

## **Chapter 6**

**Synthesis and mesomorphic properties of**

- (i) **1-[(E-4-*n*-Alkoxy- $\alpha$ -methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-*n*-dodecyloxybenzoyloxy-4-benzoates)**

**Series- 6.1**

- (ii) **1-[(E-4-*n*-Alkoxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecyloxybenzoyloxy-4-benzoates)**

**Series- 6.11**

- (iii) **1-[(E-4-*n*-Alkoxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoates)**

**Series- 6.111**

- (iv) **2-[(E-4-*n*-Alkoxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-*n*-dodecyloxybenzoyloxy-4-benzoates)**

**Series- 6.IV**

## Introduction

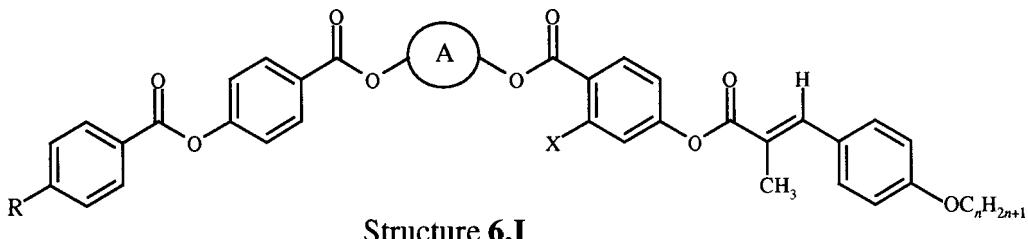
During the past few years, several hundred compounds with bent molecular shape and exhibiting mesophases have been reported [28, 29, 45, 48, 51, 53]. Most of these are derived from resorcinol, and are symmetrical about this central unit. Many bridging groups such as azomethine, azo, ester etc. have been used in the design and synthesis of such compounds with *n*-alkoxy / *n*-alkyl terminal chains. The commonly observed banana (B) phases are **B**<sub>6</sub>, **B**<sub>1</sub> and **B**<sub>2</sub> which occur in this sequence on ascending a homologous series of compounds [29, 41,581].

The occurrence of calamitic phases in conjunction with the B-phases have been observed in a number of systems [53, 54, 98-100]. This seems to depend on the bend angle between the two arms of the bent-core molecules. The occurrence of a transition from a nematic phase to a chiral mesophase is in itself an interesting phenomenon. There are only a few cases where a transition from a nematic phase to an antiferroelectric mesophase has been reported [53, 98-100].

A transition from the nematic phase to a B phase transitions has been obtained in systems containing a suitably substituted 1, 3-phenylene [53] or 2, 7-naphthylene central unit [98]. The number of reports on the mesomorphic properties of compounds derived from 2, 7-dihydroxynaphthalene are few in number [55, 98, 100-1021]. Although compounds containing two unsymmetrical arms about a central phenyl ring are known [28, 47, 99] those derived from resorcinol except [47] or 2, 7-dihydroxynaphthalene are not known.

With this in view, the synthesis and mesomorphic properties of four homologous series of unsymmetrical compounds derived from both resorcinol and 2, 7-dihydroxy-naphthalene were investigated and described in this chapter. The four homologous series (6.1, 6.11, 6.111 and **6.IV**) of unsymmetrical compounds were prepared to examine the following aspects. The effect of the lateral fluorine substituent in only one of the arms, the effect of the type of terminal chain and the nature of the central unit.

The general structure of the unsymmetrical compounds belonging to the four homologous series is shown in structure 6.1



$R = n\text{-C}_{12}\text{H}_{25}\text{O}$ ,  $A = 1, 3\text{-Phenylene}$ ,  $X = \text{H}$  Series- **6.I**

$R = n\text{-C}_{12}\text{H}_{25}\text{O}$ ,  $A = 1, 3\text{-Phenylene}$ ,  $X = \text{F}$  Series- **6.II**

$R = n\text{-C}_{12}\text{H}_{25}$ ,  $A = 1, 3\text{-Phenylene}$ ,  $X = \text{F}$  Series- **6.III**

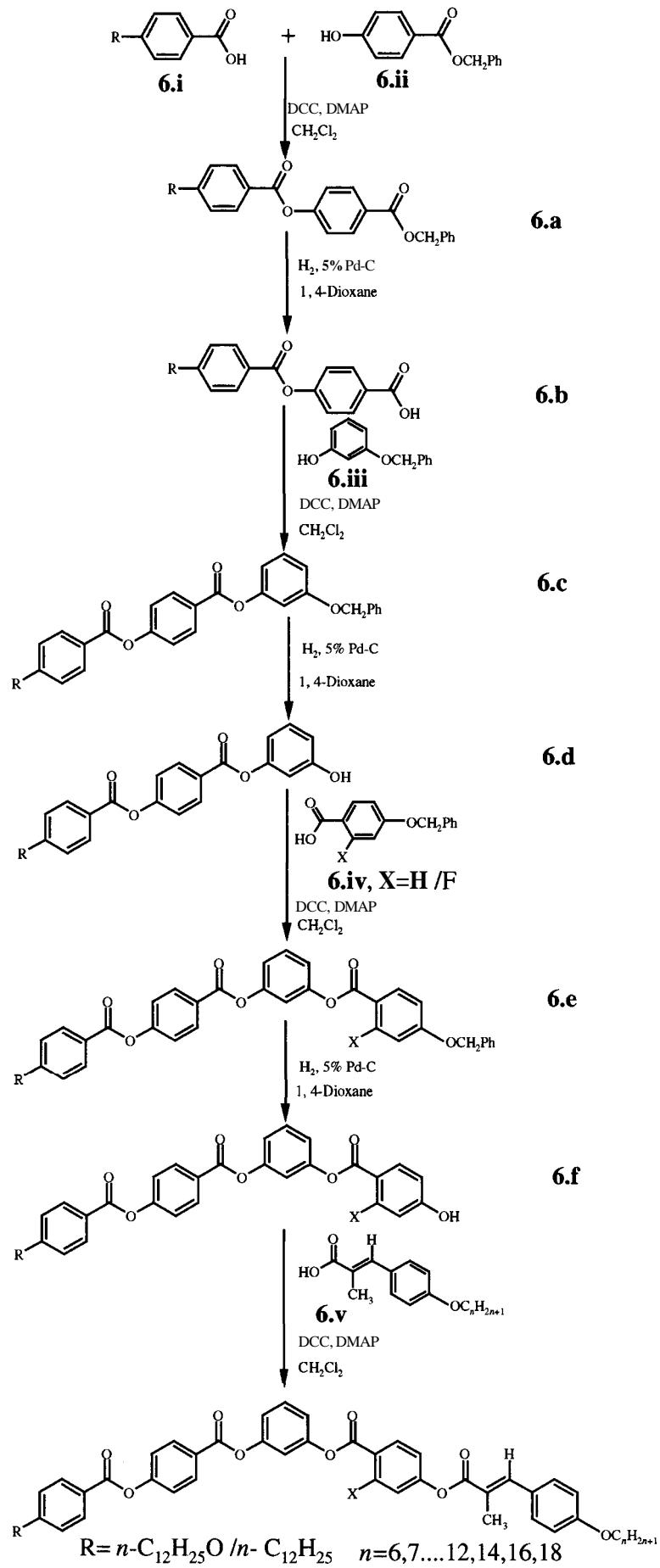
$R = n\text{-C}_{12}\text{H}_{25}\text{O}$ ,  $A = 2, 7\text{-Naphthylene}$ ,  $X = \text{F}$  Series- **6.IV**

## Synthesis

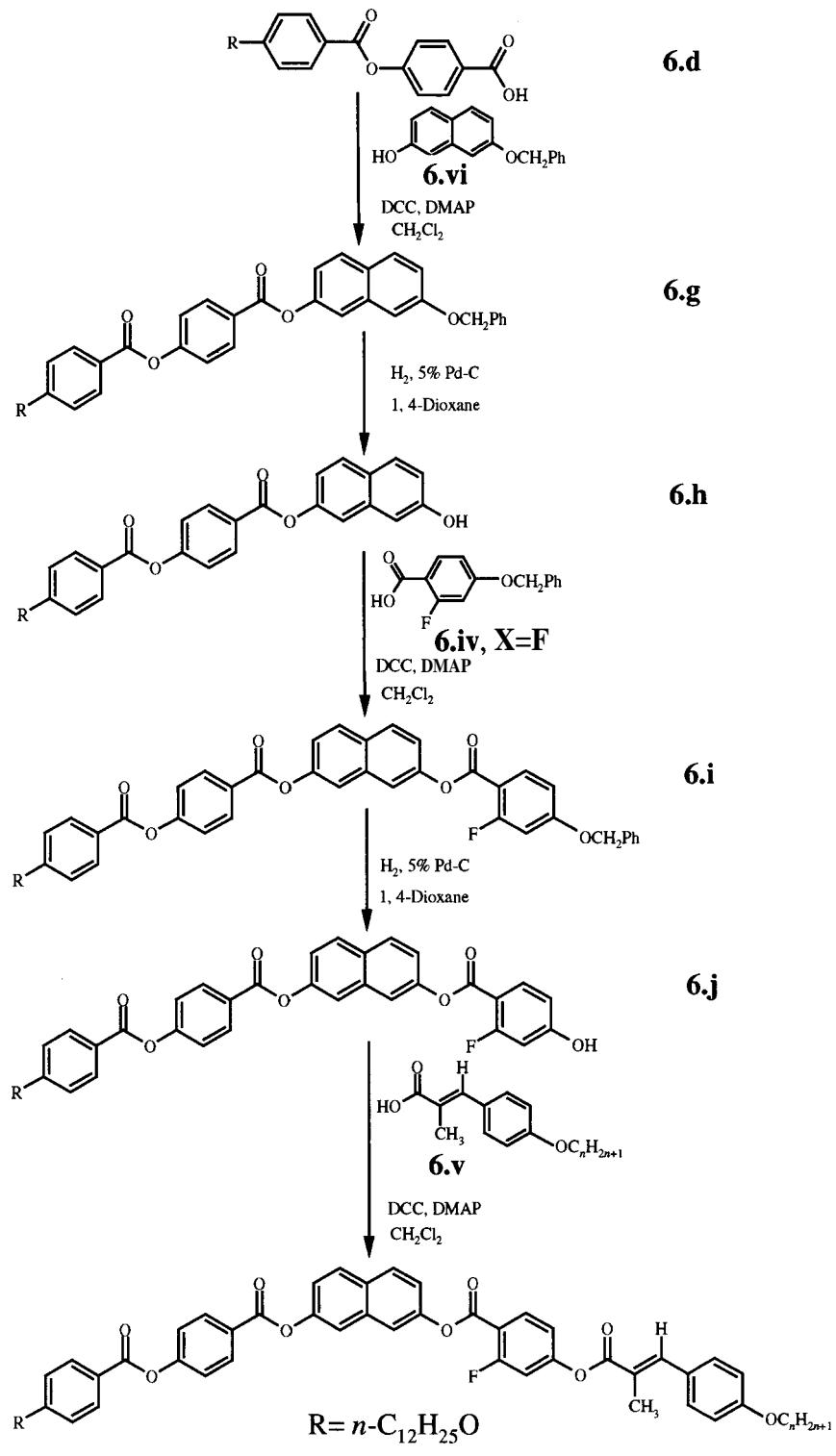
The synthetic pathway used to obtain these unsymmetrical bent-core compounds derived from resorcinol and 2, 7-dihydroxynaphthalene are shown in schemes **6.1** and **6.11** respectively. Benzyl-4-hydroxybenzoate, resorcinol and 2, 7-dihydroxynaphthalene were commercial compounds and used without further purification. 3-Benzylxylophenol was synthesized by monobenzylation of resorcinol [104]. Following the same procedure **7-benzyloxy-2-hydroxynaphthalene** was prepared from 2, 7-dihydroxynaphthalene. 4-Benzylxylobenzoic acid, **2-fluoro-4-benzyloxybenzoic acid** [59-61] and **E-4-n-alkoxy- $\alpha$ -methyl-cinnamic acids** [103] were prepared following procedures described in the literature.

## Results and discussion

The transition temperatures and the associated enthalpy values for the parent compounds (series **6.I**) are summarized in table **6.1**. Only two types of mesophases were observed in this homologous series. Compounds **6.A.1** and **6.A.2** exhibit the same type of mesophase although the latter is monotropic. When a thin film of a sample of compound **6.A.1** was cooled from the isotropic phase, mosaic texture appeared and filled the field of view. This is a characteristic feature of the two-dimensional  $B_1$  phase and the structure of this phase was confirmed using XRD studies. The X-ray diffractogram of the mesophase of compound **6.A.1** showed two reflections in the small angle region at  $d_1 = 27.6\text{\AA}$  and  $d_2 = 22.8\text{\AA}$  and a wide-angle diffuse peak at  $4.5\text{\AA}$ , the latter indicating the fluidity of the phase. The small angle reflections could be indexed to (11), (02) planes of a rectangular lattice with lattice parameters  $a = 34.7$  and  $b = 45.6$ . The X-ray angular intensity profile obtained for the mesophase of compound **6.A.1** is shown in figure **6.1**.



