D. *J. Chem. Res. Synop.* **1979**, 388. (b) Bird, T. G. C.; Fredericks, P. M.; Jones, E. R. H.; Meakins, G. D. *J. Chem. Soc., Chem. Commun.* **1979**, 65. In this case, it is reported that 12β -hydroxyandrostan-17-one gives 12β -fluoroandrostan-17-one upon DAST fluorination.

(12) Midland, M. M.; McDowell, D. C.; Hatch, L. H.; Tramontano, A. *J. Am. Chem. Soc.* **1980**, *102*, 867. The alcohol was $>95\%$ enantiomerically enriched as judged by NMR with tris[3-(heptafluoropropyl)hydroxymethylene]-(+)-camphorato]europium(III) derivative ($\text{Eu}(\text{hfc})_3$).

Scheme 11



expected for the fluoride formed with predominant *inversion* of configuration (7(R)).

In order to more fully establish the stereochemistry of the fluorination of alcohol 6, the mesylate derived from 6 was treated with CsF/18-crown-6 in refluxing THF. This process was quite inefficient and gave a low yield (1%) of pure fluoride, which must be 7(R), since this process must proceed with inversion of configuration. The measured optical rotation of fluoride 7(R) prepared in this way corroborates the above described assignment of absolute configuration of the major product of the DAST reaction and indicates the DAST process at -78°C gives highly enantiomerically enriched product (at least 69% ee) with inversion (Scheme II).

In conclusion, we have demonstrated the basic correctness of the bent cylinder model for packing in the C^* phase and have illustrated how the model can be used to establish relative and absolute configuration for very specific but interesting structures. These assignments are accomplished independently of any optical activity or crystallography measurements and are therefore to our knowledge completely unique. The compounds need not possess a C^* phase in order to apply the technique. Finally, it has been shown that DAST fluorination of epoxy alcohol 3 proceeds with predominant retention of configuration (about 3:1 at -78°C , 2:1 at 0°C), while such fluorination of unsubstituted benzylic alcohol 6 proceeds with predominant inversion of configuration at -78°C and at 0°C .

Experimental Section

General Methods. All proton and carbon NMR spectra were run on a Bruker WM-250 or a Chemagnetics A200 spectrometer. Spectra were run in CDCl_3 , which was used as an internal standard for carbon spectra. For proton spectra, residual CHCl_3 was used as the internal standard. Infrared spectra were taken on a Mattson FT-IR or a Perkin-Elmer 727B spectrometer. Mass spectra were taken on a VG 7070 EQ mass spectrometer. The reagent gas used for CI mass spectroscopy was isobutane. Optical rotations were obtained on a Perkin-Elmer 141 polarimeter. The temperature of the polarimeter cell was kept at 25°C with a Haake D8-L heating circulator bath. Elemental analyses were performed by Galbraith Labs, Knoxville, TN.

Analytical thin-layer chromatography (TLC) was performed on glass silica gel plates (0.25 mm thick E. Merck silica gel 60-F254). The components were visualized with a UV lamp (254 nm) or by anisaldehyde spray reagent (1:2:100 anisaldehyde/concentrated H_2SO_4 /ethanol). Chromatographic purifications were performed by using flash chromatography¹³ on E. Merck 40–63- μm normal-phase silica gel. All eluting solvents were distilled before use.

Conventional melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Phase-transition data were determined by using a polarizing microscope fitted with a hot stage. The temperature of the stage was controlled with an Instec mK1 temperature controller running off an Apple 2e computer.¹⁴

All reactions requiring the exclusion of water and air were run under a positive pressure of argon with a mercury bubbler in flame-dried glassware. Flame drying was accomplished by alternately flaming the reaction vessel under vacuum and filling with argon once ambient temperature was reached. All air- and moisture-sensitive reagents were handled under argon atmosphere with oven-dried Luer-Lock syringes and stainless steel cannula.¹⁵

"Dry" solvents were dried immediately prior to use. Ether and tetrahydrofuran (THF) were distilled from benzophenone and sodium, dichloromethane was distilled from phosphorus pentoxide, and dimethylformamide (DMF) was distilled from calcium hydride at reduced pressure and stored over dried 3- \AA molecular sieves prior to use. Triethylamine, toluene, and thionyl chloride were purified by a center-cut distillation and stored over dried 3- \AA molecular sieves. Methyl iodide and methanesulfonyl chloride were purchased from commercial sources and stored over dried 3- \AA molecular sieves prior to use.

Copper(I) iodide (CuI) was purified by adding 53.2 g of impure CuI to a solution of 524 g of potassium iodide (KI) in approximately 400 mL of water. Activated charcoal (2 g) was added and the mixture was heated to 60°C for 20 min. The suspension was filtered through Celite and the filtrate was poured into 3 L of water. The CuI was filtered off and transferred to a 1-L beaker and then washed with 500 mL of water, 500 mL of acetone, and 500 mL of methanol. The solid was protected from light and was dried under vacuum overnight. The CuI thus obtained was powdered and dried under vacuum for an additional 5 h. In a glove bag, under argon, the solid was transferred to small vials which were wrapped in foil.

Most reagents were obtained from commercial sources and used without further purification unless otherwise stated. Organolithium solutions were titrated with *sec*-butyl alcohol prior to use.¹⁶ (1*R*)-(+)- α -Pinene ($[\alpha]^{22} = +47.1^\circ$ (neat)) and (+)-diisopropyl L-tartrate ($[\alpha]^{24} = +17^\circ$ (neat)) were obtained from Aldrich Chemical Co. and used without further purification. *B*-[*(E)*-1-octen-1-yl]-9-BBN was prepared according to the procedure described by Brown and co-workers.¹⁷ The 4-(decyloxy)phenol was prepared according to the procedure described by Neubert and co-workers¹⁸ except dichloromethane (0.34 M) with a few drops of triethylamine was used as solvent under 15 psi of hydrogen at ambient temperature for 8–9 h to achieve the debenzoylation. Methyl 4-formylbenzoate was obtained from Fluka Chemical Corp.

For isolation by solvent extraction, the procedure generally followed was to extract the aqueous layers with several portions of the indicated solvent. The combined organic layers were dried over a combination of anhydrous sodium sulfate and anhydrous potassium carbonate unless otherwise stated. The solution was then decanted into a flask (if anhydrous magnesium sulfate was used, transfer was accomplished by filtration through Celite in a fritted funnel), and the drying agent was washed thoroughly with fresh solvent. The solvent was then removed under reduced pressure (water aspirator) by using a rotary evaporator, and the nonvolatile compounds were dried in vacuo (≈ 1 mmHg).

