Chapter 5

Synthesis and mesomorphic properties of [R]-[+]-alkoxycarbonylethoxyphenyl-4-(*trans*-4′-n-alkoxycinnamoyloxy)benzoates

Chapter 5

A brief account of the effect of molecular and phase chirality on liquid crystalline properties

The introduction of chirality into mesogenic systems can sometimes gives rise to unusual and unexpected results. Within the last few years a whole plethora of new phase types have been reported, including the TGB_A,[1-3] ferrielectric [4] and antiferroelectric [5] phases. Other unusual phenomena include helical twist inversions in both cholesteric [6] and S_C^* [7] phases, as well as inversion associated with the direction of the spontaneous polarisation in the ferroelectric S_C^* phase.[8] In order to investigate the effects of chirality on mesogenic systems, new routes and precursors that lead to materials which show a high degree of optical activity are being sought.

Recently the discovery of a new liquid crystal variant, the twisted S_A (TGB_A)[1-3] phase, was reported. In this phase the molecules are packed in layers with their long axes perpendicular on average to the layer planes. In the direction normal to the long axes of the molecules, and parallel to the layers, a macroscopic helix is formed.

Goodby and co-workers [8] have studied changes in molecular chirality with the size, shape and polarity of the lateral group at the chiral centre. They varied the substituent and the length of the two terminal chains at the chiral centre and examined how this affected the chiral properties of the mesophases formed. They found that when the terminal chiral moiety of a number of propiolate esters (series 5.A) becomes more fork-shaped in structure, the chirality of the phase would be increased due to rotational damping of the motion of the chiral centre about the long axis of the molecules. Similarly the biaxiality of the material might also be expected to increase as the lengths of the two terminal chains

are increased. When the lateral aliphatic substituent was increased in length. the antiferroelectric phase was favoured over the ferroelectric phase. The TGB_A phase also gets suppressed by increasing the length of this lateral substituent. When the two terminal chain lengths reach the same value then the material has no chirality, but it still exhibited an antiferroelectric-like phase on cooling the S_A phase.[9]

It is known that extending the aliphatic chain on the peripheral side of the chiral centre has the effect of reducing the incidence of TGB_A phase.[10] This may be due to the fact that when increasing the length of the peripheral chain, the molecular chirality initially increases because the rotation of the chiral centre about the long axis of the molecule becomes increasingly damped. As the peripheral chain is increased in length the effect of rotational damping caused by the addition of extra methylene unit will reach a maximum. This effect will then be diluted as the chain is extended further.

Slaney *et al.* [10] have studied the effect of extending the terminal aliphatic chain on the peripheral side of the chiral centre in homologous series 5.B in which derivatives of amino acids were used as the chiral building blocks. Compound 5.B.1 exhibits N*, S_A, S_C* phase sequence on cooling the isotropic liquid. It does not show TGB_A phase, because the chiral centre is associated with a relatively short alkyl chain and is able to move freely about the long axis of the molecules in the liquid crystalline state. It appears that, the compound with a short terminal chiral chain attached is more suited to give orthogonal lamellar phases rather than tilted ferroelectric S_C* phase. Compounds 5.B.2 and 5.B.3 exhibit TGB_A phase between cholesteric and smectic A phases. Stable S_C* phase also observed in these compounds, indicate that the increased length and degree of branching in the terminal chiral alkyl chain stabilises this phase.

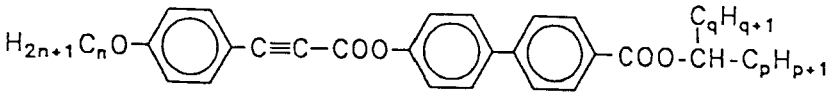
Consider the compounds of series 5.C,[11-13] which differ by a methylene unit at the terminal aliphatic chain on the peripheral side of the chiral centre show stable smectic A and S_C* phases rather than a cholesteric phase. However, only compound 5.C.2 exhibits a cholesreric to S_C* phase transition on cooling the isotropic liquid and does not exhibit S_A phase.[12]

Nabor *et al.*[14] have synthesised two homologous series of compounds 5.D.1 and 5.D.2 which differ from one another by the nature of the aliphatic chain at the chiral centre. Both of them exhibit the same N*, S_A, S_C* phase sequence on cooling the isotropic liquid.

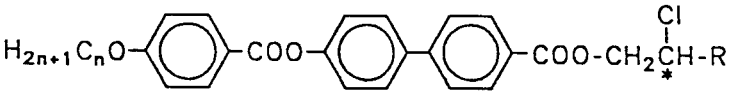
In order to investigate the effect of molecular chirality on the stabilisation of TGB_A and S_C* phases three series of substituted lactic acid derivatives were synthesised *viz.*series 5.E, 5.F and 5.G. These have the same basic molecular structure but differing in the type of alcohol used. On moving from series 5.E to 5.F to *5.G* the chirality of the compounds are believed to decrease due to the increased freedom of rotation of the chiral centre. Compounds of series 5.E have a greater restriction of rotation as compared to the compounds of series 5.F and *5.G* because it has a branching group closer to the chiral carbon. Thus these series of materials can be used to investigate the effect of molecular and phase chirality on the liquid crystalline properties.

Results and discussion

The synthesis of the compounds studied are shown schematically in figure 5.1. *trans*-4-n-Alkoxycinnamic acids were prepared following a method mentioned in chapter 2. The phenolic part of the target molecule war prepared as follows. Mitsunobu reaction [15] on 4-benzyloxyphenol with ethyl lactate in dry dichloromethane in the presence of $P(Ph)_3$ and



—5.A

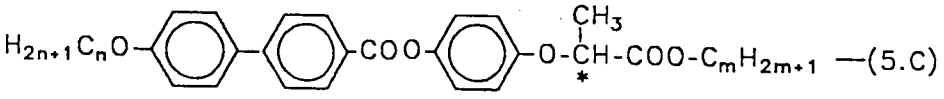


—5.B

R = $-CH_3$, 5.B.1

R = $-CH(CH_3)_2$, 5.B.2

R = $-CH_2-CH(CH_3)_2$, 5.B.3



—(5.C)

n=8, m=1; 5.C.1

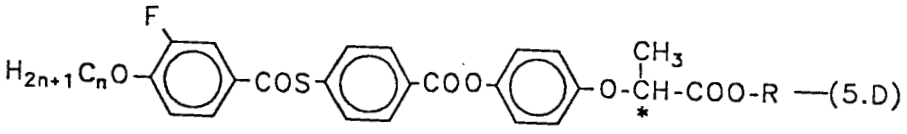
n=8, m=2; 5.C.2

n=7, m=3; 5.C.3

n=8, m=4; 5.C.4

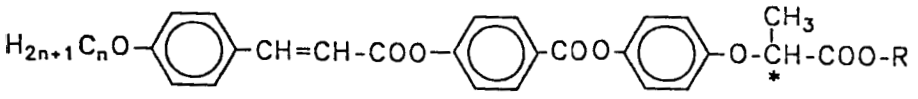
n=8, m=5; 5.C.5

n=8, m=6; 5.C.6



R = CH_2CH_3 5.D.1
R = $CH(CH_3)_2$ 5.D.2

5.D.1; n = 14, 65.3 S_C* 88.2 S_A 101.2 N* 103.8 I
5.D.2; n = 14, 73.1 S_C* 81.4 S_A 91.8 N* 96.5 I



R = $CH(CH_3)_2$, Series **5.E**
R = CH_2-$CH(CH_3)_2$, Series **5.F**
R = $(CH_2)_3$-CH_3, Series **5.G**