**Scheme 6.1:** Synthetic pathway used to prepare the unsymmetrical BC compounds derived from resorcinol.

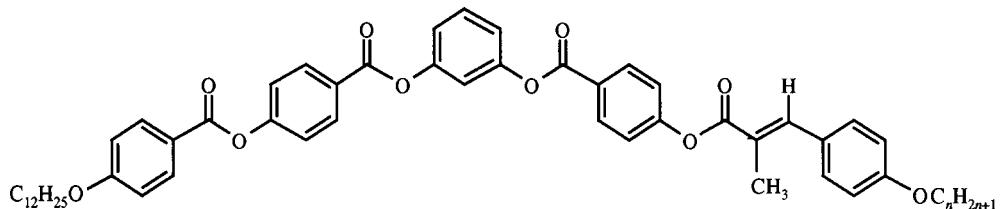


$n=5,6,7....12,14$

### Structure 6.1

**Scheme 6.2:** Synthetic pathway used to prepare the unsymmetrical BC compounds derived from 2, 7-dihdroxynaphthalene.

**Table 6.1: Transition temperatures (°C) and the associated enthalpies (kJ mol<sup>-1</sup>) for the unsymmetrical compounds of series 6.1**

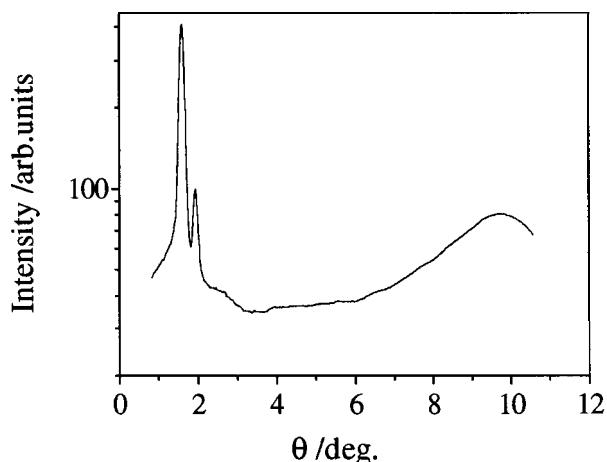


Compound	n	Cr	$\mathbf{B}_2$	$\mathbf{B}_1$	I
<b>6.A.1</b>	6	.	83.0 29.5	-	. 91.0 14.2
<b>6.A.2</b>	7	.	94.0 59.9	-	(. 90.5) 15.1
<b>6.A.3</b>	8	.	86.5 44.2	92.0 17.5	-
<b>6.A.4</b>	9	.	91.0 61.5	94.5 18.7	-
<b>6.A.5</b>	10	.	79.0 54.7	97.5 19.2	-
<b>6.A.6</b>	11	.	89.0 69.9	98.5 20.1	-
<b>6.A.7</b>	12	.	89.0 70.0	99.0 20.0	-
<b>6.A.8</b>	14	.	85.5 71.8	100.5 21.1	-
<b>6.A.9</b>	16	.	89.0 43.8	101.0 19.7	-
<b>6.A.10</b>	18	.	83.5 83.4	101.0 21.3	-

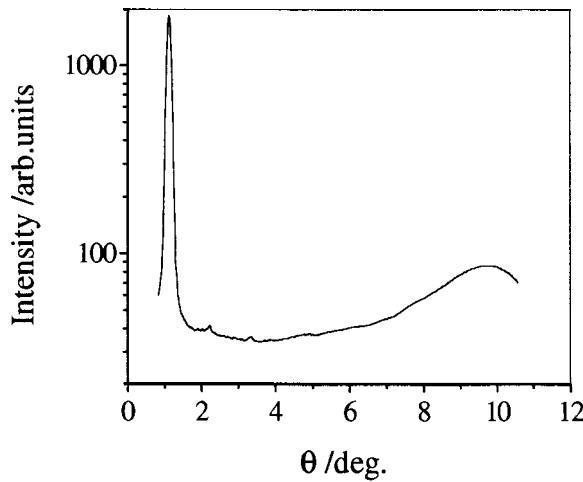
Key: Cr: crystalline phase,  $\mathbf{B}_2$ : smectic antiferroelectric banana mesophase,  $\mathbf{B}_1$ : two-dimensional rectangular banana mesophase, N: nematic mesophase, I: isotropic phase  
( ): mesophase is monotropic.

On increasing the terminal chain length, compound **6.A.3** was obtained which exhibited a lamellar  $\mathbf{B}_2$  phase. This is not surprising since for this homologue, the core-chain interaction increases resulting in the collapse of the two-dimensional lattice and any further increase in the chain length will stabilize the smectic mesophase. This general behaviour has been observed in a number of different homologous series of compounds [29, 41, 58].

Compounds **6.A.3-6.A.10** show the same types of textures under a polarizing microscope. Either a schlieren texture or a fringe pattern was observed, which is typical for the lamellar  $B_2$  phase. The clearing enthalpy value for this mesophase is in the range of 17.5 to 21.3 kJ mol<sup>-1</sup>. It is also interesting to note that the melting points are not very high and clearing temperatures are close to about 100°C unlike many other five-ring systems [28, 41, 53]. The smectic ordering of the molecules in these compounds were confirmed from XRD studies. The X-ray diffractogram of the mesophase of compound **6.A.3** showed two reflections in the ratio 1:1/2 indicating a lamellar periodicity for the phase. The d-spacings obtained from XRD studies are summarized in table **6.5**. Similar smectic reflections were observed for compound **6.A.9** and the X-ray angular intensity profile obtained for the mesophase of this compound is shown in figure **6.2**. The two polarization current peaks obtained in the triangular-wave experiments confirmed the antiferroelectric behaviour of the  $B_2$  mesophase.



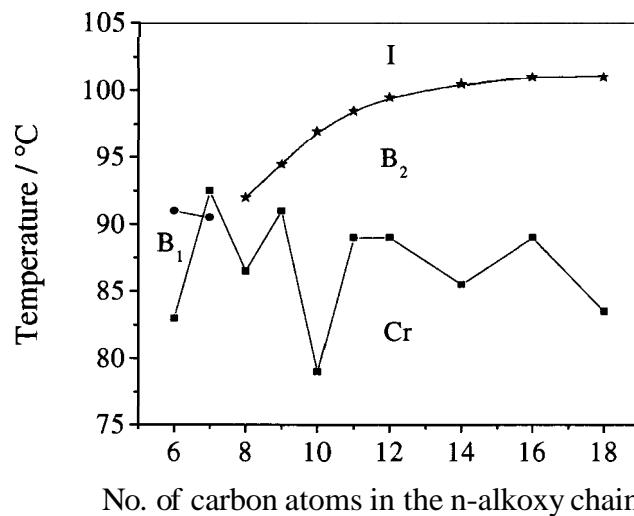
**Figure 6.1:** An X-ray angular intensity profile obtained for the  $B_1$  phase of compound **6.A.1**.



**Figure 6.2:** An X-ray angular intensity profile obtained for the  $B_2$  phase of compound 6.A.9.

A plot of transition temperatures as a function of the length of terminal n-alkoxy chain for the compounds of series 6.1 is shown in figure 6.3.

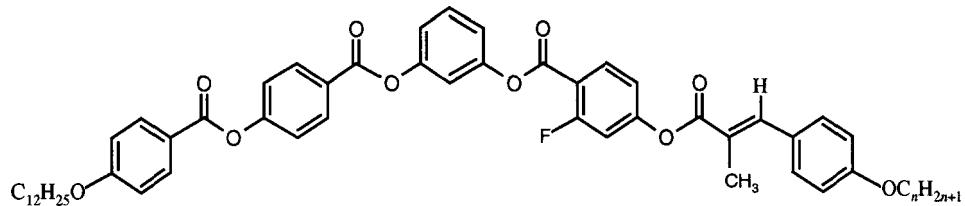
A lateral fluorine substituent appears to have a strong influence on the mesomorphic properties of banana-shaped mesogens [23, 31, 51, 58]. The mesomorphic properties of a large number of compounds having fluorine as a lateral substituent was reported from our laboratory [58]. This exhaustive and systematic investigation has indicated that the position of substitution of fluorine and its location are the determining factors for the modified properties.



**Figure 6.3:** A plot of transition temperatures as a function of the terminal chain length for compounds of series 6.1.

In order to examine the influence of fluorine as a lateral substituent, the ring hydrogen in one of the middle phenyl rings of the compounds of series **6.1** was substituted with fluorine. The transition temperatures and the associated enthalpy values obtained for these compounds (series **6.11**) are summarized in table **6.2**.

**Table 6.2:** Transition temperatures ( $^{\circ}\text{C}$ ) and the associated enthalpies ( $\text{kJ mol}^{-1}$ ) for the unsymmetrical compounds of series **6.11**

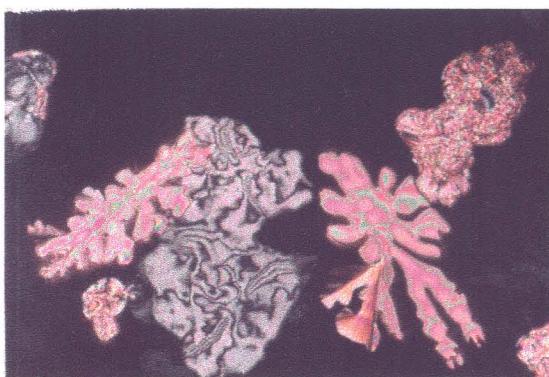


Compound	n	Cr	B <sub>2</sub>	B <sub>1</sub>	I
<b>6.B.1</b>	6	.	98.0 56.8	- (. 81.0) 14.7	.
<b>6.B.2</b>	7	.	100.0 66.7	(. 79.0) <sup>\$</sup> 14.7	.
<b>6.B.3</b>	8	.	105.0 59.6	(. 85.0) 17.9	-
<b>6.B.4</b>	9	.	105.0 65.9	(. 88.0) 18.6	-
<b>6.B.5</b>	10	.	91.0 72.5	(. 90.5) 19.5	-
<b>6.B.6</b>	11	.	89.5 31.5	. 92.0 19.6	-
<b>6.B.7</b>	12	.	93.5 89.0	(. 93.5) 20.0	-
<b>6.B.8</b>	14	.	89.0 70.1	. 95.0 21.2	-
<b>6.B.9</b>	16	.	93.0 81.1	. 96.5 21.7	-
<b>6.B.10</b>	18	.	91.0 82.8	. 97.0 22.0	-

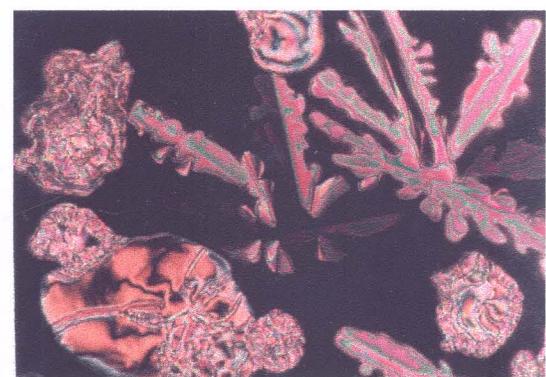
\$: on cooling the isotropic phase, both B<sub>1</sub> and B<sub>2</sub> phases appear simultaneously.

It can be seen in this table that the melting points have increased while the clearing points are reduced by 4 to 14°C as a result of fluorine substitution. Hence, some of the homologues exhibit a metastable mesophase and in others the thermal range of the mesophase has been reduced. Compound **6.B.1** shows a monotropic B<sub>1</sub> phase while

compound **6.B.2** exhibits interesting optical features. On slow cooling a thin film of this compound, both mosaic ( $B_1$  phase) as well as schlieren texture ( $B_2$  phase) appear simultaneously. These features are retained until the sample crystallizes. On heating, these textural features remain without any change until the clearing temperature is reached. The remaining compounds **6.B.3-6.B.10** showed textures characteristic of the  $B_2$  phase. Optical photomicrographs showing the simultaneous appearance of the two types of textures are shown in figure **6.4 (a)** and **(b)**. However, the possibility of a transition from  $B_1 \rightarrow B_2$  phase could not be established even on a DSC thermogram. The smectic ordering in the  $B_2$  phase of these compounds was confirmed from XRD studies. For example the reflections for compound **6.B.10** in the small angle region were in the ratio 1:1/2 indicating a smectic ordering of the bent-core molecules. The d-spacings obtained are summarized in table **6.5**.



(a)



(b)

**Figure 6.4 (a) and (b): Optical photomicrographs showing the simultaneous appearance of mosaic and schlieren textures, obtained on cooling the isotropic phase of compound **6.B.2**.**

The electro-optical behavior of the  $B_2$  phase was examined by the triangular-wave electric field experiment which was carried out on one of the representative compounds. A sample of compound **6.B.10** was taken in a cell of thickness  $13.8\mu\text{m}$ , which was coated with polyimide for homogeneous alignment. On applying a voltage of  $220\text{V}_{\text{pp}}$  at 80 Hz, two polarization current peaks for half period were obtained indicating an antiferroelectric ground state. A typical switching current response obtained for the mesophase is shown in figure **6.5**.

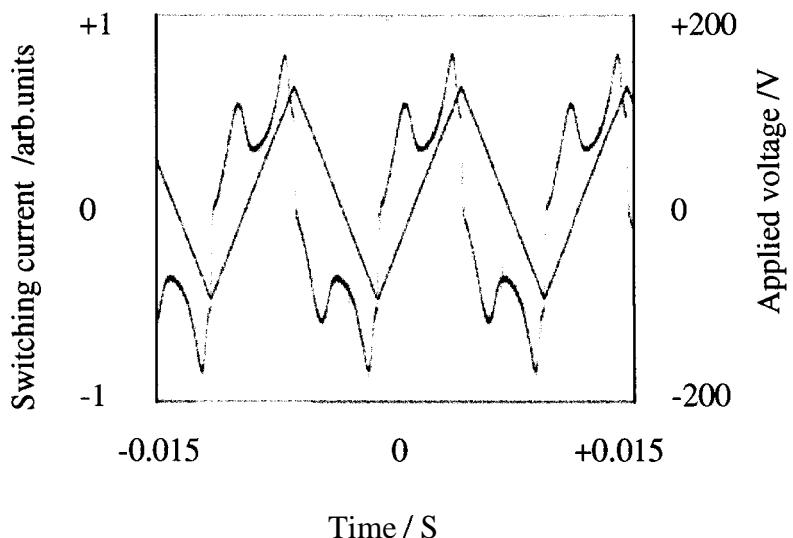


Figure 6.5: The switching current response obtained for the mesophase of compound 6.B.10 under a triangular-wave electric field (**220V<sub>pp</sub>**) at **80Hz**; cell thickness **13.8μm**; saturated polarization  $\approx 385 \text{ nC cm}^{-2}$ .