Measurement of the Sign and Magnitude of P. The magnitude of P was measured by integration of the dynamic current response of a surface-stabilized ferroelectric liquid crystal cell on reversing the applied electric field by using a slight modification of the standard methods of Martinot-Lagarde.¹⁹ The polarization-reversal current was measured after applying a triangular wave form (± 15 volts) across a 2.5- μm (Polyimide spacers) polymer-aligned²⁰ (Du Pont Elvamide 8061) SSFLC cell with indium-tin oxide (ITO) conducting glass electrodes. The signal (current vs time) was digitized with a Sony/Tektronix 390AD programmable digitizer. The current waveform showed a peak characteristic of the polarization reversal; this current peak was integrated. Division of the value of this integration (charge) by the active area of the cell af-

(16) Bergbreiter, D. E.; Pendergrass, E. *J. Org. Chem.* **1981**, *46*, 219.

(17) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96.

(18) Neubert, M. E.; Laskos, S. J.; Maurer, L. T.; Carlino, L. T.; Ferrato, J. P. *Mol. Cryst. Liq. Cryst.* **1978**, *44*, 197.

(19) (a) Martinot-Lagarde, Ph. *J. Phys. (Paris), Colloq.* **1976**, *37*, C-3, 129. (b) Martinot-Lagarde, Ph. *J. Phys. (Paris), Lett.* **1977**, *38*, L-17.

(20) Patel, J. S.; Goodby, J. W. *J. Appl. Phys.* **1986**, *59*, 2355. (b) Flatschler, K.; Skarp, K.; Lagerwall, S. T.; Stebler, B. *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 21. (c) Patel, J. S.; Leslie, T. M.; Goodby, J. W. *Ferroelectrics* **1984**, *57*, 137.

(13) Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(14) Instec, Inc., P.O. Box 7246, Boulder, CO 80306.

(15) Lane, C. F.; Kramer, G. W. *Aldrichimica Acta* **1977**, *10*, 11.

forded the magnitude of ferroelectric polarization. For all measurements, the diameter of the ITO-coated area of the cell was 0.50 in.

The sign of the polarization was determined directly from observation of molecular orientation in SSFLC cells upon application of electric fields. Thus, in a typical "well-behaved" FLC material, a smectic A phase is present at temperatures above the C* phase, the A → C* transition is second order, and the saturation tilt angle is about 20°. The materials evaluated in these experiments were well-behaved. The precise director orientation in the smectic A phase was established by rotating the cell into extinction in shear-aligned samples between crossed polarizers at an angle approximately normal to the shear direction. This method is unequivocal since for all smectic A phases known the director orients normal to the shear direction in sheared samples. The sample was then cooled into the smectic C* phase, and an electric field of known polarity was applied across the cell. The cell was rotated to extinction. The sign of the polarization was then determined on the basis of the tilt direction thus obtained for molecules in an electric field of known polarity.

Synthesis of Fluoro Epoxides 1 and 2. *4'-(n-Decyloxy)phenyl 4-Formylbenzoate.* A 1-L flame-dried flask equipped with a magnetic stirrer bar and a septum inlet was charged with 14 g of 4-(decyloxy)phenol (55.91 mmol), 9.45 g of 4-formylbenzoyl chloride (56.06 mmol), and 0.82 g of 4-pyrrolidinopyridine in 500 mL of dry THF. Triethylamine (8.6 mL, 61.70 mmol) was added while the mixture was stirred vigorously. The reaction mixture was stirred for 1.5 h, precipitated Et₃N·HCl was removed by filtration, and the filtrate was concentrated. The solid residue was dissolved in 300 mL of dichloromethane, and the resulting solution was washed with 75 mL of saturated CuSO₄ solution, 75 mL of 15% NaOH solution, 75 mL of 10% HCl solution, and 75 mL of saturated NaHCO₃ solution. The organic layer was dried over Na₂SO₄/K₂CO₃ and the solvent was removed in vacuo, affording 29 g of crude product. This solid was recrystallized from 1 L of 2-propanol and 600 mL of 33% ethyl acetate/hexanes solution to give 15.18 g of pure 4'-(n-decyloxy)phenyl 4-formylbenzoate: 58–84% yield; mp 99.9–102.0 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.86 (t, 3 H, RCH₃), 1.10–1.60 (m, 14 H, ArOCH₂CH₂(CH₂)₇CH₃), 1.77 (m, 2 H, ArOCH₂CH₂), 3.94 (t, 2 H, J = 6.5 Hz, ArOCH₂), 6.92 (d, 2 H, J = 9.1 Hz, ArH), 7.11 (d, 2 H, J = 9.0 Hz, ArH), 7.99 (d, 2 H, J = 8.2 Hz, ArH), 8.33 (d, 2 H, J = 8.2 Hz, ArH), 10.12 (s, 1 H, ArCHO); ¹³C NMR (250 MHz, CDCl₃) δ 14.00, 22.62, 26.02, 29.26, 29.35, 29.52, 29.54, 31.85, 68.55, 115.26, 122.13, 129.50, 130.64, 134.74, 139.61, 144.12, 157.19, 164.40, 191.27; IR (CDCl₃) ν 2920, 2820, 1740, 1710, 1500, 1260, 1235, 1175, 1060 cm⁻¹; mass spectrum, *m/z* (relative intensity) 382 (M⁺, 8.94), 133.4 (100); R_f 0.38 (20% ethyl acetate/hexanes). Anal. Calcd for C₂₄H₃₀O₄: C, 75.36; H, 7.91. Found: C, 75.18; H, 8.03.