DEAD afforded compound 5.1. The ester group of compound 5.1 was saponified using 2% aqueous NaOH solution followed by acidification. The acid was then esterified with an appropriate alcohol in the presence of a dehydrating agent such as DCC and DMAP as the catalyst in CH_2Cl_2. Hydrogenolysis of the resulting compound was achieved by 5% Pd-C in ethanol at room temperature. To lengthen the core, the phenol was esterified with 4-benzyloxybenzoic acid again and then the benzyl group was cleaved by hydrogenolysis reaction. Final products were obtained by esterification reaction between *trans*-4-n-alkoxycinnamic acids and the phenol.[16]

The phase assignments, transition temperatures and the associated enthalpy values for the [R]- enantiomers of the three series are listed in table 5.1 (series 5.E) and *5.2* (series 5.F and 5.G). The general mesomorphic trends of the two series of compounds (5.E and 5.F) have been plotted as a function of temperature versus the length of the terminal n-alkoxy chain and shown in figures 5.2 and 5.3 respectively. All the compounds listed in the above two tables are mesogenic and exhibit thermally stable mesophases. The phase sequence of these three series of compounds was N*, S_A, S_C*, on cooling the isotropic liquid. Higher homologues of series 5.E (compound 5.E.8) and 5.F (compound 5.F.8) do not exhibit N* phase. All the compounds of series 5.E (5.E.1 to 5.E.8) exhibit TGB_A phase and it appears between N* and S_A phases for all compounds except for compound 5.E.8, where it appears between isotropic liquid and S_A phase. The occurrence of the TGB_A phase could be seen under a polarising microscope and could not be detected by DSC measurements. The thermal range of this phase was however, very narrow (0.2^oC).

The cholesteric phase appeared from the isotropic liquid with a focal-conic or Grandjean plane texture and on further slow cooling it goes over to TGB_A phase. The

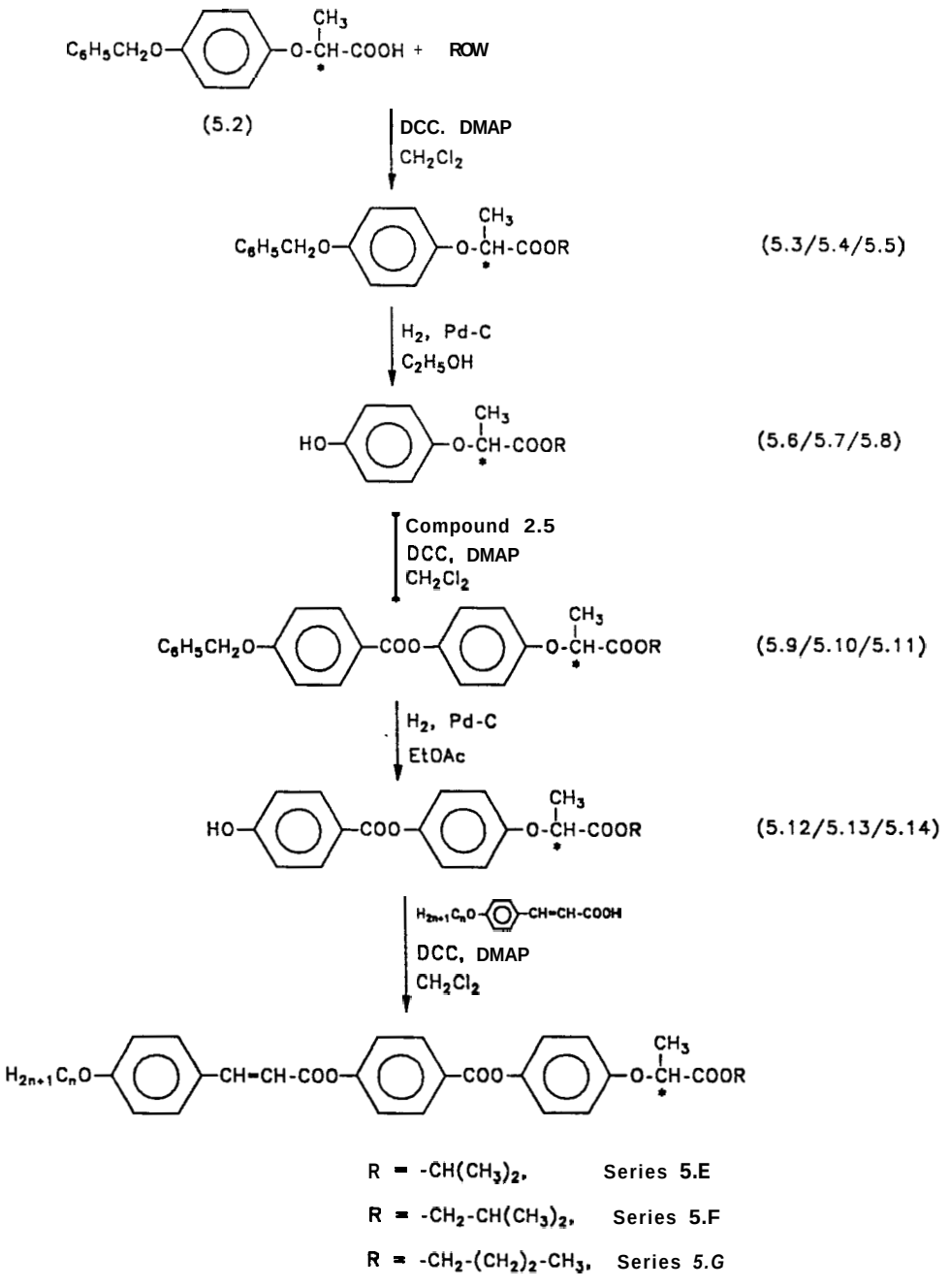
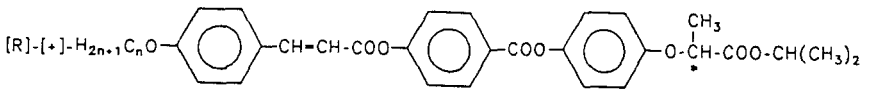


Figure 5.1. Synthetic scheme for the preparation of the compounds of series 5.E, 5.F and 5.G.