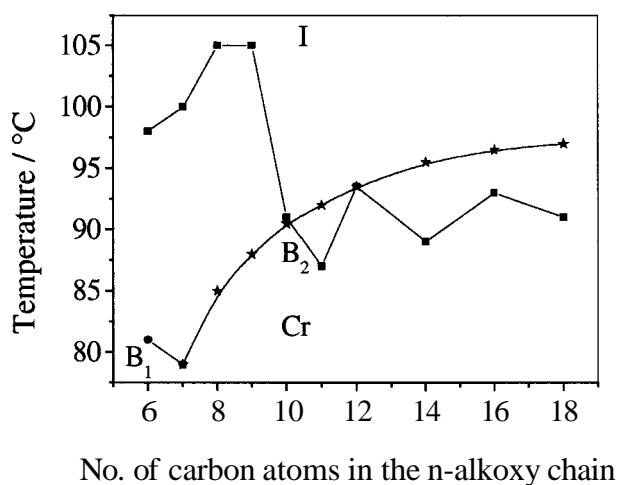


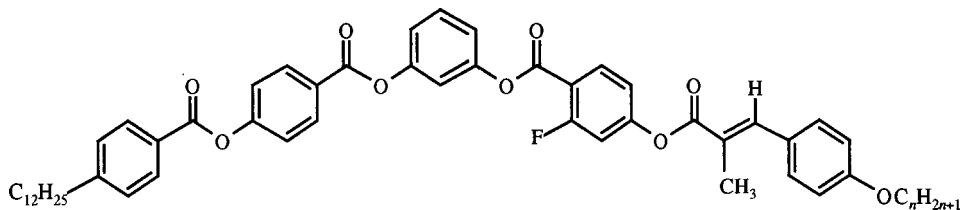
Figure 6.6: A plot of transition temperatures as a function of the terminal chain length for compounds of series **6.II**.

A plot of transition temperatures as a function of the number of carbon atoms in the n-alkoxy chain for compounds of series 6.11 is shown in figure 6.6. The clearing temperature curve for the B<sub>2</sub> phase shows the usual trend of a rising curve, which tends to level off on ascending the homologous series.

It is well known that a terminal n-alkyl chain containing compounds have generally lower transition temperatures than their corresponding n-alkoxy analogues. With a view to reduce the transition temperatures further, the n-alkoxy chain present in compounds of series

**6.11** was replaced by an n-alkyl chain in one of the arms resulted in homologous series **6.11I**. The transition temperatures and the associated enthalpy values obtained for this series of compounds are summarized in table **6.3**.

**Table 6.3:** Transition temperatures ( $^{\circ}\text{C}$ ) and the associated enthalpies (kJ mol $^{-1}$ ) for the unsymmetrical compounds of series **6.III**

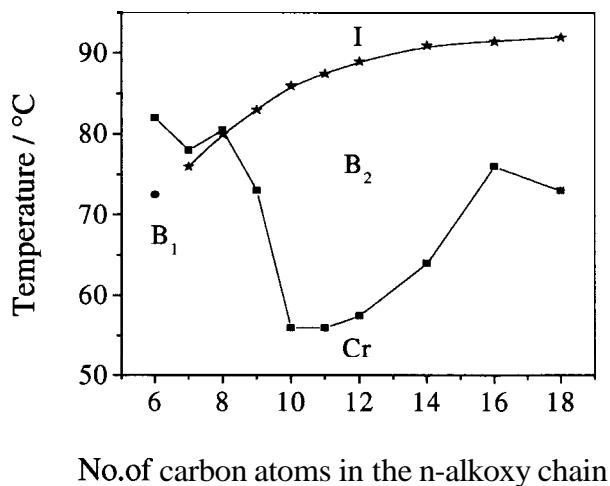


Compound	n	Cr	B <sub>2</sub>	B <sub>1</sub>	I
<b>6.C.1</b>	6	.	82.0	-	(. 72.5)
			68.3		14.3
<b>6.C.2</b>	7	.	78.0	(. 76.0)	-
			62.6	16.6	.
<b>6.C.3</b>	8	.	80.5	(. 80.0)	-
			69.2	17.6	.
<b>6.C.4</b>	9	.	73.0	. 83.0	-
			46.4	18.5	.
<b>6.C.5</b>	10	.	56.0	. 86.0	-
			33.8	19.3	.
<b>6.C.6</b>	11	.	56.0	. 87.5	-
			30.7	20.4	.
<b>6.C.7</b>	12	.	57.5	. 89.0	-
			36.2	20.4	.
<b>6.C.8</b>	14	.	64.0	. 90.5	-
			32.1	20.6	.
<b>6.C.9</b>	16	.	76.0	. 91.5	-
			34.0	20.8	.
<b>6.C.10</b>	18	.	73.0	. 92.0	-
			57.9	21.8	.

It is evident from this table, and as expected the transition temperatures are lower and the mesophases observed for compounds of series **6.11** are retained. Compound **6.C.1** showed a monotropic **B<sub>1</sub>** phase while compounds **6.C.2-6.C.10** exhibited the **B<sub>2</sub>** phase. Interestingly these homologues represent a series of bent-core compounds exhibiting the **B<sub>2</sub>** phase with the lowest melting points reported so far. For example, compound **6.C.5** melts at 56.0°C exhibiting a **B<sub>2</sub>** phase which becomes isotropic at 86.0°C. The mesophase could be easily

cooled to room temperature. In addition, the thermal range of the  $B_2$  phase also increased as a result of the introduction of n-alkyl group. The mesophase of a representative compound (**6.C.5**) was studied by XRD measurements and electro-optical switching characteristics by the triangular-wave method. The d-spacings obtained for the smectic phase of compound **6.C.5** are given in table **6.5**. The two polarization current peaks per half cycle obtained for the mesophase of compound **6.C.5** confirmed the antiferroelectric ordering of the molecules in the  $B_2$  phase.

A plot of transition temperatures as a function of the n-alkyl chain length for compounds of series **6.III** is shown in figure **6.7**. Again, a smooth rising curve, which is typical for the clearing temperatures of the  $B_2$  phase, can be seen for this series of compounds also.

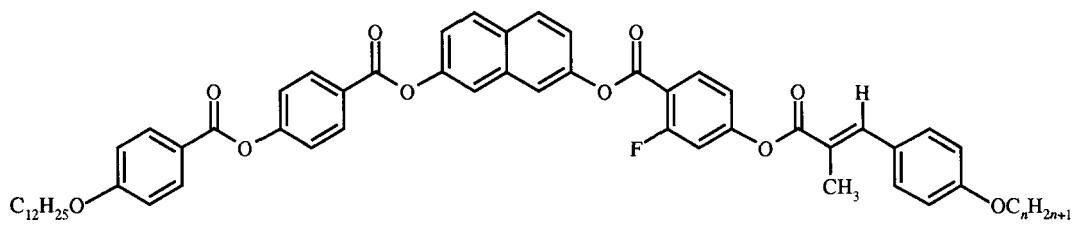


**Figure 6.7: A plot of transition temperatures as a function of the terminal chain length for compounds of series **6.III**.**

As mentioned earlier, several hundred bent-core compounds exhibiting B-phases have been reported so far. A majority of them are derived from a 1, 3-phenylene central unit. Although a few other central units have been used, derivatives from 2, 7-naphthylene system are very limited [55, 98, 100-102]. From earlier investigations [101], it was found that this group is very useful in generating banana-phases. Curiously, it has been possible to obtain banana-phases in combination with a nematic phase using this central unit. For example, a direct transition from a lamellar  $B_2$  phase to a nematic phase [53, 98-100], a two-dimensional columnar  $B_1$  phase to a nematic phase [99-101], an intercalated  $B_6$  phase to a nematic phase [100]. All these transitions were observed in symmetrical compounds. So far, there are only a

few reports of the observation of such transitions and we thought that it would be interesting to explore this feasibility in some unsymmetrical compounds derived from 2, 7-dihydroxynaphthalene. The resultant compounds obtained belong to homologous series **6.IV**, whose transition temperatures and the associated enthalpy values are summarized in table 6.4.

**Table 6.4: Transition temperatures (°C) and the associated enthalpies (kJ mol<sup>-1</sup>) for the unsymmetrical compounds of series **6.IV****

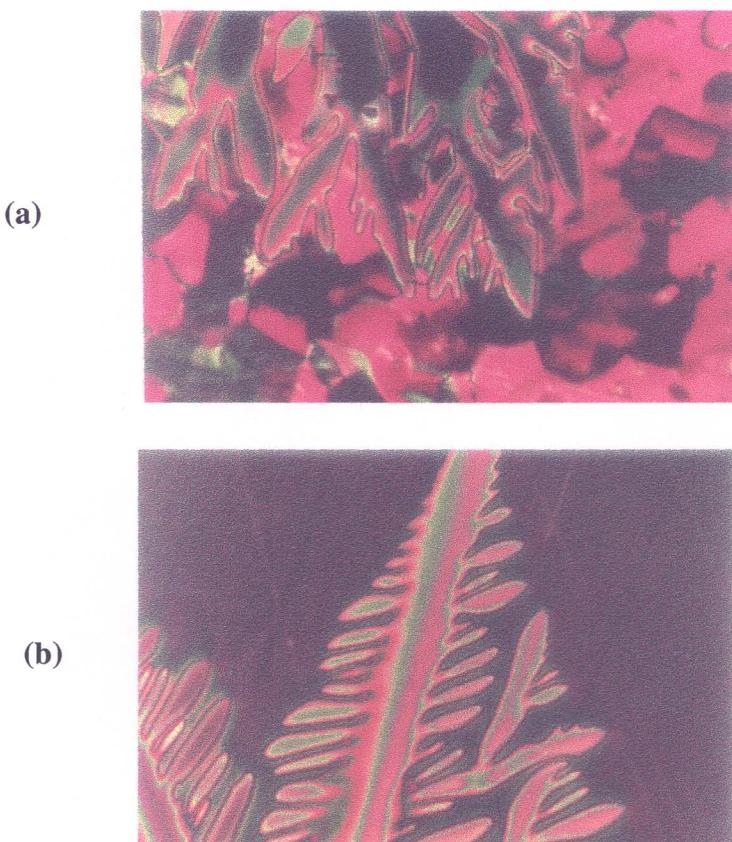


Compound	n	Cr	B <sub>2</sub>	B <sub>1</sub>	N	I
<b>6.D.1</b>	2	.	138.5 59.6	- 8.7	(. 128.0) 0.4	. 168.0
<b>6.D.2</b>	4	.	103.0 32.1	- 12.1	. 140.0 0.4	. 155.0
<b>6.D.3</b>	5	.	104.0 33.3	- 12.5	. 139.0 0.4	. 149.0
<b>6.D.4</b>	6	.	98.0 40.7	- 12.6	. 138.5 0.5	. 148.0
<b>6.D.5</b>	7	.	94.5 52.5	- 12.6	. 136.0 0.4	. 144.0
<b>6.D.6</b>	8	.	101.0 57.1	- 12.3	. 135.0 0.4	. 143.5
<b>6.D.7</b>	9	.	99.0 55.5	. 136.0 15.6	- 0.4	. 141.5
<b>6.D.8</b>	10	.	99.0 56.7	. 139.0 15.9	- 0.3	. 140.0
<b>6.D.9</b>	11	.	105.0 65.5	. 141.0 17.4	- -	.
<b>6.D.10</b>	12	.	109.0 72.1	. 142.5 17.7	- -	.
<b>6.D.11</b>	14	.	104.0 67.5	. 143.5 17.8	- -	.

Three types of mesophases viz. N, B<sub>1</sub> and B<sub>2</sub> were observed in the eleven compounds, eight of which are dimesomorphic and three are monomesomorphic. The mesomorphic behaviour along the series is somewhat unusual. Normally, the highest temperature mesophase disappears first on ascending the homologous series in calamitic liquid crystals. However, in this series, the nematic phase is retained although the lower temperature B<sub>1</sub>

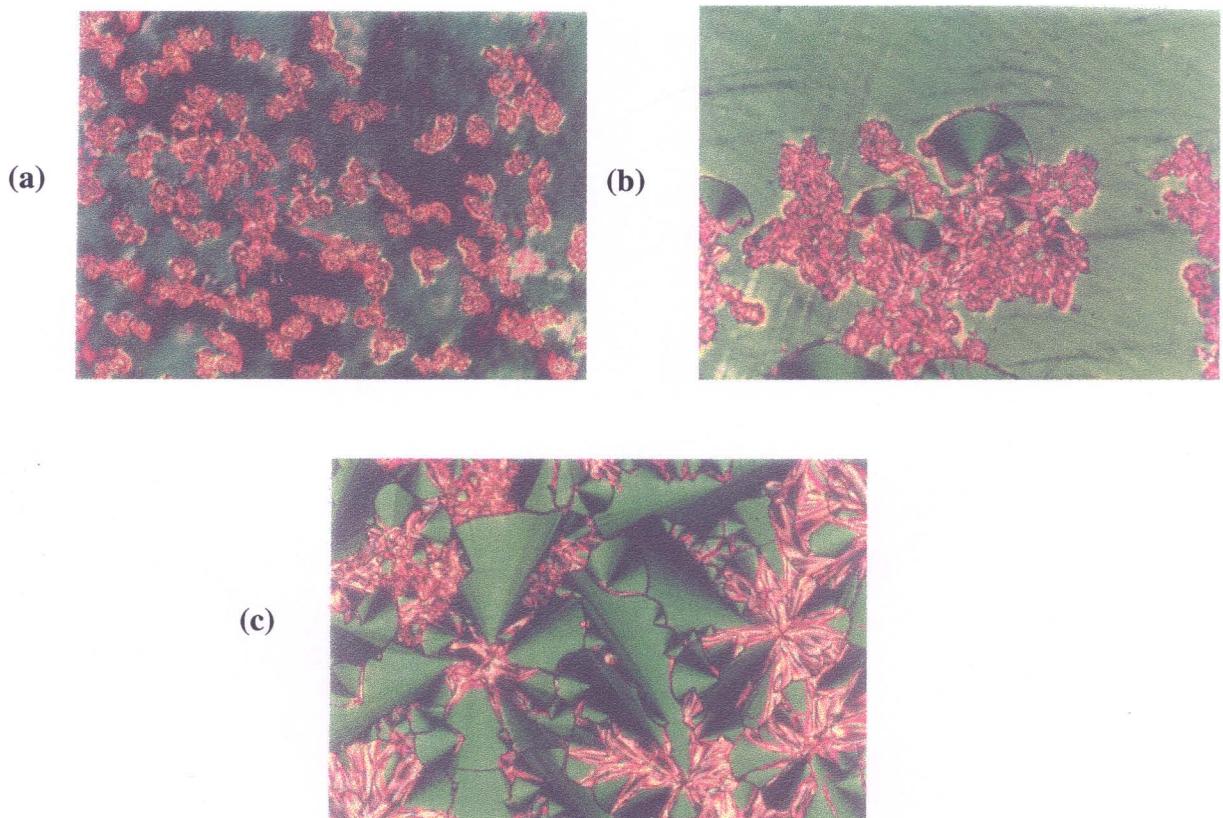
phase is eliminated in compounds **6.D.7** and **6.D.8**. This may be explained as follows. In the bent-core compounds the nematic phase is formed due to an increase in the bend angle ( $> 140^\circ$ ) between the two arms. When the terminal chain length is sufficiently long the nematic phase is transformed to a lamellar  $B_2$  phase instead of a two-dimensional  $B_1$  phase to avoid the core-chain interaction which would cost a higher energy. When a thin film of a sample of compound **6.D.3** sandwiched between two untreated glass plates was cooled from the isotropic phase, nematic droplets appeared and coalesced to give rise to a schlieren texture. On further cooling to  $138.5^\circ\text{C}$ , a mosaic texture developed on the existing nematic phase. An optical photomicrograph showing this transition is given in figure **6.8 (a)**.