4'-(n-Decyloxy)phenyl 4-(E)-1-Hydroxy-2-nonenylbenzoate. A 250-mL flame-dried flask equipped with a septum inlet and a magnetic stirrer bar was charged with 10.93 g of 4'-(n-decyloxy)phenyl 4-formylbenzoate (28.57 mmol) in 110 mL of dry THF. *B-[(E)-1-octen-1-yl]-9-BBN* (11.64 g, 32.86 mmol) was added dropwise under argon. The reaction mixture was stirred at ambient temperature for 2 h before it was heated to reflux and stirred overnight. The flask was cooled (ice/water bath), and 1.98 mL of ethanolamine (32.86 mmol) was added. The reaction mixture was stirred for 15 min, most of the solvent was removed by rotary evaporation, and the residue was triturated with 50 mL of ether. The resulting mixture was cooled with an ice/water bath and the precipitate was filtered through one inch of silica gel and washed six times with 25-mL portions of 20% ethyl acetate/hexanes. The filtrate was concentrated in vacuo and the resulting crude product was purified by flash chromatography on silica gel with 20% ethyl acetate/hexanes as eluent to afford 10.31 g of 4'-(n-decyloxy)phenyl 4-[(E)-1-hydroxy-2-nonenyl]benzoate: 61–78% yield; mp 39.2–40.8 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.87 (m, 6 H, (RCH₃)₂), 1.10–1.60 (m, 22 H, ArOCH₂CH₂(CH₂)₇CH₃, CH=CHCH₂(CH₂)₄CH₃), 1.77 (quint, 2 H, J = 7.3 Hz, ArOCH₂CH₂), 2.03 (m, 2 H, CH=CHCH₂), 3.93 (t, 2 H, J = 6.5 Hz, ArOCH₂), 5.23 (d, 1 H, J = 6.8 Hz, ArCHOH), 5.6–5.8 (m, 2 H, ArCHOHCH=CH), 6.90 (d, 2 H, J = 9.1 Hz, ArH), 7.08 (d, 2 H, J = 9.2 Hz, ArH), 7.47 (d, 2 H, J = 8.1 Hz, ArH), 8.14 (d, 2 H, J = 8.1 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.96, 14.01, 22.53, 22.62, 26.03, 28.79, 28.95, 29.27, 29.30, 29.36, 29.53, 31.62, 31.86, 32.13, 68.55, 74.79, 115.20, 122.32, 126.15, 128.78, 130.26, 131.83, 133.76, 144.42, 156.95, 165.25; IR (CDCl₃) ν 3450, 3020, 2920, 2840, 1728, 1610, 1500 cm⁻¹; mass spectrum, *m/z* (relative intensity) 494 (M⁺, 15), 245 (100); R_f 0.31 (20% ethyl acetate/hexanes). Anal. Calcd for C₃₂H₄₆O₄: C, 77.69; H, 9.37. Found: C, 77.51; H, 9.25.

4'-(n-Decyloxy)phenyl 4-[(S,S)-2,3-Epoxy-(S)-1-hydroxynonyl]benzoate (3). A 250 mL flame-dried flask equipped with a magnetic stirrer bar and a septum inlet was charged with 5.49 g of titanium(IV) isopropoxide (18.44 mmol) in 100 mL of dry dichloromethane. The solution was cooled to -30 °C while being stirred under argon. To the

flask, 4.65 mL of (+)-diisopropyl L-tartrate (22.11 mmol) was added and stirring was continued for 20 min. A cooled solution (CCl₄/dry ice) of 4'-(n-decyloxy)phenyl 4-[(E)-1-hydroxy-2-nonenyl]benzoate (9.12 g, 18.44 mmol) in 50 mL of dry dichloromethane was then added, and 34 mL of the dichloromethane was used to transfer all residual allyl alcohol. The reaction mixture was stirred for 10 min before 3.32 mL of *tert*-butyl hydroperoxide (2.5 M in toluene, 8.3 mmol) was added. The reaction flask was stored in the freezer (-25 °C) for 18 h.

A 100-mL flask was charged with a solution of 9.22 g of ferrous sulfate and 3.7 g of tartaric acid in 37 mL of water and was cooled in an ice/water bath before the contents were added to the reaction flask. The reaction material was then warmed to ambient temperature and stirred for 1 h. The two layers were separated, and the aqueous layer was washed three times with 50-mL portions of ether. The combined organic layers were dried over sodium sulfate, and the solvent was removed in vacuo. The oil obtained was dissolved in a minimum amount of 20% ethyl acetate/hexanes solution and was filtered through 2 in. of silica, which was then washed thoroughly with 20% ethyl acetate/hexanes. The combined filtrate was concentrated and purified by flash chromatography on silica with 25% ethyl acetate/hexanes as eluant. The product was then recrystallized from hexanes at -20 °C. The gel obtained was centrifuged at -20 °C and the solvent was decanted to afford 3.73 g of epoxy alcohol 3: 61–98% yield; mp 68.9–69.5 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.87 (m, 6 H, (RCH₃)₂), 1.15–1.60 (m, 24 H, ArOCH₂CH₂(CH₂)₇CH₃, CHOCH(CH₂)₅CH₃), 1.73 (quint, 2 H, J = 6.8 Hz, ArOCH₂CH₂), 2.40 (d, 1 H, J = 1.8 Hz, ArCHOH), 3.0 (t, 1 H, J = 3.0 Hz, ArCHOHCHOH), 3.12 (m, 1 H, ArCHOHCHOH), 3.94 (t, 2 H, J = 6.5 Hz, ArOCH₂), 4.97 (s, 1 H, ArCHOH), 6.91 (d, 2 H, J = 9.1 Hz, ArH), 7.08 (d, 2 H, J = 9.0 Hz, ArH), 7.50 (d, 2 H, J = 8.2 Hz, ArH), 8.18 (d, 2 H, J = 8.3 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.92, 14.01, 22.45, 22.62, 25.81, 26.04, 28.85, 29.27, 29.29, 29.36, 29.53, 31.30, 31.63, 31.86, 55.26, 61.05, 68.57, 70.74, 115.23, 115.29, 126.25, 129.54, 130.36, 144.37, 145.59, 157.01, 165.17; IR (CDCl₃) ν 3550, 3010, 2930, 2850, 1735, 1510, 1270, 1235, 1185 cm⁻¹; mass spectrum, *m/z* (relative intensity) 510 (M⁺, 0.49), 147.1 (91.98), 133.1 (100); R_f 0.19 (20% ethyl acetate/hexanes). Anal. Calcd for C₃₂H₄₆O₅: C, 75.42; H, 9.10. Found: C, 75.33; H, 9.15.