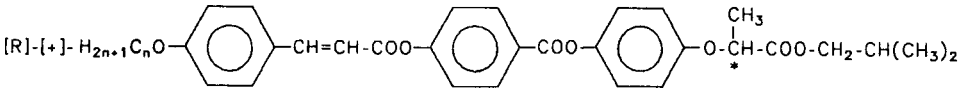
Table 5.1. Phase sequence, transition temperatures (°C) and enthalpies (Jg^{-1}) of



Compound Number	n	C		S_C*		S_A		TGB_A		N*		I
5.E.1	8	.	94.0 *30.4*	.	97.0 *0.16*	.	141.7†		142.0 *0.66*	.	153.0 *0.83*	.
5.E.2	9	.	90.0 *48.0*	.	101.0 *0.32*	.	137.6†	.	138.0 *0.55*	.	148.0 *0.7*	.
5.E.3	10	.	79.0 *42.0*	.	103.8 *0.19*	.	135.5†		135.8 *0.55*	.	144.9 *1.2*	.
5.E.4	11	.	86.0 *45.6*	.	105.9 *0.34*	.	132.7†		133.0 *0.51*	.	140.8 *1.24*	.
5.E.5	12	.	88.0 *48.6*	.	108.0 *0.33*	.	132.7†		133.0 *0.37*	.	139.3 *1.21*	.
5.E.6	14	.	95.0 *53.9*	.	110.5 *0.27*	.	130.7†	.	131.0 *0.37*	.	134.8 *1.2*	.
5.E.7	16	.	97.7 *56.0*	.	111.0 *0.21*	.	128.7†		128.8 *0.37*	.	130.6 *1.4*	.
5.E.8	18	.	96.5 *59.0*	.	110.0 *0.14*	.	127.7†	.	127.8 *3.9*	-		

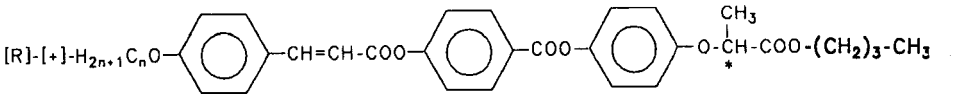
† : The enthalpy could not be measured

Table 5.2. Phase sequence, transition temperatures (°C) and enthalpies (Jg^{-1}) of



-5.F

and



-5.G

Compound Number	n	C	S_C*	S_A	N*	I
5.F.1	8	. 79.6 *50.1*	. 94.50 *0.16*	. 130.5 *1.12*	. 135.5 *0.87*	.
5.F.2	9	. 83.0 *87.3*	. 101.8 *0.25*	. 129.0 *0.83*	. 134.0 *0.91*	.
5.F.3	10	. 79.0 *53.5*	. 101.8 *0.41*	. 126.0 *0.54*	. 130.80 *1.00*	.
5.F.4	11	. 65.5 *62.2*	. 103.9 *0.45*	. 123.5 *0.58*	. 128.2 *1.42*	.
5.F.5	12	. 71.0 *55.5*	. 104.3 *0.5*	. 121.5†	. 125.50 *2.21*	.
5.F.6	14	. 68.7 *55.5*	. 106.5 *0.45*	. 120.0†	. 121.6 *3.76*	.
5.F.7	16	. 74.8 *54.3*	. 107.8 *0.45*	. 119.5†	. 119.7 *3.92*	.
5.F.8	18	. 82.3 *77.3*	. 109.5 *0.29*	. 119.3 *2.1*	-	.
5.G.1	14	. 52.2 *30.9*	. 103.5 *0.16*	. 127.5 *0.66*	. 132.5 *1.08*	.
5.G.2	14	. 55.0 *56.4*	. 107.1 *0.2*	. 125.5 *0.71*	. 128.5 *1.67*	.

†: The enthalpy could not be measured

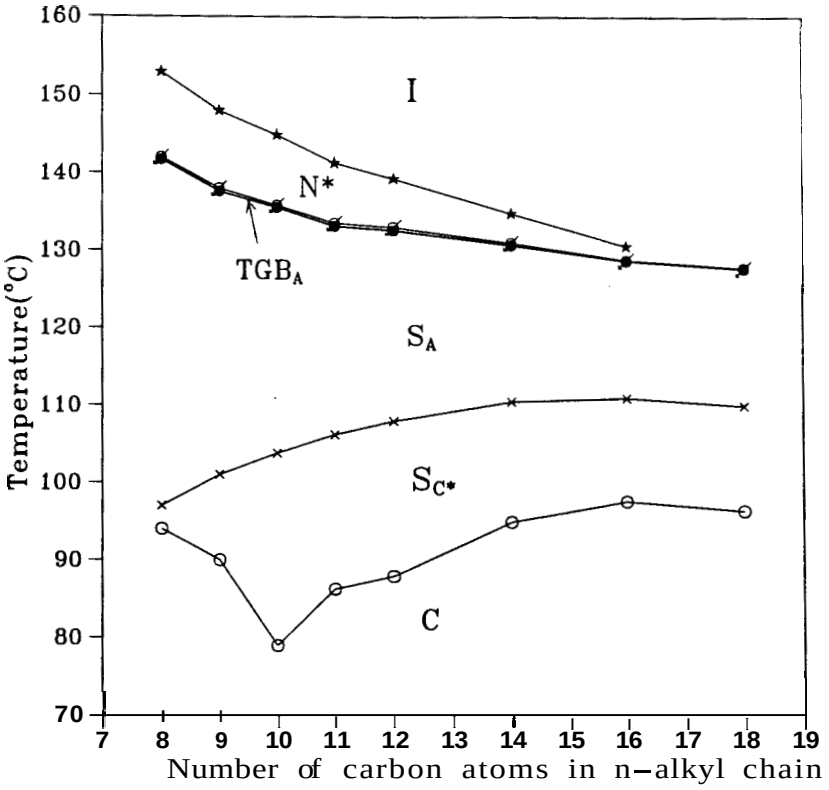


Figure 5.2. A plot of transition temperatures as a function of n-alkoxy chain length for series 5.E.