When a sample of compound **6.D.3** was sandwiched between two glass plates treated for homogeneous alignment of the sample and cooled from the isotropic phase, the nematic phase aligned very well. When the temperature reached  $138.5^\circ\text{C}$ , the  $B_1$  phase developed as a dendritic pattern and a photomicrograph of this transition is shown in figure **6.8 (b)**. Compounds **6.D.1-6.D.6** exhibited similar mesomorphic behaviour.



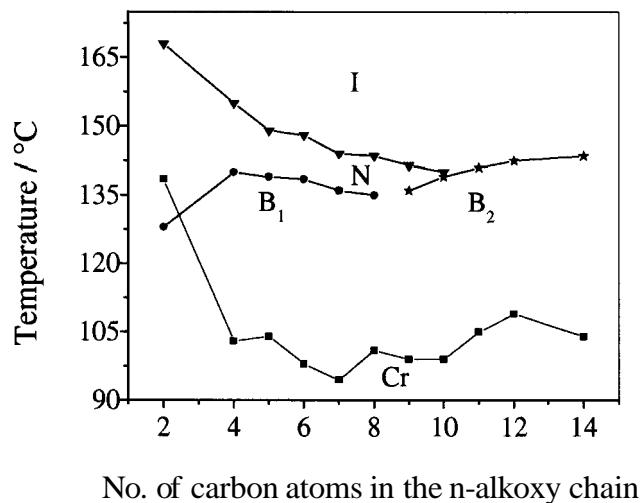
**Figure 6.8:** (a) An optical photomicrograph showing transition from a nematic phase to a  $B_1$  phase on an untreated glass plate; compound **6.D.3**; (b) the same phase transition obtained in a homeogeneously aligned cell; compound **6.D.3**.

On increasing the terminal *n*-alkoxy chain length further, compound **6.D.7** was obtained. When a thin film of a sample of this compound sandwiched between untreated glass plates was cooled from the isotropic phase, the nematic phase appeared as a marbled texture; on lowering the temperature to 135.5°C, fingerprint (fringe) texture, which is typical for a  $B_2$  phase began to develop. An optical photomicrograph illustrating the above transition is shown in figure **6.9 (a)**. When this transition was viewed for a sample sandwiched between two glass plates treated for a planar alignment, the nematic phase aligned very well and as the temperature was reduced focal-conic as well as fingerprint textures that are seen for a  $B_2$  phase appeared. An optical photomicrograph depicting this transition is shown in figure **6.9 (b)**. On cooling the sample, further the whole field of view was occupied by the spherulitic texture of the  $B_2$  phase and a photomicrograph of this is shown in figure **6.9 (c)**. On increasing the chain length further (compounds **6.D.9-6.D.11**) the compounds showed only an antiferroelectric  $B_2$  phase.



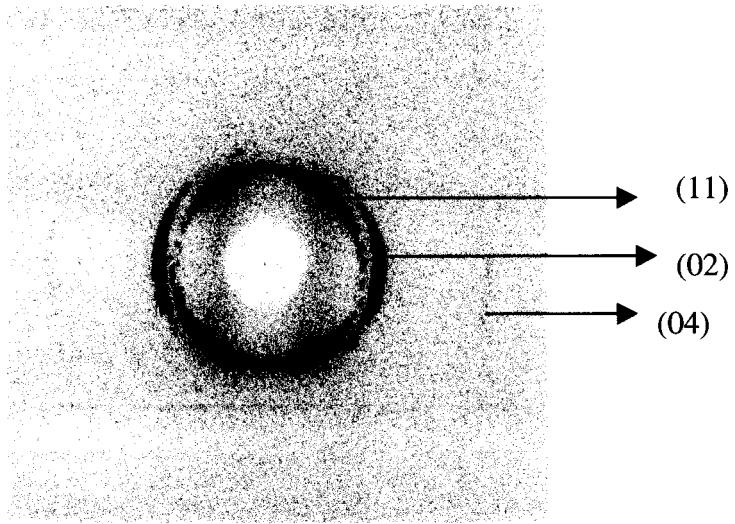
**Figure 6.9:** (a) An optical photomicrograph showing transition from a nematic phase to a  $B_2$  phase, untreated glass plates; compound **6.D.7**; (b) the same phase transition in a homogeneously aligned cell; (c) spherulitic texture obtained for the  $B_2$  phase of compound **6.D.7**.

A plot of transition temperatures as a function of the number of carbon atoms in the *n*-alkoxy chain for the compounds of series **6.IV** is shown in figure **6.10**. One can also see the odd-even effect in the nematic to isotropic transition curve, while the clearing temperature curves for the **B**<sub>1</sub> and **B**<sub>2</sub> phases follow the usual trend.



**Figure 6.10:** A plot of transition temperatures as a function of the terminal chain length for compounds of series **6.IV**.

The structures of the mesophases (**N**, **B**<sub>1</sub> and **B**<sub>2</sub>) were confirmed by detailed XRD studies. The XRD pattern of a monodomain of **B**<sub>1</sub> phase exhibited by compound **6.D.3** was obtained. On slow cooling the isotropic liquid of this compound to a nematic phase, the XRD showed a diffuse reflection, which is typical for this phase. On lowering the temperature, the **B**<sub>1</sub> phase seemed to align well. The XRD pattern of this oriented sample displayed Bragg-spots in the small as well as in the wide-angle regions. The reflections in the small angle region could be indexed to (11), (02) and (04) planes of a two-dimensional rectangular lattice. The dimension  $b=46.8$  of the crystallographic unit cell is related to the molecular length, which was measured using a molecular model ( $L= 55.3\text{\AA}$ ). The other lattice parameter was  $a=33.9$ . An XRD pattern of an oriented **B**<sub>1</sub> mesophase obtained on cooling the nematic phase of compound **6.D.3** is shown in figure **6.11**. However, we could not get a monodomain for the **B**<sub>2</sub> phase obtained on cooling the nematic phase. The unoriented XRD pattern of a sample of compound **6.D.7** showed two reflections in the small angle region, which are in the ratio of 1:1/3 indicating a smectic ordering. The d-spacings obtained are summarized in table **6.5**.

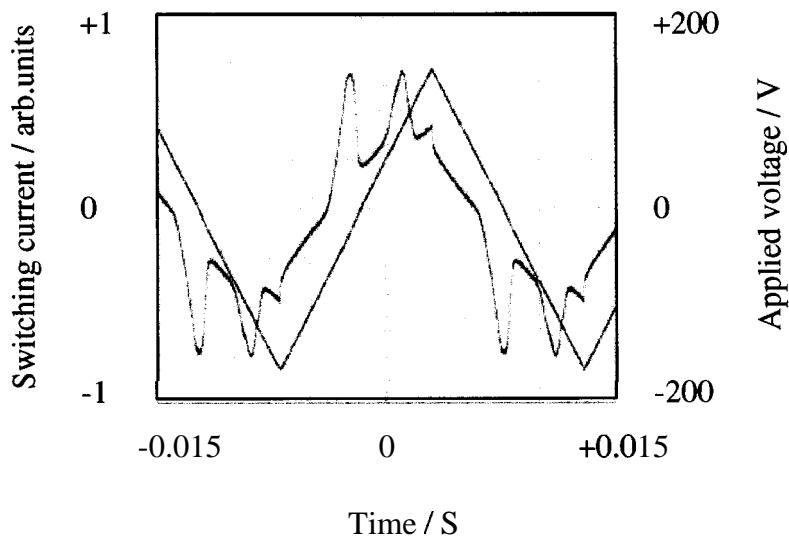


**Figure 6.11:** An XRD pattern of an oriented  $B_1$  mesophase obtained on cooling the nematic phase of compound **6.D.3**.

**Table 6.5:** Layer spacings ( $d$ ) obtained from XRD studies and the corresponding molecular length ( $L$ ) of compounds by assuming the methylene units of the n-alkoxy chain in fully extended all trans conformation

Compound	d-spacings/ $\text{\AA}$			lattice parameters/ $\text{\AA}$		Measured molecular length $L/\text{\AA}$	Phase type
	$d_1$	$d_2$	$d_3$	a	b		
<b>6.A.1</b>	27.6 (11)	22.8 (02)	-	34.7	45.6	55.0	$B_1$
<b>6.A.3</b>	34.9 (01)	17.5 (02)	-	-	-	56.6	$B_2$
<b>6.A.9</b>	39.2 (01)	19.6 (02)	-	-	-	66.2	$B_2$
<b>6.B.10</b>	39.5 (01)	-	13.3 (03)	-	-	68.2	$B_2$
<b>6.C.5</b>	35.2 (01)	17.6 (02)	-	-	-	57.1	$B_2$
<b>6.C.10</b>	38.2 (01)	-	12.7 (03)	-	-	66.1	$B_2$
<b>6.D.3</b>	27.3 (11)	23.4 (02)	11.8 (03)	33.9	46.8	55.9	$B_1$
<b>6.D.7</b>	35.3 (01)	-	17.7 (03)	-	-	58.1	$B_2$

The electro-optical behaviour of the  $B_2$  phase was investigated by triangular-wave electric field experiments. A sample of compound **6.D.7** was filled in to a cell in the isotropic state and cooled slowly under an electric field. This resulted in a reasonably good alignment of the nematic phase. On further cooling the mesophase to 134°C under a triangular-wave electric field, at a threshold of 285V<sub>pp</sub>, two-polarization current peaks were obtained which became saturated at a voltage of 313 V<sub>pp</sub> and a frequency of 50 Hz. The saturated polarization value obtained by integrating the two current peaks was about 400 nC cm<sup>-2</sup>. A typical current response obtained for compound **6.D.7** is shown in figure **6.12**, which clearly indicates the antiferroelectric nature of the mesophase.



**Figure 6.12:** The switching current response obtained for compound **6.D.7** under a triangular-wave electric field (313V<sub>pp</sub>) at 50Hz: cell thickness 10.3μm; saturated polarization ≈ 400 nC cm<sup>-2</sup>.

## **Summary**

The mesomorphic behavior of fortyone compounds unsymmetrically substituted about two central units and belonging to four different homologous series was studied. The compounds which have a 1, 3-phenylene central unit exhibit only B-phases whereas some compounds with 2, 7-naphthylene central unit show both nematic and B-phases over an extended thermal range of the mesophases. The 1, 3-phenylene system with terminal n-alkyl chain yields low melting compounds which exhibit the **B**<sub>2</sub> phase. Surprisingly fluorine substitution resulted in an increase in the melting points whereas the clearing temperature was reduced by 4 to 14°C. Hence thermal range of the mesophases was decreased. In one of the compounds of series 6.11, the **B**<sub>1</sub> and **B**<sub>2</sub> phases appeared simultaneously from the isotropic phase, which is rather unusual. The rarely observed transitions from a nematic phase to an antiferroelectric **B**<sub>2</sub> phase and from a nematic phase to a two-dimensional rectangular columnar **B**<sub>1</sub> phase have been obtained in the 2, 7-naphthylene system.

## Experimental

Resorcinol, 2, 7-dihydroxynaphthalene and benzyl-4-hydroxybenzoate were commercial compounds and used without further purification. 4-Benzoyloxybenzoic acid, **6.iv**, (X=H), 2-fluoro-4-benzoyloxybenzoic acid, **6.iv**, (X=F), [59-61] and E-4-n-alkoxy- $\alpha$ -methylcinnamic acids, **6.v** [103] were prepared according to procedures described in the literature. The partial protection of hydroxyl groups of resorcinol and 2, 7-dihydroxynaphthalene was achieved by using one equivalent of benzyl chloride in the presence of anhydrous potassium carbonate [104]. The esterification reaction was carried out by carbodiimide method and deprotection of the benzyl group was achieved by hydrogenolysis using 5% Pd-C as a catalyst.

### Benzyl-4-(4-n-dodecyloxybenzoyloxy)benzoate, **6.a** ( $R=n\text{-C}_{12}\text{H}_{25}\text{O}$ )

A mixture of 4-n-dodecyloxybenzoic acid **6.i**  $R=n\text{-C}_{12}\text{H}_{25}\text{O}$ , (9.0g, 29.4mmol), benzyl-4-hydroxybenzoate, **6.ii** (6.7g, 29.4mmol), catalytic amount of 4-(N, N-dimethylamino) pyridine (DMAP), and dry dichloromethane were stirred for ten minutes. To this N, N'-dicyclohexylcarbodiimide (DCC), (6.66g, 32.3mmol) was added and stirred overnight. The precipitated N, N'-dicyclohexylurea was filtered off and washed with dichloromethane (25 ml). The filtrate was washed successively with 5% aqueous acetic acid (2 x 25ml), 5% ice-cold sodium hydroxide solution, (2 x 25 ml), water (3 x 25 ml) and dried over anhydrous sodium sulphate. The solvent was removed to yield a residue, which was purified by column chromatography on silica gel using chloroform as an eluent. Removal of solvent from the eluate gave a white material, which was crystallized from a mixture of chloroform and acetonitrile. Yield, 13.1g (86%); m.p. 62-63°C;  $\nu_{\text{max}}$ : 2918, 2851, 1732, 1714, 1608, 1470, 1292  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ : 8.16-8.12 (m, 4H, Ar-H), 7.46-7.35 (m, 5H, Ar-H), 7.30-7.28 (d, 2H,  $^3\text{J}$ 8.72 Hz, Ar-H), 6.98-6.96 (d, 2H,  $^3\text{J}$ 8.92 Hz, Ar-H), 5.38 (s, 2H, -O-CH<sub>2</sub>-Ar), 4.06-4.02 (t, 2H,  $^3\text{J}$ 6.52Hz, Ar-O-CH<sub>2</sub>), 1.85-1.78 (quin, 2H,  $^3\text{J}$ 7.0Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>), 1.50-1.27 (m, 18H, 9 x -CH<sub>2</sub>-), 0.90-0.86 (t, 3H,  $^3\text{J}$ 6.6Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>33</sub>H<sub>40</sub>O<sub>5</sub> requires C, 76.71; H, 7.80%; found C, 76.65; H, 7.94%.