4'-(n-Decyloxy)phenyl 4-[(S,S)-2,3-Epoxy-(S)-1-fluorononyl]benzoate (1) and 4'-(n-Decyloxy)phenyl 4-[(S,S)-2,3-Epoxy-(R)-1-fluorononyl]benzoate (2). A 100-mL flame-dried flask equipped with a septum inlet and a stirrer bar was charged with 0.5 g of epoxy alcohol 3 (0.98 mmol) in 80 mL of dry dichloromethane. The flask was cooled (dry ice/acetone) before addition of 0.13 mL of (diethylamido)sulfur trifluoride (DAST, 0.98 mmol) and stirring for 2 h. The reaction was quenched by adding 7 mL of water before warming to ambient temperature. The layers were separated after addition of 10 mL of brine. The organic layer was washed with 10 mL of NaHCO₃ solution and dried over K₂CO₃/Na₂SO₄. The solvent was removed in vacuo, and the products were purified by flash chromatography on silica gel with 9% ethyl acetate/hexane as eluant. The total yield of a pure mixture of diastereomers was 0.46 g (92%, ratio of 1 to 2 by NMR was 2.85:1. The yield in this reaction varied from 78% to 92%). Further chromatography gave a pure sample of each diastereomer (0.35 g of 1 and 0.11 g of 2 isolated). 1: mp 65.3–65.4 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.89 (m, 6 H, (RCH₃)₂), 1.20–1.80 (m, 26 H, ArOCH₂(CH₂)₈CH₃, CHOCH(CH₂)₅CH₃), 3.02 (m, 2 H, ArCHFCHOH), 3.96 (t, 2 H, J = 6.5 Hz, ArOCH₂), 5.41 (d of d, 1 H, J = 4.3, 46.9 Hz, ArCHF), 6.93 (d, 2 H, J = 9.1 Hz, ArH), 7.11 (d, 2 H, J = 9.1 Hz, ArH), 7.52 (d, 2 H, J = 8.1 Hz, ArH), 8.52 (d, 2 H, J = 8.1 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.94, 14.03, 22.49, 22.66, 25.75, 26.07, 26.97, 28.94, 29.30, 29.34, 29.40, 29.56, 29.58, 31.36, 31.67, 31.90, 56.89, 56.96, 58.42, 58.92, 68.64, 90.70, 93.51, 115.30, 122.30, 126.03, 126.14, 130.37, 141.96, 142.29, 144.38, 157.11, 164.98.

2: mp 87.1–88.0 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.87 (m, 6 H, (RCH₃)₂), 1.20–1.85 (m, 26 H, ArOCH₂(CH₂)₈CH₃, CHOCH(CH₂)₅CH₃), 3.00 (m, 2 H, ArCHFCHOH), 3.94 (t, 2 H, J = 6.5 Hz, ArOCH₂), 5.27 (d of d, 1 H, J = 5.98, 47.35 Hz, ArCHF), 6.91 (d, 2 H, J = 9.1 Hz, ArH), 7.09 (d, 2 H, J = 9.1 Hz, ArH), 7.49 (d, 2 H, J = 8.2 Hz, ArH), 8.21 (d, 2 H, J = 8.2 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.90, 13.99, 22.45, 22.63, 25.70, 26.05, 28.87, 29.28, 29.32, 29.37, 29.55, 31.31, 31.62, 31.88, 55.97, 56.08, 59.09, 59.52, 68.61, 91.94, 94.76, 115.28, 122.25, 125.84, 125.95, 130.44, 141.62, 141.97, 144.35, 157.11, 164.87; IR (CDCl₃) ν 2920, 2840, 1720, 1500, 1260, 1240, 1190, 1080 cm⁻¹; mass spectrum, *m/z* (relative intensity) 512 (M⁺, 0.4), 263 (100); R_f 0.51 (20% ethyl acetate/hexanes). Anal. Calcd for C₃₂H₄₅O₄F: C, 74.97; H, 8.85; F, 3.71. Found: C, 74.93; H, 8.95; F, 3.66.

Synthesis of Ester 5. *4-[(S,S)-2,3-Epoxy-(S)-1-fluorononyl]benzoic Acid.* A 10-mL flask equipped with a stirring bar and a condenser was charged with 0.04 g (0.078 mmol) of the major diastereomer (1) obtained

from the DAST fluorination of epoxy alcohol **3** and 0.023 g of lithium hydroxide in 3 mL of methanol and 1 mL of water. The reaction mixture was heated to reflux and stirred for 30 min. The reaction flask was cooled before adding 10 mL of ether and 5 mL of water. The organic layer was separated and washed twice with 5-mL portions of 7% wt/wt NaOH solution. The combined aqueous layers were acidified and extracted three times with 10-mL portions of ether. The combined organic layers were washed twice with 5-mL portions of brine and dried over MgSO₄. The solvent was removed in vacuo, affording 0.021 g of product. Crystallization from ether or methanol gave very fine crystals of 4-(*S,S*)-2,3-epoxy-(*S*)-1-fluorononyl]benzoic acid: ¹H NMR (250 MHz, CDCl₃) δ 0.87 (t, 3 H, *J* = 6.2 Hz, RCH₃), 1.20–1.70 (m, 10 H, ArCHFCHOCH(CH₂)₂CH₃), 3.02 (t, 2 H, *J* = 4.9 Hz, ArCHFCHOCH), 5.37 (d of d, 1 H, *J* = 3.9, 46.9 Hz, ArCHF), 7.48 (d, 2 H, *J* = 7.6 Hz, ArH), 8.13 (d, 2 H, *J* = 7.5 Hz, ArH); *R*_f 0.045 (20% ethyl acetate/hexanes).

Methyl 4-[(*S,S*)-2,3-Epoxy-(*S*)-1-fluorononyl]benzoate (5). A 10-mL flask equipped with a septum inlet and a stirrer bar was charged with 0.04 g of 4-[(*S,S*)-2,3-epoxy-(*S*)-1-fluorononyl]benzoic acid (0.14 mmol), 0.008 mL of methanol (0.19 mmol), and 0.002 g of DMAP in 0.5 mL of dichloromethane. DCC (0.032 g, 0.16 mmol) was added, and the reaction mixture was stirred for 4 h at ambient temperature. The solid was filtered off through Celite, and the filtrate was diluted with 10 mL of ether. The ether solution was washed twice with 5-mL portions of 7% wt/wt NaOH solution, once with 5 mL of water, 5 mL of saturated copper(II) sulfate solution, 5 mL of water, and 5 mL of saturated NaHCO₃ solution. The organic layer was dried over MgSO₄. The solvent was removed in vacuo, giving 0.055 g of solid residue. The crude product was purified by flash chromatography to afford 0.033 g of methyl benzoate **5**: 79% yield; ¹H NMR (250 MHz, CDCl₃) δ 0.86 (t, 3 H, *J* = 6.5 Hz, ArCHFCHOCH(CH₂)₂CH₃), 1.08–1.88 (m, 10 H, ArCHFCHOCH(CH₂)₂CH₃), 2.96 (m, 1 H, ArCHFCHOCH), 3.01 (m, 1 H, ArCHFCHOCH), 3.90 (s, 3 H, ArCOOCH₃), 5.37 (d of d, 1 H, *J* = 4.0, 46.9 Hz, ArCHF), 7.43 (d, 2 H, *J* = 8.4 Hz, ArH), 8.05 (d, 2 H, *J* = 8.1 Hz, ArH); *R*_f 0.50 (20% ethyl acetate/hexanes).