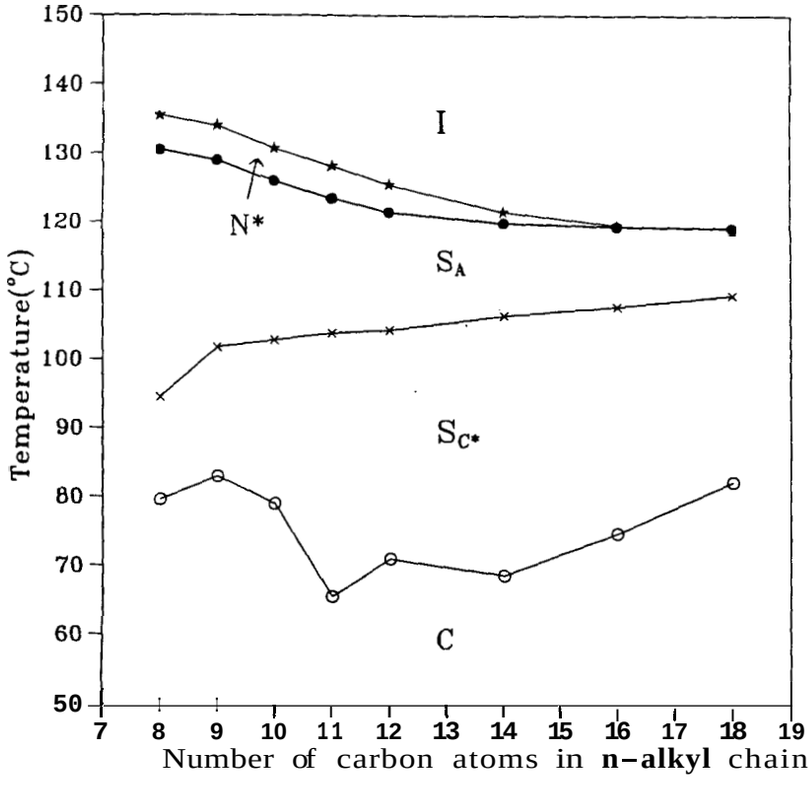


Figure 5.3. A plot of transition temperatures as a function of n-alkoxy chain length for series 5.F.

Grandjean plane texture slightly changes and the clear texture becomes somewhat blurred. When the TGB_A phase transformed to a S_A phase, several dechiralisation lines were observed followed by either a focal-conic texture or a homeotropic texture. On further slow cooling, the ferroelectric S_C^* phase appeared with a broken focal-conic or plane pseudohomeotropic or schlieren texture.

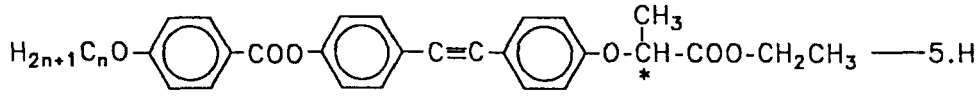
The TGB_A phase was not observed in the compounds of series 5.F and 5.G. suggesting that this phase is very sensitive to small changes in the molecular structure particularly close to the chiral centre. The two enantiomers of series 5.G have lower melting points than the corresponding analogues of series 5.E and 5.F. A comparison of the transition temperatures of the above two series of compounds shows that the phase types and sequences are about the same. The melting points as well as clearing temperatures of the latter series are much lower. In contrast the n-tetradecyl enantiomers of the series 5.G, have the lowest melting points amongst all the present compounds although the clearing points are not depressed too much. This shows that the branched isopropyl group seems to have some influence in this system for the formation of a TGB_A phase.

It can be seen in figure 5.2 that, as the terminal alkoxy chain increases in length, the smectic A to S_C^* transition temperatures rise sharply. Over the same interval of chain length the cholesteric to isotropic liquid transition temperatures fall, thereby decreasing the temperature range of the cholesteric phase. For the n-octadecyloxy homologue this effect culminates in a direct TGB_A to isotropic liquid transition.

Figure 5.3 shows that, all the homologues of series 5.F except 5.F.8 show N*, S_A and S_C* phase sequence on cooling the isotropic liquid and 5.F.8 shows S_A, S_C* phase sequence on cooling. None of the homologues of this series exhibit TGB_A phase.

Navailles *et al.*[17] have synthesised the homologous series 5.H using ethyl lactate as the chiral building block. This series of compounds exhibit the same rich polymorphism as those for series 5.E. However, they do exhibit blue phase III and blue phase I on cooling the isotropic liquid.

In conclusion, several compounds belonging to three different series containing lactic acid as the chiral group have been synthesised to examine the molecular and phase chirality on the mesomorphic properties. It is found that the nature of the alcohol group attached to the carboxyl group of the lactic acid moiety influence the type of mesophase obtained. In particular, the iospropyl group (series 5.E) seems to favour the formation of TGB_A phase compared to the n-butyl and isobutyl groups.



n =14; **C 80.0** S_C*101.0 S_A **127.1** TGB_A **128.2** N* **129.1** BPI **130.4** BPIII **133.1** I

Experimental

Ethyl-2-(4-benzyloxyphenoxy)propanoate, (5.1)

This was prepared following a procedure of Mitsunobu *et al.*[15] Thus, DEAD (19.2 g, 110 mmol) was added dropwise to a cold stirred solution of benzyloxyphenol (20.0 g, 100 mmol), [S]-[-]-ethyl lactate(14.2 g, 120 mmol), $P(Ph)_3$ (28.84 g, 110 mmol) and dichloromethane (200 ml) during two hours. The reaction mixture was then stirred at room temperature for four hours. The solid formed during the reaction was filtered off. The residue obtained on removal of solvent from the filtrate was chromatographed on silica gel and eluted with 3:1 chloroform and petroleum ether (b.p. 60-80°C). On removal of solvent from the eluate, a viscous liquid compound was obtained, (20.43 g, 68.1%), $[\alpha]_D^{25}$ =43.7 ^{o} (3.8 mg/ml in CH_2Cl_2); ν_{max} (neat): 2990, 1740, 1600, 1500, 1480, 1380, 1240 and 1050 cm^{-1}; δ: 1.2(3H, t, J=9.1 Hz, CH_3CH_2), 1.6(3H, d, J=7.6 Hz, CH_3CH), 4.2(2H, q, J=6.8 Hz, $COOCH_2CH_3$), 5.1(2H, s, $ArCH_2O$), 5.3(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 6.7-7.9(9H, m, ArH).

2-(4-Benzyloxyphenoxy)propanoic acid, (5.2)

Ethyl-2-(4-benzyloxyphenoxy)propanoate(19 g, 66.3 mmol), 2% aqueous NaOH solution(40 ml) and ethanol(40 ml) was refluxed for two hours. Ethanol was removed, the reaction mixture was cooled and acidified with dilute hydrochloric acid. The separated white solid was filtered, dried and crystallised from toluene and petroleum ether (1: 1) mixture, (12.67 g, 73.6%); m.p 96.5 "C; $[\alpha]_D^{25}$ =11.9 ^{o} (3.5 mg/ml in CH_2Cl_2); ν_{max}: 3700, 2990, 1730, 1600, 1500, 1480, 1380, 1240 and 1050 cm^{-1}; δ: 1.6(3H, d, J=8.7 Hz,

CH_3CH), 5.1(2H, s, $ArCH_2O$), 5.2 (IH, s, COOH) 5.3(1H, q, J=6.65 Hz, $OCH(CH_3)COO$), 6.7-7.9(9H, m, ArH).