### 4-n-Dodecyloxybenzoyloxy-4-benzoicacid, **6.b** ( $R=n\text{-C}_{12}\text{H}_{25}\text{O}$ )

Compound **6.a**  $R=n\text{-C}_{12}\text{H}_{25}\text{O}$ , (13.0g, 25.1mmol), was dissolved in 1, 4-dioxane (100 ml). To this solution 5% Pd-C catalyst (2.7g) was added and stirred at 40°C in an atmosphere

of hydrogen until the required quantity of hydrogen was absorbed. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure. The product thus obtained was crystallized from a mixture of 1, 4-dioxane and petroleum ether (b.p.60-80°C). Yield, 9.9g (92%); Trans. temp; Cr 120°C SmC 209°C N 220.5°C I;  $\nu_{\text{max}}$ : 3070, 2972, 2851, 2548, 1732, 1688, 1603, 1261, 1161 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.21-8.18 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 8.15-8.13 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 7.35-7.32 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 6.99-6.97 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 4.06-4.03 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 1.86-1.79 (quin, 2H, <sup>3</sup>J7.0Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.51-1.26 (m, 18H, 9 x -CH<sub>2</sub>-), 0.90-0.86 (t, 3H, <sup>3</sup>J6.48Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>26</sub>H<sub>34</sub>O<sub>5</sub> requires C, 73.21; H, 8.03%; found C, 73.61; H, 8.3%.

### **3-Benzylxyphenol, 6.iii**

This was prepared following a procedure described in the literature [104]. Yield, 55%; b.p.178-180°C / 6 mm of Hg (reported 202-210/11 mm of Hg).

### **1-Benzylxyphenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.c (R=n-C<sub>12</sub>H<sub>25</sub>O)**

This compound was prepared using the procedure as described for compound 6.a (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound 6.b R=n-C<sub>12</sub>H<sub>25</sub>O, (9.8g, 23mmol), 3-benzylxyphenol, **6.iii**, (4.6g, 23mmol), cat. amount of DMAP, DCC (5.2g, 25.3mmol), and dry dichloromethane (50ml). Yield, 12.0g (86%), m.p. 97-98°C;  $\nu$ : 2924, 2856, 1736, 1605, 1256, 1061 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.28-8.26 (d, 2H, <sup>3</sup>J8.65Hz, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 7.45-7.32 (m, 8H, Ar-H,), 7.00-6.98 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 6.92-6.84 (m, 3H, Ar-H), 5.08 (s, 2H, -O-CH<sub>2</sub>-Ar), 4.07-4.04 (t, 2H, <sup>3</sup>J6.55Hz, Ar-O-CH<sub>2</sub>-), 1.86-1.80 (quin, 2H, <sup>3</sup>J7.1Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.51-1.28 (m, 18H, 9 x -CH<sub>2</sub>-), 0.90-0.87 (t, 3H, <sup>3</sup>J6.7Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>39</sub>H<sub>44</sub>O<sub>6</sub> requires C, 76.95; H, 7.29%; found C, 76.50; H, 7.43%.

### **1-(3-Hydroxy)phenylene-4-n-dodecyloxybenzoyloxy-4-benzoate, 6.d (R=n-C<sub>12</sub>H<sub>25</sub>O)**

This compound was prepared using the procedure as described for compound 6.b (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6.c** R=n-C<sub>12</sub>H<sub>25</sub>O, (11.8g, 19.4mmol), 1, 4-dioxane (75ml), 5% Pd-C (1.8g). Yield, 9.1g (90%); m.p. 124.5-125.5°C;  $\nu_{\text{max}}$ : 3377, 3315, 2922, 2853, 1734, 1713, 1605, 1252, 1067 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 8.66 (s, 1H, Ar-OH, exchangeable with D<sub>2</sub>O), 8.27-8.25 (d, 2H, <sup>3</sup>J8.7Hz, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.9 Hz, Ar-H), 7.51-7.49 (d, 2H, <sup>3</sup>J8.7Hz, Ar-H), 7.29-7.26 (t, 1H, <sup>3</sup>J7.45Hz, Ar-H), 7.14-7.12 (d, 2H,

<sup>3</sup>58.9 Hz, Ar-H), 6.81-6.77 (m, 3H, Ar-H), 4.17-4.14 (t, 2H, <sup>3</sup>J6.5Hz, Ar-O-CH<sub>2</sub>-), 1.86-1.81 (quin, <sup>3</sup>J7.1Hz, 2H, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.54-1.30 (m, 18H, 9 × -CH<sub>2</sub>-), 0.90-0.87 (t, 3H, <sup>3</sup>J6.7Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>32</sub>H<sub>38</sub>O<sub>6</sub> requires C, 74.11; H, 7.39%; found C, 74.52; H, 7.35%.

**1-(4-Benzylbenzoyloxy)phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.e  
(R=n-C<sub>12</sub>H<sub>25</sub>O, X=H)**

This compound was prepared using the same procedure as described for compound 6.a (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound 6.d R=n-C<sub>12</sub>H<sub>25</sub>O, (5.5g, 10.6mmol), 4-benzylbenzoyloxybenzoic acid, **6.iv** (X=H) (2.42g, 10.6mmol), cat.amount of DMAP, DCC (2.40g, 11.7mmol) and dry dichloromethane (50 ml). Yield, 6.0g (78%); m.p. 119-120°C; v<sub>max</sub> 2922, 2856, 1736, 1728, 1605, 1256, 1163, 1063 cm<sup>-1</sup>; δ<sub>H</sub>: 8.28-8.26 (d, 2H, <sup>3</sup>J8.7Hz, Ar-H), 8.16-8.14 (d, 4H, <sup>3</sup>J8.0Hz, Ar-H), 7.49-7.36 (m, 8H, Ar-H), 7.17-7.15 (m, 3H, Ar-H), 7.07-7.05 (d, 2H, <sup>3</sup>J8.9Hz, Ar-H), 7.00-6.98 (d, 2H, <sup>3</sup>J8.9Hz, Ar-H), 5.16 (s, 2H, -O-CH<sub>2</sub>-Ar), 4.07-4.04 (t, 2H, <sup>3</sup>J6.5Hz, Ar-O-CH<sub>2</sub>-), 1.86-1.80 (quin, 2H, <sup>3</sup>J7.1Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.50-1.27 (m, 18H, 9 × -CH<sub>2</sub>-), 0.90-0.87 (t, 3H, <sup>3</sup>J6.65Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>46</sub>H<sub>48</sub>O<sub>8</sub> requires C, 75.80; H, 6.64%; found C, 75.37; H, 6.5%.

**1-(4-Benzyl-2-fluorobenzoyloxy)phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.e (R=n-C<sub>12</sub>H<sub>25</sub>O, X=F)**

This compound was prepared using the same procedure as described for compound 6.a (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound 6.d R=n-C<sub>12</sub>H<sub>25</sub>O, X=F, (3.5g, 6.8mmol), 2-fluoro-4-benzylbenzoyloxybenzoic acid, **6.iv** (X=F) (1.66g, 6.8mmol), cat.amount of DMAP, DCC (1.53g, 7.4mmol) and dry dichloromethane (20 ml). Yield, 3.8g (75%); m.p. 103-104°C; v<sub>max</sub> 2923, 2853, 1737, 1723, 1604, 1256, 1163, 1063 cm<sup>-1</sup>; δ<sub>H</sub>: 8.28-8.26 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 8.08-8.04 (t, 1H, <sup>3</sup>J8.6Hz, Ar-H), 7.49-7.36 (m, 7H, Ar-H), 7.18-7.16 (m, 4H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 6.88-6.85 (dd, 1H, <sup>3</sup>J8.84Hz, <sup>4</sup>J2.36Hz, Ar-H), 6.80-6.76 (dd, 1H, <sup>3</sup>J12.48Hz, <sup>4</sup>J2.28Hz, Ar-H), 5.14 (s, 2H, -O-CH<sub>2</sub>-Ar), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 1.86-1.80 (quin, 2H, <sup>3</sup>J6.92Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.50-1.27 (m, 18H, 9 × -CH<sub>2</sub>-), 0.90-0.87 (t, 3H, <sup>3</sup>J6.52Hz, -CH<sub>3</sub>).

**1-(4-Hydroxybenzoyloxy)phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate),**

**6f (R=n-C<sub>12</sub>H<sub>25</sub>O, X=H)**

This was synthesized following a procedure as described for the preparation of compound **6b** (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6e** R=n-C<sub>12</sub>H<sub>25</sub>O, X=H, (5.8g, 7.97mmol), 1, 4-dioxane (60ml), 5% Pd-C (1.lg). Yield, 4.2g (82.5%); m.p. 182-183°C;  $\nu_{\text{max}}$ : 3375, 3065, 2922, 2856, 1742, 1728, 1705, 1595, 1276, 1057 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 9.5(s, 1H, Ar-OH, exchangeable with D<sub>2</sub>O), 8.31-8.29 (d, 2H, <sup>3</sup>J8.65Hz, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 8.08-8.06 (d, 2H, <sup>3</sup>J8.7Hz, Ar-H), 7.58-7.55 (t, 1H, <sup>3</sup>J8.15Hz, Ar-H), 7.53-7.51 (d, 2H, <sup>3</sup>J8.65Hz, Ar-H), 7.31-7.24 (m, 3H, Ar-H), 7.14-7.12 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 7.02-7.00 (d, 2H, <sup>3</sup>J8.7Hz, Ar-H), 4.17-4.14 (t, <sup>3</sup>J6.5Hz, Ar-O-CH<sub>2</sub>-, 2H), 1.85-1.81 (quin, 2H, <sup>3</sup>J7.0Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.53-1.30 (m, 18H, 9 x -CH<sub>2</sub>-), 0.89-0.87 (t, 3H, <sup>3</sup>J6.5Hz -CH<sub>3</sub>). Elemental analysis: C<sub>39</sub>H<sub>42</sub>O<sub>8</sub> requires C, 73.33; H, 6.63%; found C, 73.36; H, 6.64 %.

**1-(4-Hydroxy-2-fluorobenzoyloxy)phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate),**  
**6.f(R=n-C<sub>12</sub>H<sub>25</sub>O, X=F)**

This was synthesized following a procedure as described for the preparation of compound **6b** (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6e** R=n-C<sub>12</sub>H<sub>25</sub>O, X=F, (3.5g, 7.97mmol), 1, 4-dioxane (50ml), 5% Pd-C (0.8g). Yield, 2.7g (88%); m.p. 181-182°C;  $\nu$ : 3346, 3072, 2922, 2853, 1742, 1726, 1715, 1697, 1601, 1248, 1136, 1055 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 10.1 (s, 1H, Ar-OH, exchangeable with D<sub>2</sub>O), 8.44-8.42 (dd, 2H, <sup>3</sup>J8.76Hz, <sup>4</sup>J2.0Hz, Ar-H), 8.30-8.28 (dd, 2H, <sup>3</sup>J8.92Hz, <sup>4</sup>J2.0Hz, Ar-H), 8.19-8.14 (t, 1H, <sup>3</sup>J8.68Hz, Ar-H), 7.73-7.64 (m, 3H, Ar-H), 7.46-7.38 (m, 3H, Ar-H), 7.27-7.25 (dd, 2H, <sup>3</sup>J8.92Hz, <sup>4</sup>J2.0Hz, Ar-H), 7.0-6.97 (dd, 1H, <sup>3</sup>J8.76Hz, <sup>4</sup>J2.0Hz, Ar-H), 6.90- 6.86 (dd, 1H, <sup>3</sup>J12.8Hz, <sup>4</sup>J2.8Hz, Ar-H), 4.30-4.27 (t, 2H, <sup>3</sup>J6.5Hz, Ar-O-CH<sub>2</sub>-), 1.99-1.93 (quin, 2H, <sup>3</sup>J6.92Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.53-1.30 (m, 18H, 9 x -CH<sub>2</sub>-), 1.03-1.0 (t, 3H, <sup>3</sup>J6.5Hz, -CH<sub>3</sub>).

**Benzyl-4-(4-n-dodecylbenzoyloxy)benzoate, 6a (R=n-C<sub>12</sub>H<sub>25</sub>)**

This compound was prepared using the procedure as described for compound **6a** (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: 4-n-dodecylbenzoic acid, **6i** R=n-C<sub>12</sub>H<sub>25</sub>, (5.0g, 17mmol), benzyl-4-hydroxybenzoate (3.93g, 17mmol), cat. amount of DMAP, DCC (3.85g, 18.5mmol), and dry dichloromethane (50ml). Yield, 7.3g (85%), m.p. 51-52°C;  $\nu_{\text{max}}$  (nujol): 2924, 2853, 1747, 1730, 1713, 1603, 1263 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.17-8.14 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 8.11-

8.09 (d, 2H,  $^3J$ 8.24Hz, Ar-H), 7.46-7.28 (m, 9H, Ar-H), 5.38 (s, 2H, -O-CH<sub>2</sub>-Ar), 2.23-2.69 (t, 2H,  $^3J$ 7.6Hz, Ar-CH<sub>2</sub>), 1.68-1.63 (quin, 2H,  $^3J$ 6.8Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>), 1.32-1.26 (m, 18H, 9 × -CH<sub>2</sub>-), 0.90-0.86 (t, 3H,  $^3J$ 6.52Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>33</sub>H<sub>40</sub>O<sub>4</sub> requires C, 79.17; H, 8.05%; found C, 79.16; H, 8.23%.

