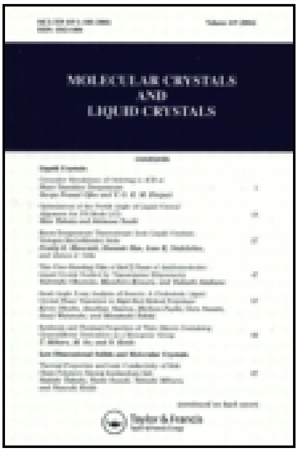

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1.3-Dioxolan-4-ones as Chiral Unit for Ferroelectric Liquid Crystals and Dopants for Induced Ferroelectric Mesophases

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1.3-Dioxolan-4-ones as Chiral Unit for Ferroelectric Liquid Crystals and Dopants for Induced Ferroelectric Mesophases

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The synthesis, phase behaviour, spontaneous polarization and response times of a new type of ferroelectric liquid crystals and dopants (for induced ferroelectric phases) containing trisubstituted 1.3-dioxolan-4-ones as chiral unit are described. Two pairs of cis respective trans 2.5.5-trisubstituted 1.3-dioxolan-4-ones are compared with respect to their ferroelectric properties. Cis configuration results in higher spontaneous polarization than trans configuration. The unbranched 2-alkylsubstituent causes higher P_S than the branched one.

Keywords: Ferroelectric liquid crystals and dopants, chiral 1.3-dioxolan-4-ones

1. INTRODUCTION

Ferroelectricity in liquid crystals was first postulated and soon afterwards experimentally demonstrated by Meyer *et al.*[1] in 1975. The principal features of *ferroelectric* liquid crystals are two stable switching states and response times in the range of microseconds. The response time is a function of spontaneous polarization and rotational viscosity respectively. To obtain high spontaneous polarization one has to consider some empirical guidelines in designing ferroelectric liquid crystals. Favourable are

1. a high dipole moment perpendicular to the molecular longitudinal axis
2. short distances between the chiral center and the lateral dipole and the mesogenic part respectively[2–4]
3. a restriction of free rotation in the chiral region.

Therefore, it seems to be attractive to incorporate the dipole and the chiral unit into a ring system, which has a *fixed* dipole and a *restricted* free rotation. Only few examples of such compounds have been presented hitherto.[5–8] There is still a need for new ferroelectric liquid crystal materials possessing high spontaneous polarization, low rotational viscosity and a broad S_C*-phase range about room temperature.[9,10]

This work presents 1.3-dioxolan-4-ones, substituted as seen below in Figure 1, as novel building block for ferroelectric liquid crystals and dopants.

The dioxolanone system was chosen because of its strong dipole and its advantageous conformation. The additional methyl group in 5-position is conditional on the following sequence of synthesis (Scheme I). It is adjacent to the mesogenic part and leads to more restriction in rotation around the molecular length axis. All synthesized examples have a three-core mesogenic unit (Rmes shown above) which has a great tendency to form broad smectic phases, especially in the case of sterically demanding chiral parts.[11]

2. SYNTHESIS

The synthesis started with the preparation of dioxolanone **1** derived from S-lactic acid and pivalaldehyde by a way first described by Seebach *et al.*[12] The electrophile **2** was obtained in three steps from 4-formyl-benzoic acid by 1) esterification with benzyl alcohol/DCCI, 2) reduction with sodium boranate, and 3) bromination of the resulting alcohol with PBr_3 in an overall yield of almost 70%. The alkylation of **1** with **2** was accomplished in presence of LiCl[13] and HMPA[14] as cosolvent. Surprisingly, the diastereomeric ratio of **3a**:**3b** was almost 2.2:1 and not, as expected,[12] about 95:5.[16] The relative conformations of **3a** and **3b** were confirmed of ^{1}H-NMR using the Nuclear Overhauser Effect (NOE). Irradiation into 2-H of **3a** leads to pos. NOE at the methylen group and the phenylic ortho-protons; irradiation into 2-H of **3b** leads to pos. NOE at the methyl group. The separation of the diastereomers was done by chromatography. Hydrogenolysis of benzylic esters **3a** and **3b** followed by esterfication of the carboxylic acids with 4-decyloxy-4′-hydroxy-biphenyl lead to dioxolanones **4a** and **4b**.