2-Propyl-2-(4-benzyloxyphenoxy)propanoate, (5.3)

A mixture of 2-(4-benzyloxyphenoxy)propanoic acid(5.5 g, 20.2 mmol), 2-propanol (1.21 g, 20.2 mmol), DCC (4.12 g, 20.2 mmol), DMAP (0.26 g, 2.0 mmol) and dry dichloromethane(20 ml) was stirred for two hours at room temperature. N,N′-Dicyclohexylurea formed was filtered off and the filtrate was washed successively with water (2X30 ml), 5% aqueous acetic acid (3X50 ml), water (3X50 ml) and dried (Na_2SO_4). The residue obtained on removal of solvent was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a liquid, (4.83 g, 76.2%); $[\alpha]_D^{25}$ =61.9 ^{o} (2.96 mg/ml in CH_2Cl_2); ν_{max} (neat): 2950, 1740, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; 6: 1.2-1.7(9H, m, $3XCH_3$), 4.2(1H, m, $COOCH(CH_3)_2$), 5.1(2H, s, $ArCH_2O$), 5.3(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 6.7-7.9(9H, m, ArH).

2-Methylpropyl-2-(4-benzyloxyphenoxy)propanoate, (5.4)

This was prepared using the same procedure as described above for compound 5.3. Yield, 71.2%; $[\alpha]_D^{25}$ = 39.5 ^{o} (5.0 mg/ml in CH_2Cl_2); ν_{max} (neat): 2950, 1740, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; *6:* 0.91-1.67(1OH, m, $3XCH_3$, $1XCH$), 4.2(2H, d, J=6.9 Hz, $COOCH_2CH$), 5.1(2H, s, $ArCH_2O$), 5.3(1H, q, J=6.64 Hz, $OCH(CH_3)COO$), 6.7-7.9(9H, m, ArH).

1-Butyl-2-(4-benzyloxyphenoxy)propanoate, (5.5)

This was prepared using the same procedure as described above for compound 5.3. Yield, 64.5%; $[\alpha]_D^{25}$ = 38.2 ^{o} (4.6 mg/ml in CH_2Cl_2); ν_{max} (neat): 2950, 1740, 1600, 1520,

1480, 1280 and 1050 cm^{-1}; 6: 0.8-1.67(10H, m, $2XCH_3$, $2XCH_2$), 4.2(2H, t, J=6.4 Hz, $COOC\underline{H}_2CH_2$), 5.1(2H, s, $ArCH_2O$), 5.3(1H, q, J=6.64 Hz, $OCH(CH_3)COO$), 6.7-7.9(9H, m, ArH).

2-Propyl-2-(4-hydroxyphenoxy)propanoate, (5.6)

To a solution of 2-propyl-2-(4-benzyloxyphenoxy)propanoate(4.5 g, 14.3 mmol) in ethanol (25 ml), 5% Pd-C catalyst(1.2 g) was added and the mixture stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was then filtered and ethanol removed by distillation under reduced pressure. The residual liquid was chromatographed on silica gel and eluted with chloroform and ethylacetate(9:1) mixture. Removal of the solvent from the eluate afforded a viscous liquid, 2.32 g, 72.3%; $[\alpha]_D^{25}$ = 49.3 ° (3.1 mg/ml in CH_2Cl_2); ν_{max} (neat): 3600, 3000, 1500, 1480, 1240 and 1050 cm^{-1}; 6: 1.22-1.68(9H, m, $3XCH_3$), 4.2(1H, m, $COOCH(CH_3)_3$), 5.3 (1H, q, J=6.58, $OCH(CH_3)COO$), 5.2(1H, s, OH), 6.7-7.9(4H, m, ArH).

2-Methylpropyl-2-(4-hydroxyphenoxy)propanoate, (5.7)

This was prepared using the same procedure as described above for compound 5.6. Yield, 68%; $[\alpha]_D^{25}$ = 47.2 ° (2.9 mg/ml in CH_2Cl_2); ν_{max} (neat): 3600, 3000, 1500, 1480, 1240 and 1050 cm^{-1}; 6: 0.9-1.6(10H, m, $3XCH_3$, 1XCH), 4.2(2H, d, J=6.88 Hz, $COOCH_2CH$), 5.3 (1H, q, J=6.4 Hz, $OCH(CH_3)COO$), 5.2(1H, s, OH), 6.7-7.9(4H, m, ArH).

1-Butyl-2-(4-hydroxyphenoxy)propanoate, (5.8)

This was prepared using the same procedure as described for compound 5.6. Yield, 68%; $[\alpha]_D^{25}$ = 43.4 ° (3.1 mg/ml in CH_2Cl_2); ν_{max} (neat): 3600, 3000, 1500, 1480, 1240 and 1050 cm^{-1}; δ :0.9-1.6(10H, m, $2XCH_3$, $2XCH_2$), 4.2(2H, t, J=6.66 Hz, $COOCH_2CH_2$), 5.3 (1H, q, J=6.4 Hz, $OCH(CH_3)COO$), 5.2(1H, s, OH), 6.7-7.9(4H, m, ArH).

2-Propyl-2-[4-(4′-benzyloxyphenylcarbonyloxy)phenoxy]propanoate,(5.9)

This was prepared according to the procedure described for compound 5.3. Yield, 79.4%; m.p. 139.7 °C; $[\alpha]_D^{25}$ =32.7 ° (3.2 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 1.1-1.62(9H, m, $3XCH_3$), 4.2(1H, m, $COOCH(CH_3)_3$), 5.1(2H, s, $ArCH_2O$), 5.3(1H, q, J=6.54 Hz, $OCH(CH_3)COO$), 6.7-7.9(13H, m, ArH).

2-Methylpropyl-2-[4-(4′-benzyloxyphenylcarbonyloxy)phenoxy]propanoate,(5.10)

This was prepared using the same procedure as described for compound 5.3. Yield, 70%; m.p. 149.5 °C; $[\alpha]_D^{25}$ =33.3 ° (3.5 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.91-1.63(10H, m, $3XCH_3$, IXCH), 4.2(2H, d, J=7.1 Hz, $COOCH_2CH$), 5.1(2H, s, $ArCH_2O$), 5.3(1H, q, J=6.62 Hz, $OCH(CH_3)COO$), 6.7-7.9(13H, m, ArH).

1-Butyl-2-[4-(4′-benzyloxyphenylcarbonyloxy)phenoxy]propanoate,(5.11)

This was prepared using the same procedure as described for compound 5.3. Yield, 64.8%; m.p. 124.8 °C; $[\alpha]_D^{25}$ =33.8 ° (2.5 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1740, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.91-1.63(10H, m, $2XCH_3$, $2XCH_2$), 4.2(2H, t, J=6.97 Hz, $COOC\underline{H}_2CH_2$), 5.1(2H, s, $ArCH_2O$), 5.3(1H, q, J=6.62 Hz, $OCH(CH_3)COO$), 6.7-7.9(13H, m, ArH).