#### **4-n-Dodecylbenzoyloxy-4-benzoicacid, 6.b (R=n-C<sub>12</sub>H<sub>25</sub>)**

This compound was prepared using the procedure as described for compound **6.b** (R= n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6.a** R= n-C<sub>12</sub>H<sub>25</sub>, (7.0g, 14mmol), was dissolved in 1,4-dioxane (100 ml). Yield, 5.15g (90%); Trans. temp; Cr 138°C N 210°C I;  $\nu_{max}$  (nujol): 2922, 2853, 2725, 1734, 1732, 1690, 1605, 1294 cm<sup>-1</sup>;  $\delta_H$ : 8.21-8.19 (dd, 2H,  $^3J$ 8.76Hz,  $^4J$ 1.92Hz, Ar-H), 8.13-8.10 (d, 2H,  $^3J$ 8.24Hz, Ar-H), 7.36-7.32 (m, 4H, Ar-H), 2.73-2.69 (t, 2H,  $^3J$ 6.52Hz, Ar-CH<sub>2</sub>-), 1.68-1.64 (quin, 2H,  $^3J$ 7.0Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.31-1.26 (m, 18H, 9 × -CH<sub>2</sub>-), 0.90-0.87 (t, 3H,  $^3J$ 6.6Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>26</sub>H<sub>34</sub>O<sub>4</sub> requires C, 76.06; H, 8.35%; found C, 75.67; H, 8.43%.

#### **1-Benzoyloxyphenylene-3-(4-n-dodecylbenzoyloxy-4-benzoate), 6.c (R=n-C<sub>12</sub>H<sub>25</sub>)**

This compound was prepared using the procedure as described for compound **6.a** (R= n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6.b** R= n-C<sub>12</sub>H<sub>25</sub>, (5.0g, 12.1mmol), 3-benzoyloxy-phenol, **6.iii** (2.44g, 12.1mmol), cat. amount of DMAP, DCC (2.74g, 13.3mmol), and dry dichloromethane (35ml). Yield, 6.0g (82%), m.p. 96-97°C;  $\nu_{max}$  (nujol): 2924, 2853, 1738, 1736, 1732, 1600, 1269 cm<sup>-1</sup>;  $\delta_H$ : 8.29-8.27 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 8.14-8.11 (d, 2H,  $^3J$ 8.24Hz, Ar-H), 7.45-7.31 (m, 8H, Ar-H,), 6.92-6.83 (m, 5H, Ar-H), 5.08 (s, 2H, -O-CH<sub>2</sub>-Ar), 2.73-2.69 (t, 2H,  $^3J$ 7.56Hz, Ar-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H,  $^3J$ 7.32Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.33-1.27 (m, 18H, 9 × -CH<sub>2</sub>-), 0.90-0.87 (t, 3H,  $^3J$ 6.52Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>39</sub>H<sub>44</sub>O<sub>5</sub> requires C, 79.02; H, 7.48%; found C, 79.15; H 7.48%.

#### **1-(3-Hydroxy)phenylene 4-n-dodecylbenzoyloxy-4-benzoate, 6.d (R=n-C<sub>12</sub>H<sub>25</sub>)**

This compound was prepared using the procedure as described for compound **6.b** (R= n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6.c** R= n-C<sub>12</sub>H<sub>25</sub>, (5.8g, 9.8mmol), 1, 4-dioxane (75ml), 5% Pd-C (1.0g). Yield, 9.1g (90%); m.p. 120.5-121.5°C;  $\nu_{max}$  (nujol): 3415, 3341, 2924, 2851, 1736, 1732, 1601, 1264, 1263 cm<sup>-1</sup>;  $\delta_H$  (CD<sub>3</sub>COCD<sub>3</sub>): 8.79 (s, 1H, Ar-OH, exchangeable with D<sub>2</sub>O), 8.43-8.40 (dd, 2H,  $^3J$ 8.76Hz,  $^4J$ 1.96Hz, Ar-H), 8.27-8.25 (d, 2H,  $^3J$ 8.24Hz, Ar-H), 7.68-7.64 (dd, 2H,  $^3J$ 8.76Hz,  $^4J$ 1.96Hz, Ar-H), 7.61-7.58 (d, 2H,  $^3J$ 8.24Hz,

Ar-H), 7.43-7.39 (t, 1H,  $^3J$ 7.88Hz, Ar-H), 6.94-6.90 (m, 3H, Ar-H), 2.92-2.88 (t, 2H,  $^3J$ 7.52Hz, Ar-CH<sub>2</sub>-), 1.87-1.81 (quin, 2H,  $^3J$ 7.24Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.52-1.43 (m, 18H, 9 x -CH<sub>2</sub>-), 1.0-0.97 (t, 3H,  $^3J$ 6.7Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>32</sub>H<sub>38</sub>O<sub>5</sub> requires C, 76.47; H, 7.62%; found C, 76.9; H, 7.84%.

**1-(4-Benzoyloxy-2-fluorobenzoyloxy)phenylene-3-(4-n-dodecylbenzoyloxy-4-benzoate)  
6e (R=n-C<sub>12</sub>H<sub>25</sub>, X=F)**

This compound was prepared using the same procedure as described for compound **6a** (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6d** R=n-C<sub>12</sub>H<sub>25</sub>, (2.5g, 4.9mmol), 2-fluoro-4-benzoyloxybenzoic acid, **6.iv** (X=F) (1.2g, 4.9mmol), cat.amount of DMAP, DCC (1.11g, 5.39mmol) and dry dichloromethane (25 ml). Yield, 2.9g (80%); m.p. 98-99°C;  $\nu_{\text{max}}$  (nujol): 2924, 2855, 1742, 1736, 1730, 1605, 1246, 1061 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.26 (dd, 2H,  $^3J$ 8.76Hz,  $^4J$ 1.84Hz, Ar-H), 8.13-8.11 (d, 2H,  $^3J$ 8.24Hz, Ar-H), 8.08-8.04 (t, 1H,  $^3J$ 8.64Hz, Ar-H), 7.49-7.32 (m, 10H, Ar-H), 7.20-7.16 (m, 3H, Ar-H), 6.88-6.85 (dd, 1H,  $^3J$ 8.88Hz,  $^4J$ 2.24Hz, Ar-H), 6.80-6.76 (dd, 1H,  $^3J$ 12.52Hz,  $^4J$ 2.36Hz, Ar-H), 5.14 (s, 2H, -O-CH<sub>2</sub>-Ar), 2.73-2.69 (t, 2H,  $^3J$ 7.64Hz, Ar-CH<sub>2</sub>-), 1.70-1.65 (quin, 2H,  $^3J$ 7.32Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.33-1.27 (m, 18H, 9 x -CH<sub>2</sub>-), 0.90-0.87 (t, 3H,  $^3J$ 6.48Hz, -CH<sub>3</sub>).

**1-(4-Hydroxy-2-fluorobenzoyloxy)phenylene-3-(4-n-dodecylbenzoyloxy-4-benzoate),  
6f (R=n-C<sub>12</sub>H<sub>25</sub>, X=F)**

This was synthesized following a procedure as described for the preparation of compound **6b** (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6e** R= n-C<sub>12</sub>H<sub>25</sub>, X=F, (2.5g, 3.42mmol), 1,4-dioxane (30ml), 5% Pd-C (0.6g). Yield, 1.8g (82%); m.p. 163.5-164.5°C;  $\nu_{\text{max}}$  (nujol): 3377, 3333, 2922, 2853, 1730, 1713, 1699, 1616, 1265 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 9.9 (s, 1H, Ar-OH, exchangeable with D<sub>2</sub>O), 8.45-8.43 (dd, 2H,  $^3J$ 8.76Hz,  $^4J$ 1.84Hz, Ar-H), 8.27-8.25 (d, 2H,  $^3J$ 8.24Hz, Ar-H), 8.19-8.14 (t, 1H,  $^3J$ 8.68Hz, Ar-H), 7.72-7.65 (m, 3H, Ar-H), 7.60-7.58 (d, 2H,  $^3J$ 8.2Hz, Ar-H), 7.46-7.37 (m, 3H, Ar-H), 7.00-6.97 (dd, 1H,  $^3J$ 8.72Hz,  $^4J$ 2.24Hz, Ar-H), 6.90-6.86 (dd, 1H,  $^3J$ 12.72Hz,  $^4J$ 2.24Hz, Ar-H), 2.91-2.87 (t, 2H,  $^3J$ 7.52Hz, Ar-CH<sub>2</sub>-), 1.85-1.81 (quin, 2H,  $^3J$ 7.12Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.42 (m, 18H, 9 x -CH<sub>2</sub>-), 1.03-1.0 (t, 3H,  $^3J$ 6.52Hz, -CH<sub>3</sub>).

### **7-Benzylxy-2-hydroxynaphthalene, 6.vi**

This was prepared by following a similar procedure that described for 3-benzylxy-phenol [104] using 2, 7-dihydroynaphthalene as starting material. Yield, 58%; m.p. 151-152°C.

### **2-Benzylxy-naphthylene-7-(4-*n*-dodecyloxybenzoyloxy-4-benzoate), 6.g (R=*n*-C<sub>12</sub>H<sub>25</sub>O)**

This compound was synthesized following a procedure as described for compound **6.a** (R=*n*-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound 6.d R=*n*-C<sub>12</sub>H<sub>25</sub>O, (2.5g, 5.8mmol), 7-Benzylxy-2-hydroxynaphthalene, **6.vi** (1.46g, 5.8mmol), cat.amount of DMAP, DCC (1.33g, 6.5mmol), dry dichloromethane (35ml). Yield, 3.2g (83%); Trans. temp. Cr 111°C N 113°C I;  $\nu_{\text{max}}$  (nujol): 2922, 2853, 1742, 1732, 1605, 1265 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.33-8.31 (d, 2H, <sup>3</sup>J8.64Hz, Ar-H), 8.17-8.15 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.84-7.82 (d, 1H, <sup>3</sup>J8.84Hz, Ar-H), 7.79-7.77 (d, 1H, <sup>3</sup>J8.72Hz, Ar-H), 7.579-7.576 (d, 1H, <sup>4</sup>J1.68Hz, Ar-H), 7.50-7.48 (d, 2H, <sup>3</sup>J7.32Hz, Ar-H), 7.43-7.21 (m, 8H, Ar-H), 7.00-6.98 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 5.19 (s, 2H, -O-CH<sub>2</sub>-Ar), 4.08-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 1.87-1.80 (quin, 2H, <sup>3</sup>J7.0Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.51-1.28 (m, 18H, 9 x -CH<sub>2</sub>-), 0.91-0.87 (t, 3H, <sup>3</sup>J6.36Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>43</sub>H<sub>46</sub>O<sub>6</sub> requires C, 78.39; H, 7.04%; found C, 78.20; H, 7.19%.

### **2-Hydroxynaphthylene-7-(4-*n*-dodecyloxybenzoyloxy-4-benzoate), 6.h (R=*n*-C<sub>12</sub>H<sub>25</sub>O)**

This compound was synthesized following a procedure as described for compound **6.b** (R=*n*-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound **6.g** R=*n*-C<sub>12</sub>H<sub>25</sub>O, (3.1g, 4.7mmol), 5% Pd-C (0.6g), 1, 4-dioxane (50ml). Yield, 2.1g (80%); Trans. temp. Cr 146°C N 184°C I;  $\nu_{\text{max}}$  (nujol): 3412, 2922, 2849, 1740, 1720, 1603, 1254, 1163, 1067 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 8.93 (s, 1H, Ar-OH, exchangeable with D<sub>2</sub>O), 8.47-8.45 (dd, 2H, <sup>3</sup>J8.76Hz, <sup>4</sup>J1.96Hz, Ar-H), 8.31-8.29 (dd, 2H, <sup>3</sup>J8.92Hz, <sup>4</sup>J1.96Hz, Ar-H), 8.04-8.02 (d, 1H, <sup>3</sup>J8.8Hz, Ar-H), 7.99-7.97 (d, 1H, <sup>3</sup>J8.8Hz, Ar-H), 7.742-7.738 (d, 1H, <sup>4</sup>J2.08Hz, Ar-H), 7.68-7.66 (d, 2H, <sup>3</sup>J8.64Hz, Ar-H) 7.40-7.29 (m, 3H, Ar-H), 7.28-7.26 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 4.31-4.28 (t, 2H, <sup>3</sup>J6.48Hz, Ar-O-CH<sub>2</sub>-), 2.0-1.94 (quin, 2H, <sup>3</sup>J6.48Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.65-1.43 (m, 18H, 9 x -CH<sub>2</sub>-), 1.03-1.0 (t, 3H, <sup>3</sup>J6.36Hz, -CH<sub>3</sub>). Elemental analysis: C<sub>36</sub>H<sub>40</sub>O<sub>6</sub> requires C, 76.03; H, 7.09%; found C, 75.76; H, 6.86%.

**2-(4-Benzylxy-2-fluorobenzoyloxy)naphthylene-7-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.i (R=n-C<sub>12</sub>H<sub>25</sub>O)**

This compound was synthesized following a procedure as described for compound 6.a (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound 6.h R=n-C<sub>12</sub>H<sub>25</sub>O, (2.0g, 3.5mmol), 2-fluoro-4-benzylxybenzoic acid, **6.iv**, X=F, (0.87g, 3.5mmol), cat.amount of DMAP, DCC (0.79g, 3.9mmol) dry dichloromethane (25 ml). Yield, 2.25g (80%); m.p. 137-138°C;  $\nu_{\text{max}}$  (nujol): 2922, 2853, 1734, 1728, 1717, 1605, 1271 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.34-8.32 (d, 2H, <sup>3</sup>J8.64Hz, Ar-H), 8.17-8.15 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 8.13-8.09 (t, 1H, <sup>3</sup>J8.6Hz, Ar-H), 7.94-7.91 (rn, 2H, Ar-H), 7.69-7.36 (m, 11H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 6.90-6.87 (dd, 1H, <sup>3</sup>J8.84Hz, <sup>4</sup>J2.24Hz, Ar-H), 6.82-6.77 (dd, 1H, <sup>3</sup>J12.48Hz, <sup>4</sup>J2.28Hz, Ar-H), 5.18 (s, 2H, -O-CH<sub>2</sub>-Ar), 4.08-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 1.87-1.80 (quin, 2H, <sup>3</sup>J7.0Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.28 (m, 18H, 9 x -CH<sub>2</sub>-), 0.90-0.87 (t, 3H, <sup>3</sup>J6.48Hz, -CH<sub>3</sub>).