Synthesis of (1-Fluorononyl)benzoate 7. **Methyl 4-[1-Hydroxy-2-nonyl]benzoate.** A 250-mL flame-dried flask equipped with a magnetic stirrer bar and a septum inlet was charged with 9.5 mL of 1-octyne (64.40 mmol) in 60 mL of dry THF and then cooled with a dry ice/acetone bath. A solution of *n*-butyllithium in hexane (1.53 M, 39.81 mL, 60.91 mmol) was then added over a period of 15 min. The reaction mixture was stirred for an additional 30 min before the solution was decanted slowly (0.5 h) into a cooled (dry ice/acetone) 500 mL flame-dried flask containing 10 g of methyl 4-formylbenzoate (60.92 mmol) in 300-mL of dry THF. The resulting faint yellow solution was stirred for 30 min before quenching by the addition of 50 mL of concentrated NH₄Cl solution and warming to ambient temperature. Anhydrous sodium sulfate was then added to the reaction mixture until the aqueous layer became pasty. The organic layer was decanted and the paste was washed three times with 20-mL portions of ether. The combined organic layers were dried over Na₂SO₄/K₂CO₃, and the solvent was removed in vacuo. The oil thus obtained was distilled in a Kugelrohr oven to afford 13.03 g of methyl 4-[1-hydroxy-2-nonyl]benzoate between 145 and 160 °C at 0.45 mmHg: 78% yield; ¹H NMR (250 MHz, CDCl₃) δ 0.88 (t, 3 H, *J* = 6.6 Hz, ArCHOHC≡C(CH₂)₂CH₃), 1.00–1.70 (m, 8 H, ArCHOHC≡CCH₂(CH₂)₂CH₃), 2.24 (d of t, 2 H, *J* = 2.0, 7.1 Hz, ArCHOHC≡CCH₂), 2.45 (d, 2 H, *J* = 6.1 Hz, ArCHOH), 3.91 (s, 3 H, CH₃OCOAr), 5.49 (d, 1 H, *J* = 5.9 Hz, ArCHOHC≡C), 7.60 (d, 2 H, *J* = 8.1 Hz, ArH), 8.02 (d, 2 H, *J* = 8.3 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.65, 18.52, 22.22, 28.27, 31.02, 51.74, 63.82, 87.53, 126.22, 129.35, 129.46, 146.41, 166.70; IR (CDCl₃) ν 3530–3340, 2950, 2940, 2830, 2210, 2190, 1725, 1275 cm⁻¹; mass spectrum, *m/z* (relative intensity) 274.2 (M⁺, 0.3), 273.1 (M⁺ - 1.167), 241.1 (31.15), 213.1 (36.14), 163.0 (100); *R*_f 0.22 (20% ethyl acetate/hexanes). Anal. Calcd for C₁₇H₂₂O₃: C, 74.42; H, 8.02. Found: C, 74.37; H, 7.65.

Methyl 4-[1-Oxo-2-nonyl]benzoate. A 500-mL Erlenmeyer flask equipped with a stirrer bar was charged with 13 g of methyl 4-[1-hydroxy-2-nonyl]benzoate (47.38 mmol) in 300 mL of acetone. The solution was cooled with an ice/water bath and 60 mL of Jones reagent was added dropwise with vigorous stirring until the orange color persisted. The addition of the reagent was discontinued and the reaction mixture was stirred for an additional 30 min with cooling. The reaction was quenched by addition of 2-propanol dropwise until the solution turned blue. The mixture was warmed to ambient temperature and stirred for 30 min before addition of Na₂SO₄/K₂CO₃ until the bottom layer became pasty. The resulting mixture was stirred until the top layer became clear. The organic layer was decanted, and the paste was washed two times with 50-mL portions of ether. The combined organic layers were filtered through 1 in. of Florisil, and the filtrate was concentrated in vacuo. The resulting crude oil was recrystallized two times from 30-mL portions of

hexane at -20 °C to afford 9.7 g of methyl 4-[1-oxo-2-nonyl]benzoate: 75% yield; bp 140–180 °C at 0.4 mmHg; ¹H NMR (250 MHz, CDCl₃) δ 0.88 (t, 3 H, *J* = 6.5 Hz, ArCOC≡C(CH₂)₂CH₃), 1.20–1.60 (m, 6 H, ArCOC≡C(CH₂)₂(CH₂)₂CH₃), 1.66 (m, 2 H, *J* = 7.6 Hz, ArCOC≡CCH₂CH₂), 2.49 (t, 2 H, *J* = 7.1 Hz, ArCOC≡CCH₂), 3.93 (s, 3 H, CH₃OCOAr), 8.14 (d of d, 4 H, *J* = 6.5, 7.4 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.79, 19.16, 22.35, 27.69, 28.54, 31.11, 52.23, 79.70, 97.81, 129.57, 134.50, 140.10, 166.00, 177.09; IR (CDCl₃) ν 2960, 2930, 2860, 2210, 2190, 1725, 1650, 1275 cm⁻¹; mass spectrum, *m/z* (relative intensity) 272.1 (M⁺, 5.95), 163.0 (100); *R*_f 0.41 (20% ethyl acetate/hexanes). Anal. Calcd for C₁₇H₂₀O₃: C, 74.96; H, 7.41. Found: C, 74.88; H, 7.45.