2-Propyl-2-[4-(4′-hydroxyphenylcarbonyloxy)phenoxy]propanoate, (5.12)

This was prepared according to the procedure described for compound 5.6. Yield, 77.3%; m.p. 113.4°C; $[\alpha]_D^{25}$ = 41.7 ° (4.4 mg/ml in CH_2Cl_2); ν_{max}: 3600, 3000, 1500, 1480, 1240 and 1050 cm^{-1}; δ : 1.24-1.68(9H, m, $3XCH_3$), 4.2(1H, m, $COOCH(CH_3)_2$), 5.3(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 6.7-7.9(8H, m, ArH), 7.5(s, 1H, OH);

Elemental analysis: Found, C, 66.25; H, 5.83% $C_{19}H_{20}O_6$ requires C, 66.28; H, 5.81%.

2-Methylpropyl-2-[4-(4′-hydroxyphenylcarbonyloxy)phenoxy]propanoate, (5.13)

This was prepared according to the procedure described for compound 5.6. Yield, 73.2%; m.p. 107.9°C; $[\alpha]_D^{25}$=50.8 ° (19.8 mg/ml in CH_2Cl_2); ν 3600, 3000, 1500, 1480, 1240 and 1050 cm^{-1}; δ : 0.91-1.64(10H, $3XCH_3$, 1XCH), 4.2(2H, d, J=7.23 Hz, $COOCH_2CH$), 5.3(1H, q, J=6.64 Hz, $OCH(CH_3)COO$), 6.7-7.9(8H, m, ArH), 7.5(1H, s, OH);

Elemental analysis: Found, C, 66.04; H, 6.13% $C_{20}H_{22}O_6$ requires C, 67.03; H, 6.14%.

1-Butyl-2-[4-(4′-hydroxyphenylcarbonyloxy)phenoxy]propanoate, (5.14)

This was prepared according to the procedure described for compound 5.6. Yield, 73.2%; m.p. 89.9 °C; $[\alpha]_D^{25}$ =38.8 ° (3.2 mg/ml in CH_2Cl_2); ν_{max}: 3600, 3000, 1500, 1480, 1240 and 1050 cm^{-1}; δ : 0.91-1.64(10H, $2XCH_3$, $2XCH_2$), 4.2(2H, t, J=7.02 Hz, $COOC\underline{H}_2CH_2$), 5.3(1H, q, J=6.64 Hz, $OCH(CH_3)COO$), 6.7-7.9(8H, m, ArH), 7.5(1H, s, OH);

Elemental analysis: Found, C, 67.05; H, 6.17% $C_{20}H_{22}O_6$ requires C, 67.03; H, 6.14%.

[R]-[+]-(2-Propyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-decyloxycinnamoyloxy)benzoate, (5.E.3)

This was prepared according to the procedure described above for compound 5.3 Yield, 72%; m.p. 79.0 °C; $[\alpha]_D^{25}$ = 22.0 ° (5.8 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.71-1.71 (28H, m, $4XCH_3$, $8XCH_2$), 4.02(2H, t, J=6.4 Hz, $ArOCH_2$), 4.71(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 5.14(1H, m, $COOCH(CH_3)_2$), 6.48 and 7.85(2H, AB q, J= 17.4 Hz, CH=CH-COO), 6.85 and 7.51(4H, AB q, J=10.1 Hz, ArH), 6.97(4H, s, ArH), 7.32 and 8.24(4H, AB q, J=9.8 Hz, ArH);

Elemental analysis: Found, C, 72.33; H, 7.38% $C_{38}H_{46}O_8$ requires C, 72.38; H, 7.30%.

The physical data of the cognate preparations of the other [R]-[+]-(2-propyloxycarbonyl)ethoxyphenyl 4-(*trans*-4′-n-alkoxycinnamoyloxy)benzoates are given below.

[R]-[+]-(2-Propyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-octyloxycinnamoyloxy)benzoate, (5.E.1)

Yield, 68%; m.p. 94.0°C; $[\alpha]_D^{25}$ = 23.1 ^{o} (4.5 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.71-1.71 (24H, m, $4XCH_3$, $6XCH_2$), 4.02(2H, t, J=6.4 Hz, $ArOCH_2$), 4.71(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 5.14(1H, m, $COOCH(CH_3)_2$), 6.48 and 7.85(2H, AB q, J= 17.4 Hz, CH=CH-COO), 6.85 and 7.51(4H, AB q, J=10.1 Hz, ArH), 6.97(4H, s, ArH), 7.32 and 8.24(4H, AB q, J=9.8 Hz, ArH);

Elemental analysis: Found, C, 71.78; H, 7.08% $C_{36}H_{42}O_8$ requires C, 71.76; H, 6.97%.

[R]-[+]-(2-Propyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-nonyloxycinnamoyloxy)benzoate, (5.E.2)

Yield, 74%; m.p. 90.0°C; $[\alpha]_D^{25}$ = 19.5 ^{o} (5.5 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.71-1.71 (26H, m, $4XCH_3$, $7XCH_2$), 4.02(2H, t, J=6.4 Hz, $ArOCH_2$), 4.71(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 5.14(1H, m, $COOCH(CH_3)_2$), 6.48 and 7.85(2H, AB q, J= 17.4 Hz, CH=CH-COO), 6.85 and 7.51(4H, AB q, J=10.1 Hz, ArH), 6.97(4H, s, ArH), 7.32 and 8.24(4H, AB q, J=9.8 Hz, ArH);

Elemental analysis: Found, C, 71.87; H, 7.26% $C_{37}H_{44}O_8$ requires C, 72.07; H, 7.14%.

[R]-[+]-(2-Propyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-undecyloxy-cinnamoyloxy)benzoate, (5.E.4)