Dioxolanones with linear alkylsubstituents in 2-position were obtained by the following pathway: Dioxolanone **3a** was saponified to hydroxy diacid **5** either by acid or by base. Then, α-hydroxy acid **5** was recyclisized with n-butanale to give dioxolanone **6**, which was formed in cis/trans ratio of almost 1:1. This can be explained by the same steric influence of the methyl and benzylic group on the newly formed stereogenic center. The recyclization can be accomplished with many other aldehydes under acid condtions, except for allylic or benzylic aldehydes. In this case another way of cyclization is necessary.[15] With aldehydes having, α-protones large excess of the aldehyde was needed, because large amounts of aldol condensation products were formed. The last two steps of this pathway were esterification with 4-decyloxy-4′-hydroxy-biphenyl/dicyclohexyl carbodiimide (DCCI)

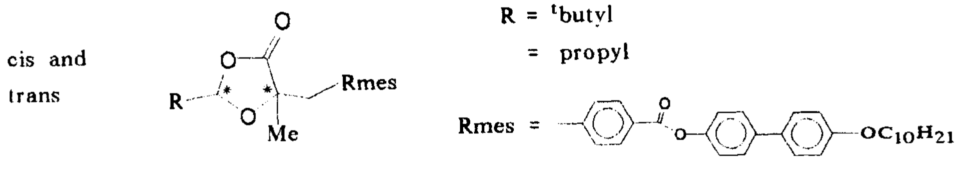
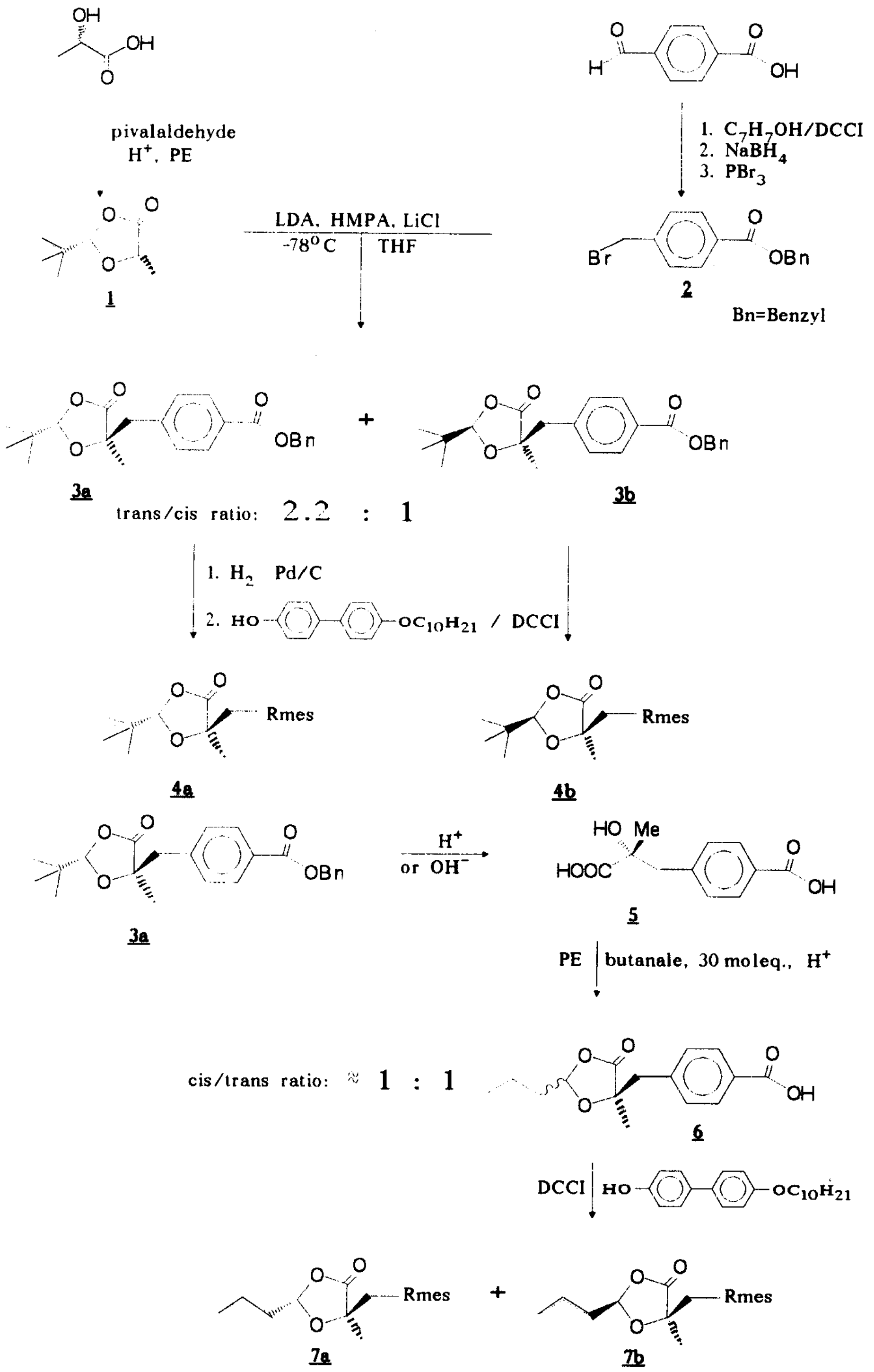