Methyl 4-[1(*R*)-Hydroxy-2-nonyl]benzoate. A flame-dried three-necked 50-mL flask equipped with a stirrer bar and a septum inlet was charged with 6.53 g of 9-BBN (53.5 mmol) and 10.8 mL of (1*R*)-(+)- α -pinene (67.70 mmol) in a glove bag under a positive flow of argon. The reaction mixture was heated to 65 °C and stirred for 5 h. The clear solution was then cooled to ambient temperature and 7.3 g of methyl 4-[1-oxo-2-nonyl]benzoate (26.80 mmol) was added. The reaction mixture was stirred for 4 days at ambient temperature and quenched by injection of 5 mL of acetaldehyde. The resulting mixture was allowed to stir for 30 min before all the volatile material was removed under vacuum. The residue was then triturated with 20 mL of ether. The flask was cooled with an ice bath and 3.2 mL of ethanolamine (57.69 mmol) and added. Stirring was continued for 30 min and the resulting white precipitate was filtered off through Celite and washed with 100 mL of cold ether. The combined filtrates were washed three times with 20-mL portions of brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the oil thus obtained was distilled with a Kugelrohr oven to afford 6.66 g of methyl 4-[1(*R*)-hydroxy-2-nonyl]benzoate (bp 170–220 °C, 1 mmHg). The oil was then crystallized once from 50 mL of pentane at -20 °C and once more from 100 mL of pentane at 0 °C to provide 4.63 g of fine needles: 63% yield; mp 33.9–34.1 °C; bp 370 °C. The spectral data are the same as for the racemic alcohol.

4-[1(*R*)-Hydroxy-2-nonyl]benzoic Acid. A 250-mL flask equipped with a stirrer bar and a septum inlet was charged with 4.5 g of methyl 4-[1(*R*)-hydroxy-2-nonyl]benzoate (16.40 mmol) in 123 mL of methanol and 41 mL of water. Lithium hydroxide (1.57 g, 65.55 mmol) was then added and the reaction mixture was stirred vigorously for 14 h. The solution was diluted with 200 mL of 3.5% (wt/wt) NaOH solution and was washed twice with 50-mL portions of ether. The aqueous layer was acidified by adding concentrated hydrochloric acid with ice and was extracted four times with 50-mL portions of ether. The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to afford 4.27 g of 4-[1(*R*)-hydroxy-2-nonyl]benzoic acid as a solid which was taken to the next step without further purification: 100% yield; mp 84.9–86.9 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.86 (t, 3 H, *J* = 6.7 Hz, ArCHOHC≡C(CH₂)₂CH₃), 1.15–1.65 (m, 8 H, ArCHOHC≡CCH₂(CH₂)₂CH₃), 2.24 (d of t, 2 H, *J* = 2.0, 7.1 Hz, ArCHOHC≡CCH₂), 5.50 (s, 1 ArCHOH), 7.60 (d, 2 H, *J* = 8.3 Hz, ArH), 8.07 (d, 2 H, *J* = 8.3 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.92, 18.79, 22.48, 28.48, 28.53, 31.26, 64.35, 79.47, 88.51, 126.59, 129.08, 130.46, 147.05, 171.54; IR (CDCl₃) ν 3550–3050, 2950, 2930, 2840, 2210, 1690, 1425, 1275 cm⁻¹; mass spectrum, *m/z* (relative intensity) 260 (M⁺, 14.8), 215.15 (100); *R*_f 0.22 (50% ethyl acetate/hexanes + 1 drop of acetic acid). Anal. Calcd for C₁₆H₂₀O₃: C, 73.82; H, 7.74. Found: C, 73.80; H, 7.90.

4-(*n*-Decyloxy)phenyl 4-[1(*R*)-Hydroxy-2-nonyl]benzoate. A flame-dried 250-mL flask equipped with stirrer bar and a septum inlet was charged with 4.27 g of 4-[1(*R*)-hydroxy-2-nonyl]benzoic acid (16.40 mmol), 4.30 g of 4-(*n*-decyloxy)phenol (17.18 mmol), and 0.2 g of DMAP (1.64 mmol) in 164 mL of dry dichloromethane. 1,3-dicyclohexylcarbodiimide (4.06 g, 19.67 mmol) was added, and the reaction mixture was left stirring for 24 h. The dicyclohexylurea was filtered off and the filtrate was extracted with 7% (wt/wt) NaOH solution (2 × 50 mL), 10% (v/v) HCl solution (4 × 50 mL), and saturated sodium bicarbonate solution (2 × 50 mL). The organic layer was dried over Na₂SO₄/K₂CO₃ and the solvent was removed in vacuo. The resulting crude product was purified by flash chromatography with 18% ethyl acetate/hexane as eluant to afford 6.9 g of solid. The solid was then recrystallized from 75 mL of hexane at 0 °C, giving 5.79 g of 4-(*n*-decyloxy)phenyl 4-[1(*R*)-hydroxy-2-nonyl]benzoate as a white solid: 72% yield; mp 66.9–68.9 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.91 (m, 6 H, ArCHOHC≡C(CH₂)₂CH₃, ArO(CH₂)₉CH₃), 1.20–1.90 (m, 24 H, ArCHOHC≡CCH₂(CH₂)₂CH₃, ArOCH₂(CH₂)₉CH₃), 2.25 (m, 3 H, ArCHOHC≡CCH₂), 3.96 (t, 2 H, *J* = 6.4 Hz, ArOCH₂), 5.51 (d, 1 H, *J* = 5.9 Hz, ArCHC≡C), 6.90 (d, 2 H, *J* = 9.0 Hz, ArH), 7.15 (d, 2 H, *J* = 9.0 Hz, ArH), 7.70 (d, 2 H, *J* = 9.0 Hz, ArH), 7.70 (d, 2 H, *J* = 9.0 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 14.08, 18.76, 22.50,

22.60, 26.01, 28.44, 28.52, 29.30, 29.38, 29.54, 31.25, 31.86, 64.22, 68.42, 79.43, 88.31, 115.05, 122.30, 126.58, 129.25, 130.32, 144.17, 146.74, 156.87, 165.24; IR (CDCl₃) ν 3570–3230, 2950, 2930, 2840, 2220, 1735, 1500, 1275 cm⁻¹; mass spectrum, m/z (relative intensity) 492 (M⁺, 3.1), 243 (100); R_f 0.28 (20% ethyl acetate/hexanes). Anal. Calcd for C₃₂H₄₄O₄: C, 78.01; H, 9.00. Found: C, 77.93; H, 9.04.