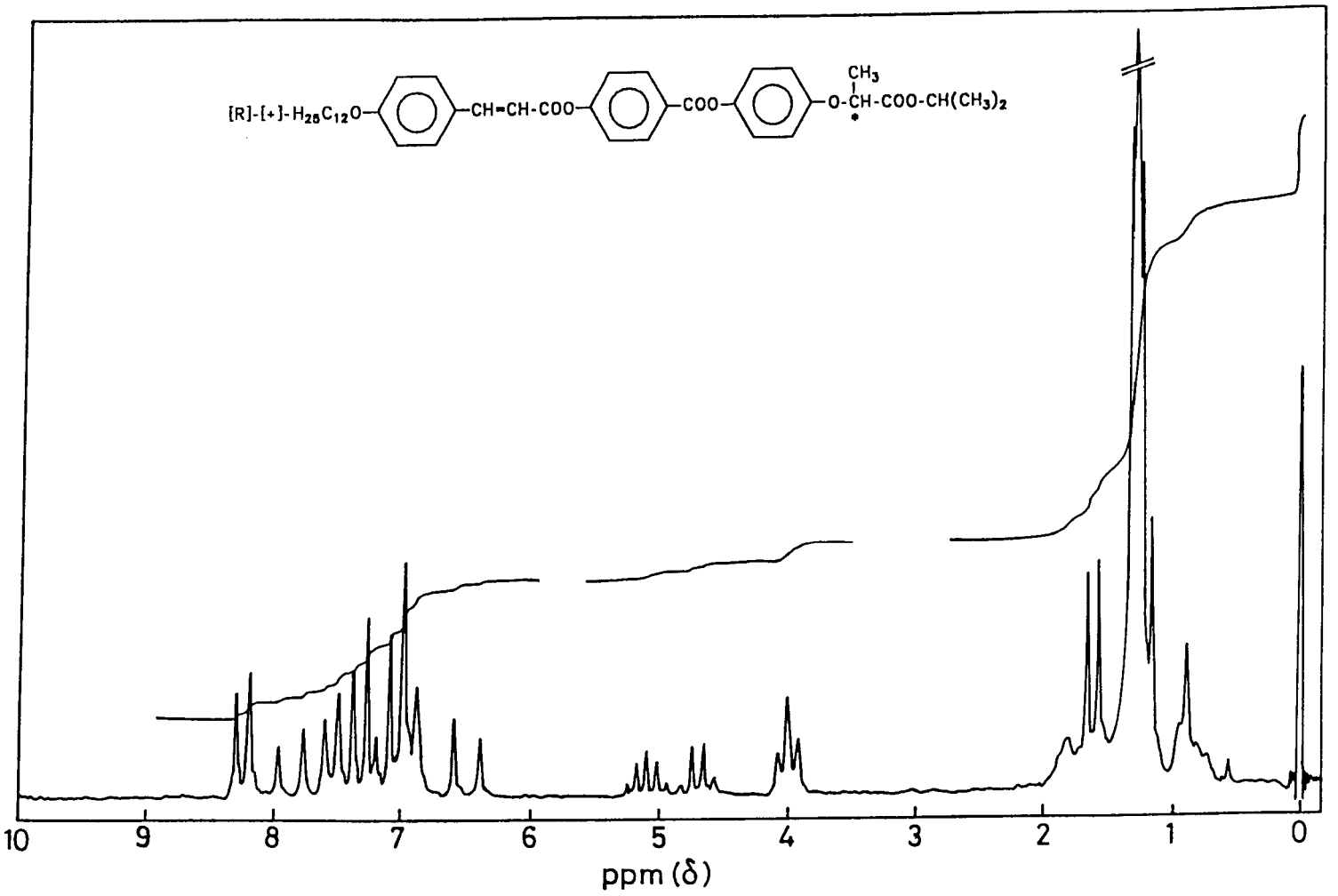
Yield, 71%; m.p. 86.0°C; $[\alpha]_D^{25}$ = 21.6 ° (3.6 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.71-1.71 (30H, m, $4XCH_3$, $9XCH_2$), 4.02(2H, t, J=6.4 Hz, $ArOCH_2$), 4.71(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 5.14(1H, m, $COOCH(CH_3)_2$), 6.48 and 7.85(2H, AB q, J= 17.4 Hz, CH=CH-COO), 6.85 and 7.51(4H, AB q, J=10.1 Hz, ArH), 6.97(4H, s, ArH), 7.32 and 8.24(4H, AB q, J=9.8 Hz, ArH);

Elemental analysis: Found, C, 72.55; H, 7.55% $C_{39}H_{48}O_8$ requires C, 72.67; H, 7.45%.

[R]-[+]-(2-Propyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-dodecyloxy-cinnamoyloxy)benzoate, (5.E.5)

Yield, 65%; m.p. 88.0°C; $[\alpha]_D^{25}$ = 20.1 ° (4.7 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.71-1.71 (32H, m, $4XCH_3$, $10XCH_2$), 4.02(2H, t, J=6.4 Hz, $ArOCH_2$), 4.71(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 5.14(1H, m, $COOCH(CH_3)_2$), 6.48 and 7.85(2H, AB q, J= 17.4 Hz, CH=CH-COO), 6.85 and 7.51(4H, AB q, J=10.1 Hz, ArH), 6.97(4H, s, ArH), 7.32 and 8.24(4H, AB q, J=9.8 Hz, ArH);

Elemental analysis: Found, C, 72.56; H, 7.74% $C_{40}H_{50}O_8$ requires C, 72.94; H, 7.59%.



^{1}H NMR spectrum for compound 5.E.5

[R]-[+]-(2-Propyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-tetradecyloxy-cinnamoyloxy)benzoate, (5.E.6)

Yield, 73%; m.p. 95.0°C; $[\alpha]_D^{25}$ = 20.8 ° (5.0 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.71-1.71 (36H, m, $4XCH_3$, $12XCH_2$), 4.02(2H, t, J=6.4 Hz, $ArOCH_2$), 4.71(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 5.14(1H, m, $COOCH(CH_3)_2$), 6.48 and 7.85(2H, AB q, J= 17.4 Hz, CH=CH-COO), 6.85 and 7.51(4H, AB q, J=10.1 Hz, ArH), 6.97(4H, s, ArH), 7.32 and 8.24(4H, AB q, J=9.8 Hz, ArH);

Elemental analysis: Found, C, 73.32; H, 7.94% $C_{42}H_{54}O_8$ requires C, 73.46; H, 7.87%.

[R]-[+]-(2-Propyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-hexadecyloxy-cinnamoyloxy)benzoate, (5.E.7)

Yield, 70%; m.p. 97.7°C; $[\alpha]_D^{25}$ = 19.6 ° (4.8 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.71-1.71 (40H, m, $4XCH_3$, $14XCH_2$), 4.02(2H, t, J=6.4 Hz, $ArOCH_2$), 4.71(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 5.14(1H, m, $COOCH(CH_3)_2$), 6.48 and 7.85(2H, AB q, J= 17.4 Hz, CH=CH-COO), 6.85 and 7.51(4H, AB q, J=10.1 Hz, ArH), 6.97(4H, s, ArH), 7.32 and 8.24(4H, AB q, J=9.8 Hz, ArH);

Elemental analysis: Found, C, 73.71; H, 8.29% $C_{44}H_{58}O_8$ requires C, 73.95; H, 8.12%.

[R]-[+]-(2-Propyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-octadecyloxy-cinnamoyloxy)benzoate, (5.E.8)

Yield, 73%; m.p. 96.5°C; $[\alpha]_D^{25}$ = 21.9 ° (4.3 mg/ml in CH_2Cl_2); ν_{max}: 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; 6 : 0.71-1.71 (44H, m, $4XCH_3$, $16XCH_2$), 4.02(2H, t, J=6.4 Hz, $ArOCH_2$), 4.71(1H, q, J=6.6 Hz, $OCH(CH_3)COO$), 5.14(1H, m, $COOCH(CH_3)_2$), 6.48 and 7.85(2H, AB q, J= 17.4 Hz, CH=CH-COO), 6.85 and 7.51(4H, AB q, J=10.1 Hz, ArH), 6.97(4H, s, ArH), 7.32 and 8.24(4H, AB q, J=9.8 Hz, ArH);

Elemental analysis: Found, C, 73.98; H, 8.31% $C_{46}H_{62}O_8$ requires C, 74.39; H, 8.35%.