FIGURE 1


pivalaldehyde
H⁺, PE
1
1. C7H7OH/DCCI
2. NaBH4
3. PBr3
2
Bn=Benzyl
LDA, HMPA, LiCl
-78°C
THF
3a
3b
trans/cis ratio: 2.2 : 1
1. H2 Pd/C
2. HO–(C6H4)–(C6H4)–OC10H21 / DCCI
Rmes
4a
4b
H⁺
or OH⁻
HO Me
HOOC
OH
5
PE
butanale, 30 moleq., H⁺
cis/trans ratio: ≈ 1 : 1
6
DCCI
HO–(C6H4)–(C6H4)–OC10H21
7a
7b
OBn
Br

SCHEME I

and separation of the diastereomers over silica chromatography, to give in this case **7a** and **7b**.

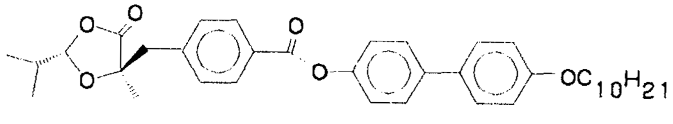
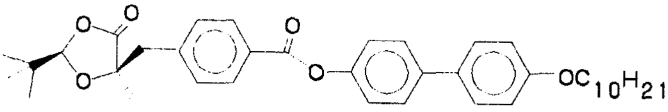
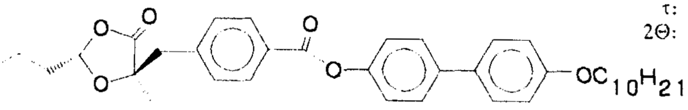
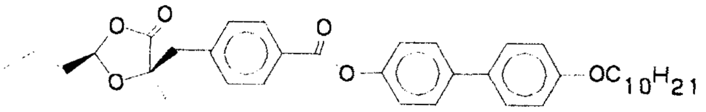
3. RESULTS AND DISCUSSION

3.1. Phase Behavior

Only dioxolanone **7a** has mesomorphic properties. It shows a cholesteric and a supercoolable S_C*-phase, which exhibits ferroelectric switching. The analogous cis-isomer has no liquid crystal properties. This observation corresponds to the results, observed at cis and trans oxirane esters which were synthesized and investigated by J. Gay.[6] Dioxolanones **4a** and **4b**, too, have no liquid crystal properties because of their very bulky terminal unit, leading to the collapse of the mesomorphism.