**2-(4-Hydroxy-2-fluorobenzoyloxy)naphthylene-7-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.j (R=n-C<sub>12</sub>H<sub>25</sub>O)**

This compound was synthesized following a procedure as described for compound 6.b (R=n-C<sub>12</sub>H<sub>25</sub>O). Quantities: compound 6.i R=n-C<sub>12</sub>H<sub>25</sub>O, (2.1g, 2.6mmol), 5% Pd-C (0.45g), 1, 4-dioxane (40ml). Yield, 1.5g (81%); m.p. 198.5-199.5°C;  $\nu_{\text{max}}$  (nujol): 3344, 2922, 2853, 1740, 1724, 1797, 1601, 1274, 1163, 1057 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CD<sub>3</sub>COCD<sub>3</sub>): 9.94 (s, 1H, Ar-OH, exchangeable with D<sub>2</sub>O), 8.49-8.44 (dd, 2H, <sup>3</sup>J8.76Hz, <sup>4</sup>J1.96Hz, Ar-H), 8.31-8.29 (dd, 2H, <sup>3</sup>J8.92Hz, <sup>4</sup>J2.0Hz, Ar-H), 8.25-8.20 (m, 3H, Ar-H), 8.021-8.017 (d, 1H, <sup>4</sup>J2.04Hz, Ar-H), 7.973-7.968 (d, 1H, <sup>4</sup>J2.08Hz, Ar-H), 7.69-7.59 (m, 4H, Ar-H), 7.28-7.26 (d, 2H, <sup>3</sup>J8.96Hz, Ar-H), 7.03-7.0 (dd, 1H, <sup>3</sup>J8.72Hz, <sup>4</sup>J2.28Hz, Ar-H), 6.92-6.89 (dd, 1H, <sup>3</sup>J12.72Hz, <sup>4</sup>J2.28Hz, Ar-H), 4.31-4.28 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 2.01-1.94 (quin, 2H, <sup>3</sup>J6.96Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.67-1.43 (m, 18H, 9 x -CH<sub>2</sub>-), 1.03-1.0 (t, 3H, <sup>3</sup>J6.6Hz, -CH<sub>3</sub>).

**1-[(E-4-n-Hexyloxy- $\alpha$ -methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-n-dodecyl-oxybenzoyloxy-4-benzoate), 6.A.1**

A mixture of 6f R= n-C<sub>12</sub>H<sub>25</sub>O, X=H, (0.15g, 0.024mmol), E-4-n-hexyloxy- $\alpha$ -methylcinnamic acid, **6.v**, n=6, (0.063g, 0.024mmol) catalytic amount of 4-(N, N-dimethylamino) pyridine (DMAP), and dry dichloromethane were stirred for ten minutes. To this N, N'-dicyclohexylcarbodiimide (DCC), (0.055g, 0.026mmol) was added and stirred overnight. The reaction mixture was diluted with dichloromethane and the precipitated N, N'

dicyclohexylurea was filtered off. The filtrate was washed successively with 5% aqueous acetic acid (15ml x 2), 5% ice-cold sodium hydroxide solution, (15 ml x 2), water (15 ml x 3) and dried over anhydrous sodium sulphate. The solvent was removed to yield a product, which was purified by column chromatography on silica gel using chloroform as an eluent. Removal of solvent from the eluate gave a white material, which was crystallized from a mixture of chloroform and acetonitrile. Yield, 0.14g (71%); m.p. 83.0°C v<sub>max</sub>: 3073, 2922, 2853, 1738, 1728, 1603, 1256, 1128, 1061 cm<sup>-1</sup>; δ<sub>H</sub>: 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.52-7.46 (m, 3H, Ar-H), 7.39-7.36 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>), 4.03-3.99 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>), 2.273-2.270 (d, 3H, <sup>3</sup>J1.1Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.50-1.27 (m, 24H, 12 × -CH<sub>2</sub>-), 0.93-0.87 (m, 6H, 2 ×-CH<sub>3</sub>). Elemental analysis: C<sub>55</sub>H<sub>62</sub>O<sub>10</sub> requires C, 74.81; H, 7.08%; found C, 74.87; H, 7.17%.

**1-[(E-4-n-Heptyloxy-α-methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-n-dodecyl-oxybenzoyloxy-4-benzoate), 6.A.2**

Yield, 73%; m.p. 94.0°C; v<sub>max</sub>: 3073, 2922, 2853, 1736, 1730, 1603, 1256, 1128, 1061 cm<sup>-1</sup>; δ<sub>H</sub>: 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.52-7.46 (m, 3H, Ar-H), 7.39-7.36 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>), 4.03-3.99 (t, 2H, <sup>3</sup>J6.6Hz, Ar-O-CH<sub>2</sub>), 2.276-2.273 (d, 3H, <sup>3</sup>J1.1Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 26H, 13 x -CH<sub>2</sub>-), 0.92-0.87 (m, 6H, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>56</sub>H<sub>64</sub>O<sub>10</sub> requires C, 74.98; H, 7.19%; found C, 75.17; H, 7.28%.

**1-[(E-4-n-Octyloxy-α-methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-n-dodecyloxy-benzoyloxy-4-benzoate), 6.A.3**

Yield, 69%; m.p. 86.5°C; v<sub>max</sub>: 3073, 2922, 2853, 1736, 1730, 1603, 1256, 1128, 1061 cm<sup>-1</sup>; δ<sub>H</sub>: 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.52-7.46 (m, 3H, Ar-H), 7.39-7.36 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>), 4.03-3.99 (t, 2H, <sup>3</sup>J6.6Hz, Ar-

O-CH<sub>2</sub>-), 2.276-2.273 (d, 3H, <sup>3</sup>J1.1Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 28H, 14 x -CH<sub>2</sub>-), 0.92-0.87 (m, 6H, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>57</sub>H<sub>66</sub>O<sub>10</sub> requires C, 75.14; H, 7.30%; found C, 75.48; H, 7.29%.

**1-[*(E*-4-*n*-Nonyloxy- $\alpha$ -methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-*n*-dodecyl-oxybenzoyloxy-4-benzoate),**6.A.4****

Yield, 71%; m.p. 91.0°C;  $\nu_{\text{max}}$ : 3088, 2920, 2851, 1732, 1730, 1605, 1256, 1138, 1070 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 7.91 (s, 1H, =C(H) ), 7.52-7.46 (m, 3H, Ar-H), 7.39-7.36 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.277-2.274 (d, 3H, <sup>3</sup>J1.12Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 30H, 15 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>58</sub>H<sub>68</sub>O<sub>10</sub> requires C, 75.30; H, 7.41%; found C, 75.67; H, 7.48%.

**1-[*(E*-4-*n*-Decyloxy- $\alpha$ -methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-*n*-dodecyloxy-benzoyloxy-4-benzoate),**6.A.5****

Yield, 73%; m.p. 79.0°C;  $\nu_{\text{max}}$ : 3088, 2920, 2851, 1732, 1730, 1605, 1256, 1138, 1070 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 7.91 (s, 1H, =C(H) ), 7.52-7.46 (m, 3H, Ar-H), 7.39-7.36 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.96Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.273 (d, 3H, <sup>3</sup>J1.16Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 32H, 16 × -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>59</sub>H<sub>70</sub>O<sub>10</sub> requires C, 75.45; H, 7.51%; found C, 75.04; H, 7.53%.

**1-[*(E*-4-*n*-Undecyloxy- $\alpha$ -methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-*n*-dodecyl-oxybenzoyloxy-4-benzoate),**6.A.6****

Yield, 78%; m.p. 89.0°C;  $\nu_{\text{max}}$ : 3088, 2920, 2855, 1732, 1730, 1603, 1258, 1136, 1070 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 7.91 (s, 1H, =C(H) ), 7.52-7.46 (m, 3H, Ar-H), 7.39-7.36 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-

O-CH<sub>2</sub>-), 2.276-2.274 (d, 3H, <sup>3</sup>J1.0Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 34H, 17 × -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>60</sub>H<sub>72</sub>O<sub>10</sub> requires C, 75.60; H, 7.61%; found C, 75.17; H, 7.27%.

**1-[*(E*-4-*n*-Dodecyloxy-α-methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-*n*-dodecyl-oxybenzoyloxy-4-benzoate), 6.A.7**

Yield, 67%; m.p. 89.0°C; v<sub>max</sub>: 3088, 2920, 2851, 1732, 1730, 1605 1256, 1138, 1070 cm<sup>-1</sup>; δ<sub>H</sub>: 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 7.91 (s, 1H, =C(H) ), 7.52-7.46 (m, 3H, Ar-H), 7.39 7.36 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0- 6.98 (d, 2H, <sup>3</sup>J8.96Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.274 (d, 3H, <sup>3</sup>J1.08Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 36H, 18 × -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>61</sub>H<sub>74</sub>O<sub>10</sub> requires C, 75.75; H, 7.71%; found C, 75.58; H, 7.67%.

**1-[*(E*-4-*n*-Tetradecyloxy-α-methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-*n*-dodecyloxybenzoyloxy-4-benzoate), 6.A.8**

Yield, 64%; m.p. 85.5°C; v<sub>max</sub>: 3089, 2920, 2851, 1732, 1730, 1605 1256, 1138, 1070 cm<sup>-1</sup>; δ<sub>H</sub>: 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.91 (s, 1H, =C(H) ), 7.52- 7.46 (m, 3H, Ar-H), 7.39-7.36 (d, 2H, <sup>3</sup>J8.64Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.64Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.274 (d, 3H, <sup>3</sup>J1.0Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 40H, 20 × -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>63</sub>H<sub>78</sub>O<sub>10</sub> requires C, 76.03; H, 7.90%; found C, 76.45; H, 8.04%.

**1-[*(E*-4-*n*-Hexadecyloxy-α-methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-*n*-dodecyloxybenzoyloxy-4-benzoate), 6.A.9**

Yield, 69%; m.p. 89.0°C; v<sub>max</sub>: 3089, 2920, 2851, 1738, 1736, 1732, 1605 1256, 1138, 1070 cm<sup>-1</sup>; δ<sub>H</sub>: 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.91 (s, 1H, =C(H) ), 7.52-7.46 (m, 3H, Ar-H), 7.39- 7.36 (d, 2H, <sup>3</sup>J8.64Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.6Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.52Hz,

Ar-O-CH<sub>2</sub>-), 2.276-2.273 (d, 3H, <sup>3</sup>J1.08Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 44H, 22 x -CH<sub>2</sub>-), 0.89-0.86 (m, 6H, 2 x -CH<sub>3</sub>). Elemental analysis: C<sub>65</sub>H<sub>82</sub>O<sub>10</sub> requires C, 76.29; H, 8.08%; found C, 76.23; H, 8.02%.

**1-[*(E*-4-*n*-Octadecyloxy- $\alpha$ -methylcinnamoyloxy)-4-benzoyloxy]phenylene-3-(4-*n*-dodecyloxybenzoyloxy-4-benzoate), 6.A.10**

Yield, 71%; m.p. 83.5°C;  $\nu_{\text{max}}$ : 3078, 2918, 2851, 1732, 1730, 1605, 1254, 1163, 1076 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.26 (m, 4H, Ar-H), 8.16-8.14 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 7.91 (s, 1H, =C(H) ), 7.52-7.46 (m, 3H, Ar-H), 7.39-7.36 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.96Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 2.275-2.273 (d, 3H, <sup>3</sup>J0.96Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.25 (m, 48H, 24 x -CH<sub>2</sub>-), 0.89-0.86 (m, 6H, -CH<sub>3</sub>). Elemental analysis: C<sub>67</sub>H<sub>76</sub>O<sub>10</sub> requires C, 76.54; H, 8.24%; found C, 75.61; H, 8.26%.

**1-[*(E*-4-*n*-Hexyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecyloxybenzoyloxy-4-benzoate), 6.B.1**

Yield, 65%; m.p. 98.0°C;  $\nu_{\text{max}}$ : 3078, 2920, 2851, 1744, 1734, 1603, 1250, 1132, 1061 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H) ), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 2.266-2.263 (d, 3H, <sup>3</sup>J1.12Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.52-1.27 (m, 24H, 12 x -CH<sub>2</sub>-), 0.94-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[*(E*-4-*n*-Heptyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecyloxybenzoyloxy-4-benzoate), 6.B.2**

Yield, 69%; m.p. 100.0°C;  $\nu_{\text{max}}$ : 3076, 2920, 2851, 1744, 1732, 1603, 1250, 1132, 1061 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 8.19-8.14 (rn, 3H, Ar-H), 7.89 (s, 1H, =C(H) ), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.96Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.266-2.263 (d, 3H, <sup>3</sup>J1.2Hz,

=C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 26H, 13 x -CH<sub>2</sub>-), 0.92-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Octyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.B.3**

Yield, 68%; m.p. 105.0°C;  $\nu_{\text{max}}$ : 3076, 2920, 2851, 1744, 1736, 1603, 1250, 1132, 1061 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.267-2.265 (d, 3H, <sup>3</sup>J1.12Hz, CH=C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.28 (m, 28H, 14 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Nonyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.B.4**

Yield, 70%; m.p. 105.0°C;  $\nu_{\text{max}}$ : 3076, 2920, 2851, 1744, 1732, 1603, 1250, 1132, 1061 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.96Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.266-2.263 (d, 3H, <sup>3</sup>J1.2Hz, =C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.28 (m, 30H, 15 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Decyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.B.5**

Yield, 66%; m.p. 91.0°C;  $\nu_{\text{max}}$ : 3090, 2920, 2853, 1744, 1734, 1605, 1256, 1142, 1061 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 7.0-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.07-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 2.267-2.264 (d, 3H, <sup>3</sup>J1.12Hz, CH=C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.28 (m, 32H, 16 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Undecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate),6.B.6**

Yield, 63%; m.p. 89.5°C;  $\nu_{\text{max}}$ : 3090, 2920, 2853, 1746, 1734, 1605, 1256, 1142, 1065 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 7.22-7.12 (m, 5H, Ar-H), 7.0-6.98 (d, 2H,  $^3J$ 8.96Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.8Hz, Ar-H), 4.07-4.04 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 2.268-2.265 (d, 3H,  $^3J$ 1.04Hz, CH=C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.28 (m, 34H, 17 x -CH<sub>2</sub>-), 0.91-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Dodecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.B.7**