[R]-[+]-(2-Methylpropyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-decyl-oxycinnamoyloxy)benzoate, (5.F.3)

This was prepared using the same procedure as described above for compound 5.E.3. Yield, 69%; m.p. 79.0°C; $[\alpha]_D^{25}$ = 21.2 ° (1.8 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; 6 : 0.57-1.73 (29H, m, $4XCH_3$, $8XCH_2$, IXCH), 3.98(2H, t, J=6.8 Hz, $COOCH_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.1 Hz, ArH);

Elemental analysis: Found, C, 72.96; H, 7.51% $C_{39}H_{48}O_8$ requires C, 72.67; H, 7.45%.

The physical data of the cognate preparations of the other [R]-[+]-(2-methylpropyloxy-carbonyl)ethoxyphenyl-4-(*trans*-4′-n-alkoxycinnamoyloxy)benzoates are given below.

(2-Methylpropyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-octyloxycinnamoyloxy)benzoate, (5.F.1)

Yield, 69%; m.p. 79.6°C; $[\alpha]_D^{25}$ = 21.8 ° (1.74 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.57-1.73 (25H, m, $4XCH_3$, $6XCH_2$, 1XCH), 3.98(2H, t, J=6.8 Hz, $COOCH_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.1 Hz, ArH);

Elemental analysis: Found, C, 72.11; H, 7.13% $C_{37}H_{44}O_8$ requires C, 72.07; H, 7.14%.

(2-Methylpropyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-nonyloxycinnamoyloxy)benzoate, (5.F.2)

Yield, 73%; m.p. 83.0°C; $[\alpha]_D^{25}$ = 21.2 ° (1.7 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.57-1.73 (27H, m, $4XCH_3$, $7XCH_2$, 1XCH), 3.98(2H, t, J=6.8 Hz, $COOCH_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.1 Hz, ArH);

Elemental analysis: Found, C, 72.32; H, 7.42% $C_{38}H_{46}O_8$ requires C, 72.38; H, 7.30%.

(2-Methylpropyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-undecyloxy-cinnamoyloxy)benzoate, (5.F.4)

Yield, 68.0%; m.p. 65.5°C; $[\alpha]_D^{25}$ = 20.1 ° (3.22 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.57-1.73 (31H, m, $4XCH_3$, $9XCH_2$, IXCH), 3.98(2H, t, J=6.8 Hz, $COOC\underline{H}_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.1 Hz, ArH);

Elemental analysis: Found, C, 73.10; H, 7.69% $C_{40}H_{50}O_8$ requires C, 72.94; H, 7.59%.

(2-Methylpropyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-dodecyloxy-cinnamoyloxy)benzoate, (5.F.5)

Yield, 74%; m.p. 71.0°C; $[\alpha]_D^{25}$ = 19.8 ° (2.7 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.57-1.73 (33H, m, $4XCH_3$, $10XCH_2$, IXCH), 3.98(2H, t, J=6.8 Hz, $COOC\underline{H}_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.1 Hz, ArH);

Elemental analysis: Found, C, 73.33; H, 7.80% $C_{41}H_{52}O_8$ requires C, 73.21; H, 7.73%.

(2-Methylpropyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-tetradecyloxy-cinnamoyloxy)benzoate, (5.F.6)

Yield, 70%; m.p. 68.7°C; $[\alpha]_D^{25}$ = 27.1 ° (2.2 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm''; δ : 0.57-1.73 (37H, m, $4XCH_3$, $12XCH_2$, IXCH), 3.98(2H, t, J=6.8 Hz, $COOC\underline{H}_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.I Hz, ArH);

Elemental analysis: Found, C, 73.58; H, 8.13% $C_{43}H_{56}O_8$ requires C, 73.71; H, 8.0%.

(2-Methylpropyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-hexadecyloxy-cinnamoyloxy)benzoate, (5.F.7)

Yield, 65%; m.p. 74.8°C; $[\alpha]_D^{25}$ = 18.4 ° (2.06 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.57-1.73 (41H, m, $4XCH_3$, $14XCH_2$, IXCH), 3.98(2H, t, J=6.8 Hz, $COOC\underline{H}_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.I Hz, ArH);

Elemental analysis: Found, C, 74.18; H, 8.19% $C_{45}H_{60}O_8$ requires C, 74.15; H, 8.24%.

(2-Methylpropyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-octadecyloxy-cinnamoyloxy)benzoate, (5.F.8)

Yield, 78%; m.p. 82.3°C; $[\alpha]_D^{25}$ = 20.9 ° (2.93 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480,1280 and 1050 cm^{-1}; 6 : 0.57-1.73 (45H, m, $4XCH_3$, $16XCH_2$, 1XCH), 3.98(2H, t, J=6.8 Hz, $COOC\underline{H}_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.1 Hz, ArH);

Elemental analysis: Found, C, 74.79; H, 8.36% $C_{47}H_{64}O_8$ requires C, 74.60 H, 8.46%.

(1-Butyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-dodecyloxycinnamoyl-oxy)benzoate, (5.G.1)

This was prepared using the same procedure as described above for compound **5.E.3.** Yield, 71%; m.p. 52.2°C; $[\alpha]_D^{25}$ = 23.07 ° (1.0 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.57-1.73 (33H, m, $3XCH_3$, $12XCH_2$), 3.98(2H, t, J=6.65 Hz, $COOC\underline{H}_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)$ COO), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.1 Hz, ArH);

Elemental analysis: Found, C, 73.19; H, 7.78% $C_{41}H_{52}O_8$ requires C, 73.21; H, 7.73%.

(1-Butyloxycarbonyl)ethoxyphenyl-4-(*trans*-4′-n-tetradecyloxycinnamoyloxy)benzoate, (5.G.2)

Yield, 71%; m.p. 55.0°C; $[\alpha]_D^{25}$ = 23.07 ° (1.0 mg/ml in CH_2Cl_2); ν_{max} : 2950, 1738, 1600, 1520, 1480, 1280 and 1050 cm^{-1}; δ : 0.57-1.73 (37H, m, $3XCH_3$, $14XCH_2$), 3.98(2H, t, J=6.65 Hz, $COOC\underline{H}_2CH_2$), 4.01(2H, t, $ArOCH_2$), 4.78(1H, q, J=6.48 Hz, $OCH(CH_3)COO$), 6.51 and 7.81(2H, AB q, J= 17.3 Hz, CH=CH-COO), 6.84 and 7.53(4H, AB q, J=9.62 Hz, ArH), 6.98(4H, s, ArH), 7.34 and 8.21(4H, AB q, J=9.1 Hz, ArH);

Elemental analysis: Found, C, 73.73; H, 7.78% $C_{43}H_{56}O_8$ requires C, 73.71; H, 7.99%.

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