TABLE I

Mesomorphic properties and P_S-values of dioxolanones **4a**, **4b** and **7a**, **7b**

		P_S
4a	 Cr 144 I	40
4b	 Cr 113 I	116
7a	τ: 150 μs 2Θ: 70°  Cr (55) 71 S_C* 75 N* 85 I	64* 66⁺
7b	 Cr 103 I	181

⁺ P_S measured in neat compound; * P_S measured in 5 mol% solution in M89/85 and extrapolated.

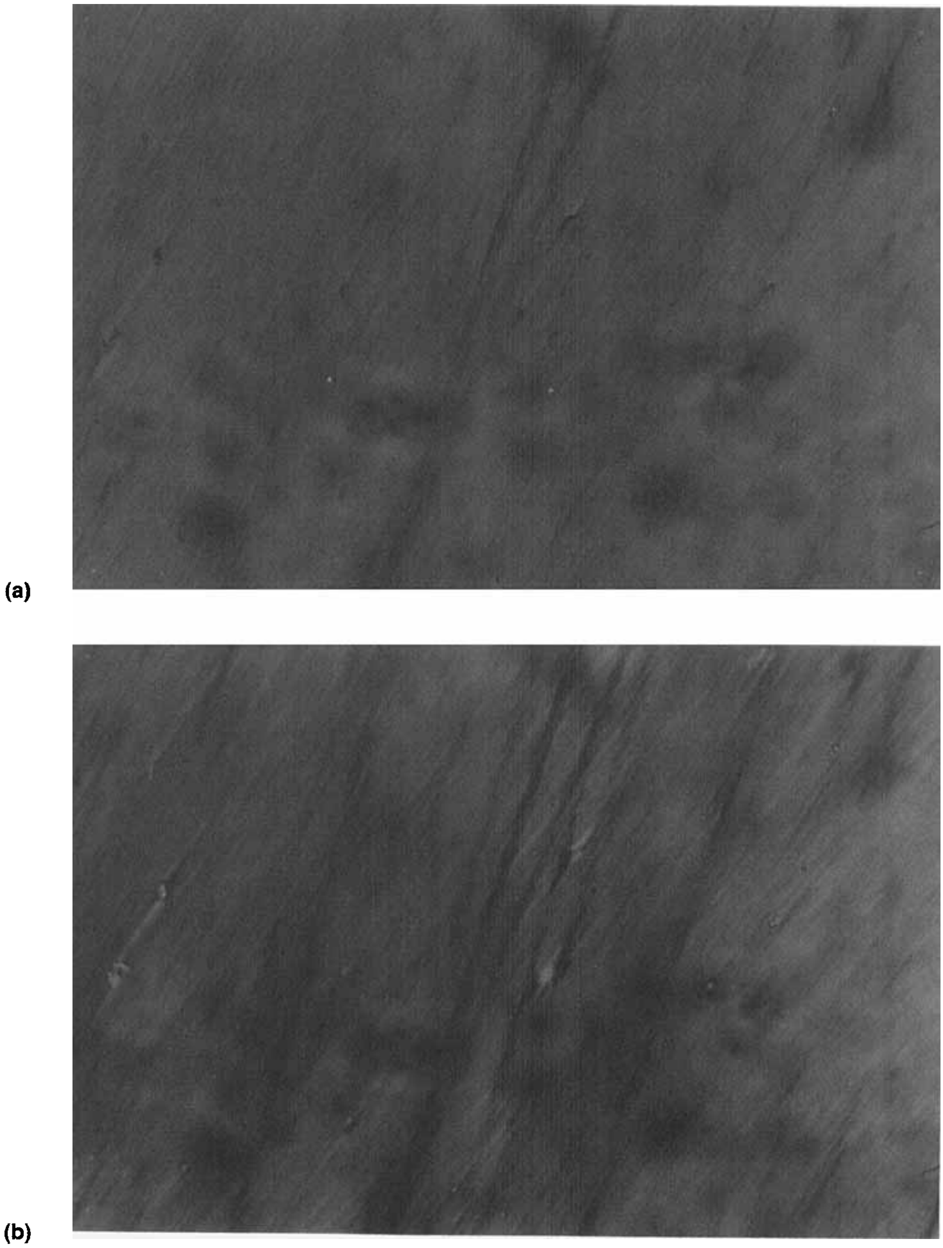


FIGURE 2 The two switching states a) and b) in the S_C*-phase of dioxolanone **7a**. See Color Plate I.