4'-(*n*-Decyloxy)phenyl 4-[(*S*)-1-Hydroxynonyl]benzoate (6). A 250-mL flask equipped with a stirrer bar was charged with 4.79 g of 4'-(*n*-decyloxy)phenyl 4-[(*R*)-1-hydroxy-2-nonyl]benzoate (9.72 mmol), 0.24 g of 10% palladium on carbon, 97 mL of ethyl acetate, and 0.0002 g of DMAP. The resulting suspension was placed under a positive hydrogen pressure (15 psi) and stirred rapidly. After 25 min the hydrogen pressure was released, and the reaction mixture was filtered through Celite. The solvent was removed in vacuo and the crude product was purified by flash chromatography with 18% ethyl acetate/hexane as eluant to afford 5.71 g of benzyl alcohol 6. This material was purified further by recrystallization from 80 mL of ethanol to afford 3.73 g of a white solid: 77% yield; mp 64.2–65.2 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.87 (m, 6 H, ArCH(OH)(CH₂)₇CH₃, ArO(CH₂)₉CH₃), 1.10–1.90 (m, 30 H, ArCHOH(CH₂)₇CH₃, ArOCH₂(CH₂)₈CH₃), 2.02 (d, 1 H, J = 2.6 Hz, ArCHOH), 3.94 (t, 2 H, J = 6.5 Hz, ArOCH₂), 4.74 (br s, 1 H, ArCHOH), 6.90 (d, 2 H, J = 9.0 Hz, ArH), 7.08 (d, 2 H, J = 9.0 Hz, ArH), 7.44 (d, 2 H, J = 8.3 Hz, ArH), 8.13 (d, 2 H, J = 8.3 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.97, 13.98, 22.57, 22.60, 25.56, 26.01, 29.17, 29.25, 29.27, 29.35, 29.44, 29.50, 29.52, 31.79, 31.85, 31.19, 68.53, 74.04, 115.17, 122.28, 125.90, 128.74, 130.21, 144.39, 150.86, 156.92, 165.27; IR (CDCl₃) ν 3550–3100, 2920, 2830, 1725, 1610, 1490, 1450, 1260, 1240, 1175 cm⁻¹; mass spectrum, m/z (relative intensity) 496.3 (M⁺, 17.77), 247.2 (100); R_f 0.31 (20% ethyl acetate/hexanes). Anal. Calcd for C₃₂H₄₈O₄: C, 77.38; H, 9.74. Found: C, 77.64; H, 9.54.

When the racemic alcohol 6 (0.0035 g in 0.5 mL of CDCl₃) was treated with 2.33 molar equiv of the Eu shift reagent tris[3-[(heptafluoropropyl)hydroxymethyl]enyl]-*d*-camphorato]europium(III), the resonances for the benzylic proton at C-1 of the hydroxynonyl grouping of the two enantiomers appeared as two broad singlets centered at δ 11.4 ($\Delta\delta \approx 0.02$). Similar treatment of the enantiomerically enriched material prepared as described above showed only one singlet at δ 11.8 (no trace of the other absorption could be observed), establishing the enantiomeric purity of the material as >95%.

4'-(*n*-Decyloxy)phenyl 4-[(*R*)-1-Fluorononyl]benzoate (7) by DAST Fluorination of Benzylic Alcohol 6. A 10-mL flame-dried flask equipped with a stirring bar and a septum inlet was charged with 0.12 mL of (diethylamido)sulfur trifluoride (0.91 mmol) in 1 mL of dry dichloromethane. The flask was cooled in a dry ice/acetone bath before a solution of 0.43 g (0.87 mmol) of enantiomerically enriched alcohol 6 in 1 mL of dry dichloromethane was added dropwise. After 2 h of stirring, 5 mL of water was added, and the reaction mixture was warmed to ambient temperature. The organic layer was separated and washed twice with 2-mL portions of brine. It was then dried over sodium sulfate and solvent was removed in vacuo. The resulting crude product was purified by flash chromatography with 7% ethyl acetate/hexanes as eluant. The product was then separately crystallized from 50 mL of acetonitrile, 30 mL of ether, and 50 mL of hexane at -20 °C to give 0.35 g of benzylic fluoride 7: 79% yield; ¹H NMR (250 MHz, CDCl₃) δ 0.87 (m, 6 H, ArCHF(CH₂)₇CH₃, ArO(CH₂)₉CH₃), 1.10–2.20 (m, 30 H, ArCHF(C-H₂)₇CH₃, ArOCH₂(CH₂)₈CH₃), 3.94 (t, 2 H, J = 6.5 Hz, ArOCH₂), 5.50 (d of t, 1 H, J = 47.6, 2.4 Hz, ArCHF), 6.90 (d, 2 H, J = 9.0 Hz, ArH), 7.09 (d, 2 H, J = 9.0 Hz, ArH), 7.42 (d, 2 H, J = 8.1 Hz, ArH), 8.18 (d, 2 H, J = 8.1 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 14.00, 14.02, 22.61, 22.65, 24.84, 24.90, 26.05, 29.16, 29.32, 29.39, 29.56, 31.81, 31.89, 37.06, 37.43, 68.59, 92.53, 95.27, 115.23, 122.31, 125.34, 125.46, 129.52, 130.27, 144.38, 146.20, 146.51, 157.02, 165.12; IR (CDCl₃) 2920, 2840, 1730, 1500, 1270, 1250, 1190, 1050 cm⁻¹; mass spectrum, m/z (relative intensity) 498 (M⁺, 3.1), 249 (36.6), 57.06 (100); R_f 0.59 (20% ethyl acetate/hexanes); $[\alpha]_D^{25} = +8.9 \pm 1.0^\circ$ (18.8 mg/mL CHCl₃); $[\alpha]_D^{25} = +10.9 \pm 2.0^\circ$ (2.3 mg/mL CHCl₃). Anal. Calcd for C₃₂H₄₇O₃F: C, 77.06; H, 9.50; F, 3.80. Found: C, 76.66; H, 9.46; F, 3.66.

A similar fluorination run at -98 °C gave material with an observed $[\alpha]_D^{25} = +8.5 \pm 1.0^\circ$ (19.5 mg/mL CHCl₃), while fluorination at 0 °C gave compound 7 with $[\alpha]_D^{25} = +4.6 \pm 1.0^\circ$ (19.6 mg/mL CHCl₃).