3.2. Ferroelectric Properties

The spontaneous polarization was measured in a 10 mol% solution in a smectic C material. For comparision **7a** was also measured as neat compound (Figure 2 shows the two stable switching states of **7a**, well orientated between two polyimide coated glass plates of a 4 μm cell). The host used for the cis-isomers was HOAB (Merck; phase sequence: Cr 74.7 S_C 94.0 N 123.5 I); the host for the trans-isomers was M 89/85 (Hoechst AG, phase sequence: Cr 10 S_C 84.5 S_A 93.5 N 105 I). The different hosts we had to use for solubility reasons. The values given (Table I) are extrapolated from those obtained in the described mixtures. Assuming the induced spontaneous polarization in HOAB and M 89/85 to be comparable, the cis-isomers have almost three times higher P_S-values than the corresponding trans-isomers. The same facts were observed by J. Gay[6] with oxirane esters, where he also found higher P_S-values with the cis-isomers. The dioxolanones with the ^{t}butyl group, **4a** and **4b**, have lower P_S-values than dioxolanones **7a** and **7b**, which seem to allow a better polar ordering in the mesomorphic state. Because of the bulkiness of the ^{t}butyl group in **7a** and **7b** a parallel orientation of the molecular length axis is hindered. In the case of **7a**, the P_S-value of the neat compound shows a remarkably good agreement with the extrapolated value, measured at almost the same temperature. The response time of **7a** is about 150 μs in an applied field of 4.7 V/μm. Probably a relative high rotational viscosity is responsible for this comparatively long switching time.

4. EXPERIMENTAL PART

General: The spectra were reocrded using the following instruments: Perkin-Elmer PE 257.–^{1}H-NMR: Bruker WM 400.–MS: Varian MAT 711 (70 eV).–Specific optical rotation: Perkin Elmer PE 241 polarimeter.–Texture observations and melting points: Jenapol polarizing microscope and Linkam heating stage THM 600.–Measurements of spontaneous polarization: in test cells with a spacing of 2 μm or 4 μm. The glass substrates of the cells were coated with polyimide and both substrates were rubbed. The cells were filled by capillary action. Spontaneous polarization was obtained by the Diamant bridge: applied voltage: 5–20 V, frequency: 50–500 Hz.–Response time (τ) was determined by applying a rectangular wave of /+5 V/μm and is defined as time difference between voltage reversal and 90% change in optical transmission. Phase transitions were determined using a Perkin-Elmer DSC 7 apparatus. Chromatographic purifications were performed using flash liquid chromatography (FLC) on ICN Biomedicals silica (32–63 μm).

Solvents: CH_2Cl_2 was dried by distillation over KOH, THF by distillation over sodium/benzophenone, EtOH by distillation over magnesia ethanolate.
Petroleum ether (PE): b.p.: 40–60°C

General Procedure for Esterification. A solution of carboxylic acid (10 mmol), N,N-dicyclohexyl-carbodiimide (DCCI) (10.5 mmol) the hydroxy compound (10 mmol) and 4,4-dimethylamino-pyridine (1.5 mmol) in dry CH_2Cl_2 (100 ml) is stirred at room temperature overnight. The N,N-dicyclohexyl-urea is filtered off, and the filtrate is concentrated in vacuo. Products are purified by FLC with changing solvent mixtures. The details for the individual cases are described below.

(2R,5R)-(+)-5-(4-Benzyloxycarbonyl-phenylmethyl)-2-(t-butyl)-5-methyl-1.3-dioxolan-4-one **(3b)** *and (2S, 5R)-(+)-5-(4-Benzyloxycarbonyl-phenylmethyl)-2-(t-butyl)-5-methyl-1.3-dioxolan-4-one* **(3a)**. 2.7 g (27 mmol) diisopropylamide and 1.13 g (27 mmol) LiCl were dissolved in 80 ml dry THF, cooled to −78°C and treated with 16.8 ml butyllithium (1.6 N in hexane). The pale yellow solution was stirred for 15 minutes. Then 3.79 g (24 mmol) (2S, 5S)-(+)-2-(t-butyl)-5-methyl-1.3-dioxolan-4-one **1**, dissolved in 10 ml dry THF, was added slowly. After 10 minutes 15 ml distilled HMPA was added, and the enolate solution was stirred for another 20 minutes. Thereafter 7.6 g (25 mmol) benzyl-4-brommethyl-benzoate **2** in 10 ml dry THF was added. The reaction mixture was stirred at −78°C for 6 hours and then allowed to warm up to room temperature overnight. The solution was poured into cold diluted HCl. The aqueous layer was extracted with ether, the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The diastereomers were first purified by FLC (CH_2Cl_2) and then separated by FLC (Et_2O:PE 1:12). Yield: **3b** 1.57 g (17%); **3a** 3.45 g (38%), both are colourless liquids.

3b: $[\alpha]_D^{26} = +21.1° \ c = 2.45$ ($CHCl_3$)
IR ($CHCl_3$): 2970 (CH); 1790, 1715 (C═O); 1615 (C═C); 1380; 1280; 1110; 990
^{1}H-NMR ($CDCl_3$): $\delta = 0.77$ (*s*; 9H), 1.40 (*s*; 3H), 3.04 (*d*, $J = 14$ Hz; 1H); 3.21 (*d*, $J = 14$ Hz; 1H), 5.13 (*s*; 1H), 5.35 (*s*; 2H), 7.34–7.46 (*m*; 5H), 7.32; 8.00 (AA'BB', $J = 8$ Hz, 4H)
MS (Ref.): m/e = 382 (1.5%, M^+), 325 (5.5, M-^{t}Bu), 275 (35, M-BnO), 269 (41), 226 (49), 161 (36), 118 (56), 91 (100).

3a: $[\alpha]_D^{20} = +51.2 \ c = 2.47$ ($CHCl_3$)
IR ($CHCl_3$): 2970 (CH); 1795, 1715 (C═O); 1615 (C═C); 1280; 1110; 980
^{1}H-NMR ($CDCl_3$): $\delta = 0.86$ (*s*; 9H), 1.47 (*s*; 3H), 2.96 (*d*, $J = 14$ Hz, 1H), 3.17 (*d*, $J = 14$ Hz; 1H), 4.52 (*s*; 1H), 5.36 (*s*; 2H), 7.34–7.46 (*m*; 5H), 7.32; 8.03 (AA'BB', $J = 8$ Hz; 4H)
MS (Ref.): m/e = 382 (1%, M^+), 325 (5.5, M-^{t}Bu), 275 (38, M-BnO), 269 (40), 226 (50), 161 (35), 118 (60), 91 (100).

(2R, 5R)-(+)-2-(t-Butyl)-5-(4-decyloxy-biphenyl-4'-yl-oxy-4"-carbonyl-phenylmethyl)-5-methyl-1.3-dioxolan-4-one **(4b)** *and (2S, 5R)-(+)-2-(t-Butyl)-5-(4-decyloxy-biphenyl-4'-yl-oxy-4"-carbonyl-phenylmethyl) - 5-methyl-1.3-dioxolan-4-one* **(4a)**. To a solution of 900 mg (3.1 mmol) of the carboxylic acid, obtained from **3b** by hydrogenolysis in EtOH/Pd/C 1.01 g (3.1 mmol) 4-decyloxy-4'-hydroxy-biphenyl and 56 mg DMAP in 30 ml dry CH_2Cl_2, 0.66 g (3.2 mmol) DCCI was added. Purification by FLC ($CHCl_3$:PE 1:3) yielded 1.3 g (70%) of **4b**.