Attempted Resolution of Fluorononyl Compound 7. Racemic 7 was prepared as described above for the enantiomerically enriched material, except that racemic alcohol 6 was utilized as substrate for the fluorination. A J. T. Baker Bakerbond DNBPG (covalent) chiral column (particle size 5 μ m, pore size 110 Å) was used in the attempts to separate

the two enantiomers in a racemic mixture. Pure hexane (0.5 and 1 mL/min), 2% ethyl acetate in hexane (0.5 mL/min), 3% ethyl acetate in hexane (0.5 mL/min), 5% ethyl acetate in hexane (0.5 mL/min), and 9% ethyl acetate in hexane (0.5 mL/min) were used with UV detection, and no separation of the enantiomers was obtained. Attempts to separate the enantiomers with a Diacel Chemicals Chiralpac op(+) (no. 98-1-1-4-001209) and pure hexane (0.3 and 0.5 mL/min) also failed. Finally, the two enantiomeric fluorides proved indistinguishable by ¹H and ¹⁹F NMR with a saturated solution of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol in CDCl₃ as a chiral solvating agent.

4'-(*n*-Decyloxy)phenyl 4-[(*S*)-1-[(Methylsulfonyl)oxy]nonyl]benzoate. A 25-mL flame-dried flask equipped with a stirrer bar and a septum inlet was charged with 1.5 g of benzyl alcohol 6 (3.02 mmol), 0.5 mL of triethylamine (3.59 mmol), and 0.04 g of DMAP (0.16 mmol) in 10 mL of dry dichloromethane. The reaction flask was cooled in ice/water bath before 0.28 mL of methanesulfonyl chloride (3.62 mmol) was added slowly. The reaction material was stirred for 2 h in the ice/water bath before it was quenched with 10 mL of 10% (v/v) HCl solution. The layers were separated, and the organic layer was washed with two 10-mL portions of 10% (v/v) HCl solution and with 10 mL of saturated sodium bicarbonate solution. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The resulting crude product was purified by flash chromatography eluting with 20% ethyl acetate/hexanes as eluant to give 1.7 g of 4'-(*n*-decyloxy)phenyl 4-[(*S*)-1-[(methylsulfonyl)oxy]nonyl]benzoate: 98% yield; mp 49.5–50.5 °C; ¹H NMR (250 MHz, CDCl₃) δ 0.87 (m, 6 H, ArCH(CH₂)₇CH₃, ArO(CH₂)₉CH₃), 1.10–2.20 (m, 30 H, ArCH(CH₂)₇CH₃, ArOCH₂(CH₂)₈CH₃), 2.74 (s, 3 H, ArCHOSO₂CH₃), 3.94 (t, 2 H, J = 6.5 Hz, ArOCH₂), 5.57 (t, 1 H, J = 6.9 Hz, ArCHOSO₂CH₃), 6.90 (d, 2 H, J = 9.0 Hz, ArH), 7.08 (d, 2 H, J = 9.0 Hz, ArH), 7.49 (d, 2 H, J = 8.3 Hz, ArH), 8.19 (d, 2 H, J = 8.3 Hz, ArH); ¹³C NMR (250 MHz, CDCl₃) δ 13.86, 13.89, 22.44, 22.51, 25.07, 25.93, 28.96, 29.15, 29.19, 29.25, 29.42, 31.63, 31.75, 37.02, 38.87, 68.45, 83.48, 115.14, 122.12, 126.62, 130.24, 130.51, 144.23, 144.25, 156.98, 164.61; IR (CDCl₃) ν 2930, 2850, 1720, 1605, 1499, 1360, 1260, 1230, 1180, 1075 cm⁻¹; mass spectrum, m/z (relative intensity) 547 (M⁺, 325 (1), 229 (7), 79 (100); R_f 0.35 (20% ethyl acetate/hexanes).

4'-(*n*-Decyloxy)phenyl 4-[(*R*)-1-Fluorononyl]benzoate (7) by Fluoride Displacement of Mesylate. A 10-mL flame-dried flask equipped with a condenser and a stirrer bar was charged with 0.33 g of cesium fluoride (2.17 mmol), 0.02 g of 18-crown-6 (0.076 mmol), and 0.25 g of 4'-(*n*-decyloxy)phenyl 4-[(*S*)-1-[(methylsulfonyl)oxy]nonyl]benzoate (0.43 mmol) in 4 mL of dry THF. The suspension was left heating at reflux for 12 h. The reaction mixture was cooled to ambient temperature and the excess cesium fluoride was filtered off. The solvent was removed in vacuo, and the resulting residue was purified by flash chromatography with 7% ethyl acetate/hexanes as eluant to afford 0.048 g (22%) of benzylic fluoride 7. The product was then crystallized once from ether and once from hexane to afford 2.3 mg (1%) of a white solid suitable for rotation measurements; $[\alpha]_D^{25} = +9.5^\circ \pm 2.0^\circ$ (2.3 mg/mL CHCl₃).

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Registry No. 1, 117438-57-0; 2, 117556-70-4; 3, 117438-58-1; 4, 92950-96-4; 5, 117469-77-9; 5 (free acid), 117438-62-7; 6, 113248-18-3; 7(R), 117438-59-2; 4-(decyloxy)phenol, 35108-00-0; 4'-(*n*-decyloxy)phenyl 4-formylbenzoate, 117438-60-5; 4'-(*n*-decyloxy)phenyl 4-[(*E*)-1-hydroxy-2-nonyl]benzoate, 117438-61-6; 4'-(*n*-decyloxy)phenyl 4-[(*R*)-1-hydroxy-2-nonyl]benzoate, 113301-59-0; 4-formylbenzoyl chloride, 16173-52-7; *B*-[(*E*)-1-octen-1-yl]-9-BBN, 73062-42-7; methyl 4-[1-hydroxy-1-nonyl]benzoate, 117438-63-8; 1-octyne, 629-05-0; methyl 4-formylbenzoate, 1571-08-0; methyl 4-[1-oxo-2-nonyl]benzoate, 117438-64-9; methyl 4-[(1*R*)-hydroxy-2-nonyl]benzoate, 117557-89-8; 4-[(1*R*)-hydroxy-2-nonyl]benzoic acid, 117438-65-0; 4'-(*n*-decyloxy)phenyl 4-[(*S*)-1-(methylsulfonyloxy)nonyl]benzoate, 117469-78-0.

Supplementary Material Available: Details of the crystal-structure determination of compound 5 (including an ORTEP drawing (Figure 1) and listings of bond lengths and angles, torsion angles, and anisotropic temperature factors (Tables 1–5)) (9 pages). Ordering information is given on any current masthead page.