m.p.: 113°C
$[\alpha]_D^{23} = +15.2° \ c = 2.50$ ($CHCl_3$)
IR (KBr): 2920, 2860 (CH); 1790, 1745 (C═O), 1615, 1500 (C═C); 1215; 1080; 810
^{1}H-NMR ($CDCl_3$): $\delta = 0.81$ (*s*; 9H), 0.89 (*t*, $J = 7$ Hz; 3H), 1.23–1.41 (*m*; 12H), 1.43 (*s*, 3H), 1.47 (quintbr, $J = 7$ Hz; 2H), 1.81 (quint, $J = 7$ Hz; 2H), 3.09 (*d*, $J = 14$ Hz; 1H), 3.27 (*d*, $J = 14$ Hz; 1H), 4.00 (*t*, $J = 7$ Hz; 2H), 5.16 (*s*; 1H),

6.97; 7.51 (AA'BB', J = 9 Hz; 4H), 7.25; 7.59 (AA'BB', J = 9 Hz; 4H), 7.41; 8.14 (AA'BB', J = 8 Hz; 4H)
MS (180°C): m/e = 600 (32%, M$^+$), 487 (3), 326 (31), 275 (100), 186 (90), 161 (32), 56 (67, ^{t}Bu$^+$).

In similar manner, 550 mg of the carboxylic acid obtained from **3a** by hydrogenolysis was converted into the ester **4a** Yield: 880 mg (78%).

m.p.: 144°C
$[\alpha]^{23}_{D}$ = +36.0° c = 2.75 ($CHCl_3$)
IR (KBr): 2925, 2860 (CH); 1795, 1725 (C=O); 1615, 1500 (C=C); 1275; 1185; 1085; 815
^{1}H-NMR ($CDCl_3$): δ = 0.89 (*t*, J = 7 Hz; 3H), 0.90 (*s*; 9H), 1.24–1.41 (*m*; 12H), 1.47 (quintbr, J = 7 Hz; 2H), 1.51 (*s*, 3H), 1.81 (quint, J = 7 Hz; 2H), 3.02 (*d*, J = 14 Hz; 1H), 3.22 (*d*, J = 14 Hz; 1H), 4.00 (*t*, J = 7 Hz; 2H), 4.59 (*s*; 1H), 6.97; 7.51 (AA'BB', J = 9 Hz; 4H), 7.26; 7.59 (AA'BB', J = 9 Hz; 4H), 7.41; 8.17 (AA'BB', J = 8 Hz; 4H)
MS (180°C): m/e = 600 (38%, M$^+$), 487 (2), 326 (27), 275 (94), 186 (100), 161 (32), 57 (67, ^{t}Bu$^+$).

(2R)-(+)-3-(4-Carboxy-phenyl)-2-hydroxy-2-methyl-propionic acid (**5**). 2.45 g (6.4 mmol) of ester **4a** was emulgated in 30 ml 6 N HCl and heated under reflux for 18 hours. The aqueous layer was extracted with CH_2Cl_2/CH_3OH 3:1. The combined organic layers were dried over $MgSO_4$ and evaporated. The crude product was dissolved in a small amount of CH_3OH, precipitated with ether and filtrated. Yield: 1.3 g (90%)

m.p.: 241°C (dec.)
$[\alpha]^{25}_{D}$ = +10.4° c = 2.18 (CH_3OH)
IR (KBr): 3560–2100 (OH); 2920, 2850 (CH); 1710, 1685 (C=O); 1615, 1580 (C=C); 1430; 1300; 1200; 960
^{1}H-NMR (CD_3OD): δ = 1.41 (*s*; 3H), 2.98 (*d*, J = 13.5 Hz; 1H), 3.12 (*d*, J = 13.5 Hz; 1H), 7.36; 7.90 (AA'BB', J = 8 Hz; 4H)
MS (190°C); m/e = 224 (2.5%, M$^+$), 206 (7, M-H_2O), 179 (100), 136 (58)

(2R/S, 5R)-5-(4-Carboxy-phenylmethyl)-5-methyl-2-propyl-1.3-dioxolan-4-one (**6**). To a suspension of 1.30 g (5.8 mmol) di-acid **5**, 0.5 g p-TsOH, 20 ml conc. HCl in 200 ml PE, 11.1 g (150 mmol) freshly distilled butanal and two drops conc. H_2SO_4 were added. The mixture was heated under reflux and the water removed azeotropically. After removal of PE, the diastereomers were purified by FLC (Et_2O:PE 1:3) without separation. Yield: 1.05 g (65%)
No spectra were recorded of the unseparated diastereomers.

(2R, 5R)-(+)-5-(4-Decyloxy-biphenyl-4'-yl-oxy-4''-carbonyl-phenylmethyl)-5-methyl-2-propyl-1.3-dioxolan-4-one (**7b**) *and (2S, 5R)-(+)-5-(4-Decyloxy-biphenyl-4'yl-oxy-4''-carbonyl-phenyl-methyl)-5-methyl-2-propyl-1.3-dioxolan-4-one* (**7a**). In the same manner as described in the general procedure, 950 mg (3.4 mmol) of the diastereomeric acid **6**, 1.11 g (3.4 mmol) 4-decyloxy-4'-hydroxy-biphenyl, and 62 mg

DMAP in 34 ml dry CH_2Cl_2 were treated with 700 mg (3.4 mmol) DCCI. Purification and separation of the crude diastereomers by FLC (Et_2O:$CHCl_3$:PE 2:1:12) yielded 860 mg (43%) of **7b** and 740 mg (37%) of **7a**.

7b: m.p.: 103°C
$[\alpha]_D^{25} = +27.3° \; c = 2.75 \; (CHCl_3)$
IR ($CHCl_3$): 3015, 2940, 2870 (CH); 1795, 1740 (C=O); 1615, 1500 (C=C); 1275; 1175; 1085
^{1}H-NMR ($CDCl_3$): δ = 0.89 (*t*, *J* = 7 Hz; 3H), 0.90 (*t*, *J* = 7.5 Hz; 3H), 1.48 (*s*; 3H), 1.23–1.53 (*m*; 18H), 1.81 (quint, *J* = 7 Hz; 2H), 3.08 (*d*, *J* = 14 Hz; 1H), 3.22 (*d*, *J* = 14 Hz; 1H), 4.00 (*t*, *J* = 7 Hz; 2H), 5.51 (*t*, *J* = 5 Hz; 1H) 6.97; 7.51 (AA'BB', *J* = 9 Hz; 4H), 7.25; 7.59 (AA'BB', *J* = 9 Hz; 4H), 7.40; 8.15 (AA'BB', *J* = 8 Hz; 4H)
MS (220°C): 586 (42%, M^+), 326 (5), 261 (100), 186 (14), 161 (17).

7a: m.p. 72°C
$[\alpha]_D^{25} = +15.6° \; c = 1.78 \; (CHCl_3)$
IR ($CHCl_3$): 3015, 2940, 2860 (CH); 1790, 1740 (C=O); 1615, 1500 (C=C); 1275; 1185; 1085
^{1}H-NMR ($CDCl_3$): δ = 0.89 (*t*, *J* = 7 Hz; 3H), 0.93 (*t*, *J* = 7.5 Hz; 3H) 1.24–1.50 (*m*, 16), 1.53 (*s*; 3H), 1.64–1.70 (*m*; 2H), 1.81 (quint, *J* = 7 Hz; 2H), 3.01 (*d*, *J* = 14 Hz; 1H), 3.22 (*d*, *J* = 14 Hz; 1H), 4.00 (*t*, *J* = 7 Hz; 2H), 4.97 (*t*, *J* = 5 Hz; 1H), 6.97; 7.51 (AA'BB', *J* = 9 Hz; 4H), 7.25; 7.59 (AA'BB', *J* = 9 Hz; 4H), 7.41; 8.17 (AA'BB', *J* = 8 Hz; 4H)
MS (210°C): 586 (24%, M^+), 326 (5), 261 (100), 186 (13), 161 (10).

Acknowledgment

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