Yield, 71%; m.p. 93.5°C;  $\nu_{\text{max}}$ : 3090, 2920, 2853, 1746, 1734, 1605, 1256, 1142, 1065 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 7.22-7.12 (m, 5H, Ar-H), 7.0-6.98 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.8Hz, Ar-H), 4.07-4.04 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.267-2.264 (d, 3H,  $^3J$ 1.04Hz, CH=C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 36H, 18 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Tetradecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate),6.B.8**

Yield, 69%; m.p. 89.0°C;  $\nu_{\text{max}}$ : 3090, 2920, 2853, 1744, 1734, 1605, 1256, 1142, 1067 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 7.22-7.12 (m, 5H, Ar-H), 7.0-6.98 (d, 2H,  $^3J$ 8.96Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.8Hz, Ar-H), 4.07-4.04 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.267-2.265 (d, 3H,  $^3J$ 1.04Hz, CH=C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 40H, 20 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Hexadecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate),6.B.9**

Yield, 71%; m.p. 93.0°C;  $\nu_{\text{max}}$ : 3088, 2918, 2851, 1746, 1734, 1605, 1256, 1142, 1067 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 7.23-7.11 (m, 5H, Ar-H), 7.0-6.98 (d, 2H,  $^3J$ 8.96Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.84Hz, Ar-H), 4.07-4.04 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.267-2.263 (d, 3H,  $^3J$ 1.24Hz, CH=C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 44H, 22 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Octadecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecyloxybenzoyloxy-4-benzoate),6.B.10**

Yield, 68%; m.p. 91.0°C;  $\nu$ : 3089, 2918, 2851, 1744, 1734, 1605, 1256, 1142, 1067 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 8.19-8.14 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 7.23-7.11 (m, 5H, Ar-H), 7.0-6.98 (d, 2H,  $^3J$ 8.96Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.84Hz, Ar-H), 4.07-4.04 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 4.03-3.99 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.267-2.264 (d, 3H,  $^3J$ 1.24Hz, CH=C(CH<sub>3</sub>)-), 1.86-1.77 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 48H, 24 x -CH<sub>2</sub>-), 0.90-0.86 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-n-Hexyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-n-dodecylbenzoyloxy-4-benzoate),6.C.1**

Yield, 63%; m.p. 82.0°C;  $\nu_{\text{max}}$ : 3078, 2922, 2851, 1746, 1736, 1605, 1512, 1259, 1132, 1076 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 7.34-7.32 (d, 2H,  $^3J$ 8.16Hz, Ar-H), 7.22-7.12 (m, 5H, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 4.03-3.99 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 2.73-2.69 (t, 2H,  $^3J$ 7.52Hz, Ar-CH<sub>2</sub>-), 2.266-2.263 (d, 3H,  $^3J$ 1.12Hz, =C(CH<sub>3</sub>)-), 1.85-1.77 (quin, 2H,  $^3J$ 6.96Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H,  $^3J$ 7.0Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.50-1.27 (m, 24H, 12 x -CH<sub>2</sub>-), 0.94-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-*n*-Heptyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.2**

Yield, 67%; m.p. 78.0°C;  $\nu_{\text{max}}$ : 3080, 2920, 2851, 1744, 1736, 1605, 1512, 1250, 1132, 1061 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 7.34-7.32 (d, 2H,  $^3J$ 8.08Hz, Ar-H), 7.22-7.12 (m, 5H, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 4.03-3.99 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>), 2.73-2.69 (t, 2H,  $^3J$ 7.48Hz, Ar-CH<sub>2</sub>), 2.266-2.263 (d, 3H,  $^3J$ 1.08Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H,  $^3J$ 7.0Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H,  $^3J$ 7.08Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.27 (m, 26H, 13 x -CH<sub>2</sub>), 0.92-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-*n*-Octyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.3**

Yield, 71%; m.p. 80.5°C;  $\nu_{\text{max}}$ : 3080, 2922, 2853, 1744, 1736, 1603, 1512, 1250, 1132, 1060 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 7.34-7.32 (d, 2H,  $^3J$ 8.16Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 4.03-3.99 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>), 2.73-2.69 (t, 2H,  $^3J$ 7.52Hz, Ar-CH<sub>2</sub>), 2.266-2.264 (d, 3H,  $^3J$ 1.04Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H,  $^3J$ 6.96Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H,  $^3J$ 7.2Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.27 (m, 28H, 14 x -CH<sub>2</sub>), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-*n*-Nonyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.4**

Yield, 66%; m.p. 73.0°C;  $\nu_{\text{max}}$ : 3080, 2922, 2853, 1744, 1736, 1603, 1512, 1250, 1132, 1060 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 7.34-7.32 (d, 2H,  $^3J$ 8.2Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 4.03-3.99 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>), 2.73-2.69 (t, 2H,  $^3J$ 7.52Hz, Ar-CH<sub>2</sub>), 2.267-2.264 (d, 3H,  $^3J$ 1.0Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H,  $^3J$ 6.96Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H,  $^3J$ 6.96Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.27 (m, 30H, 15 x -CH<sub>2</sub>), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-*n*-Decyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.5**

Yield, 71%; m.p. 56.0°C;  $\nu_{\text{max}}$ : 3080, 2920, 2853, 1744, 1732, 1605, 1510, 1250, 1132, 1060 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.2Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.73-2.69 (t, 2H, <sup>3</sup>J7.52Hz, Ar-CH<sub>2</sub>-), 2.266-2.263 (d, 3H, <sup>3</sup>J1.16Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H, <sup>3</sup>J6.88Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H, <sup>3</sup>J7.24Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.27 (m, 32H, 16 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-*n*-Undecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.6**

Yield, 69%; m.p. 56.0°C;  $\nu_{\text{max}}$ : 3072, 2920, 2851, 1736, 1730, 1605, 1510, 1256, 1142, 1065 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.2Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.03-3.99 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.73-2.69 (t, 2H, <sup>3</sup>J7.52Hz, Ar-CH<sub>2</sub>-), 2.267-2.263 (d, 3H, <sup>3</sup>J1.04Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H, <sup>3</sup>J6.96Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H, <sup>3</sup>J7.24Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 34H, 17 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[(E-4-*n*-Dodecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.7**

Yield, 70%; m.p. 57.5°C;  $\nu_{\text{max}}$ : 3071, 2920, 2851, 1740, 1730, 1607, 1510, 1258, 1136, 1065 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.16Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 4.03-3.99 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 2.73-2.69 (t, 2H, <sup>3</sup>J7.56Hz, Ar-CH<sub>2</sub>-), 2.267-2.263 (d, 3H, <sup>3</sup>J0.96Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H, <sup>3</sup>J6.96Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H, <sup>3</sup>J7.24Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 36H, 18 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[*(E*-4-*n*-Tetradecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.8**

Yield, 66%; m.p. 64.0°C;  $\nu_{\text{max}}$ : 3074, 2920, 2851, 1732, 1605, 1512, 1256, 1139, 1065 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.35-7.33 (d, 2H, <sup>3</sup>J8.24Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.76Hz, Ar-H), 4.03-3.99 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 2.73-2.69 (t, 2H, <sup>3</sup>J7.56Hz, Ar-CH<sub>2</sub>-), 2.267-2.265 (d, 3H, <sup>3</sup>J1.08Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H, <sup>3</sup>J6.92Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H, <sup>3</sup>J7.32Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 40H, 20 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[*(E*-4-*n*-Hexadecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.9**

Yield, 71%; m.p. 76.0°C;  $\nu_{\text{max}}$ : 3082, 2920, 2851, 1748, 1732, 1605, 1508, 1261, 1139, 1057 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 7.34-7.32 (d, 2H, <sup>3</sup>J8.12Hz, Ar-H), 7.22-7.11 (m, 5H, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 4.03-3.99 (t, 2H, <sup>3</sup>J6.48Hz, Ar-O-CH<sub>2</sub>-), 2.73-2.69 (t, 2H, <sup>3</sup>J7.52Hz, Ar-CH<sub>2</sub>-), 2.267-2.265 (d, 3H, <sup>3</sup>J1.08Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H, <sup>3</sup>J6.92Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H, <sup>3</sup>J7.48Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 44H, 22 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**1-[*(E*-4-*n*-Octadecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]phenylene-3-(4-*n*-dodecylbenzoyloxy-4-benzoate), 6.C.10**

Yield, 64%; m.p. 73.0°C;  $\nu_{\text{max}}$ : 3082, 2920, 2851, 1746, 1734, 1605, 1510, 1261, 1139, 1057 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.29-8.27 (d, 2H, <sup>3</sup>J8.64Hz, Ar-H), 8.19-8.11 (m, 3H, Ar-H), 7.89 (s, 1H, =C(H)), 7.51-7.45 (m, 3H, Ar-H), 7.39-7.37 (d, 2H, <sup>3</sup>J8.64Hz, Ar-H), 7.35-7.33 (d, 2H, <sup>3</sup>J8.12Hz, Ar-H), 7.22-7.12 (m, 5H, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 4.03-3.99 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 2.73-2.69 (t, 2H, <sup>3</sup>J7.52Hz, Ar-CH<sub>2</sub>-), 2.268-2.265 (d, 3H, <sup>3</sup>J1.04Hz, =C(CH<sub>3</sub>)-), 1.84-1.77 (quin, 2H, <sup>3</sup>J6.92Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.68-1.63 (quin, 2H, <sup>3</sup>J7.2Hz, Ar-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.27 (m, 48H, 24 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**2-[*(E*-4-Ethoxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-**

(4-n-dodecyloxybenzoyloxy-4-benzoate),6.D.1

Yield, 76%; m.p. 138.5°C;  $\nu_{\text{max}}$ : 3060, 2924, 2853, 1744, 1736, 1734, 1603, 1232, 1059 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 8.25-8.21 (t, 1H,  $^3J$ 8.64Hz, Ar-H), 8.18-8.15 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.721-7.717 (d, 1H,  $^4J$ 2.0Hz, Ar-H), 7.703-7.698 (d, 1H,  $^4J$ 2.0Hz, Ar-H), 7.49-7.46 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.0-6.98 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 4.12-4.04 (rn, 4H, 2 x Ar-O-CH<sub>2</sub>), 2.276-2.273 (d, 2H,  $^3J$ 1.2Hz, =C(CH<sub>3</sub>)), 1.85-1.79 (quin, 2H,  $^3J$ 6.88Hz, Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47-1.27 (m, 21H, 9 x -CH<sub>2</sub>-, 1 x -CH<sub>3</sub>), 0.90-0.87 (t, 3H,  $^3J$ 6.88Hz, -CH<sub>3</sub>).

**2-[*(E*-4-n-Butyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-**

(4-n-dodecyloxybenzoyloxy-4-benzoate),6.D.2

Yield, 78%; m.p. 103.0°C;  $\nu_{\text{max}}$ : 3080, 2922, 2851, 1740, 1736, 1724, 1603, 1232, 1055 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 8.25-8.21 (t, 1H,  $^3J$ 8.64Hz, Ar-H), 8.18-8.15 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.722-7.717 (d, 1H,  $^4J$ 2.04Hz, Ar-H), 7.704-7.698 (d, 1H,  $^4J$ 2.04Hz, Ar-H), 7.48-7.46 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.18-7.14 (m, 2H, Ar-H), 7.01-6.98 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 4.07-4.00 (m, 4H, 2 x Ar-O-CH<sub>2</sub>), 2.276-2.273 (d, 2H,  $^3J$ 1.2Hz, =C(CH<sub>3</sub>)), 1.85-1.79 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.54--1.27 (m, 20H, 10 x -CH<sub>2</sub>), 1.01-0.98 (t, 3H,  $^3J$ 7.40Hz, -CH<sub>3</sub>), 0.90-0.87 (t, 3H,  $^3J$ 6.60Hz, -CH<sub>3</sub>).

**2-[*(E*-4-n-Pentyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-**

(4-n-dodecyloxybenzoyloxy-4-benzoate),6.D.3

Yield, 73%; m.p. 104.0°C;  $\nu_{\text{max}}$ : 3080, 2922, 2853, 1740, 1738, 1728, 1603, 1232, 1055 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 8.25-8.21 (t, 1H,  $^3J$ 8.64Hz, Ar-H), 8.18-8.15 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.722-7.717 (d, 1H,  $^4J$ 1.92Hz, Ar-H), 7.703-7.699 (d, 1H,  $^4J$ 1.92Hz, Ar-H), 7.48-7.46 (d, 2H,  $^3J$ 8.76Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.01-6.98 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 4.07-4.04 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>), 4.03-4.00 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>), 2.276-2.273 (d, 2H,  $^3J$ 1.08Hz, =C(CH<sub>3</sub>)), 1.85-1.79 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.50-1.27 (m, 22H, 11 x -CH<sub>2</sub>), 0.96-0.93 (t, 3H,  $^3J$ 7.08Hz, -CH<sub>3</sub>), 0.90-0.87 (t, 3H,  $^3J$ 6.56Hz, -CH<sub>3</sub>).

**2-[(E-4-n-Hexyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-n-dodecyloxybenzoyloxy-4-benzoate),6.D.4**

Yield, 77%; m.p. 98.0°C;  $\nu_{\text{max}}$ : 3080, 2922, 2853, 1740, 1736, 1719, 1603, 1232, 1055 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 8.25-8.21 (t, 1H,  $^3J$ 8.48Hz, Ar-H), 8.18-8.15 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.722-7.717 (d, 1H,  $^4J$ 2.0Hz, Ar-H), 7.703-7.698 (d, 1H,  $^4J$ 2.0Hz, Ar-H), 7.48-7.46 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.01-6.98 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 4.07-4.04 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-4.00 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.274 (d, 2H,  $^3J$ 1.08Hz, =C(CH<sub>3</sub>)), 1.85-1.79 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 24H, 12 x -CH<sub>2</sub>-), 0.94-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**2-[(E-4-n-Heptyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-n-dodecyloxybenzoyloxy-4-benzoate),6.D.5**

Yield, 75%; m.p. 94.5°C;  $\nu_{\text{max}}$ : 3098, 2922, 2853, 1744, 1734, 1732, 1605, 1240, 1055 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 8.25-8.21 (t, 1H,  $^3J$ 8.68Hz, Ar-H), 8.18-8.15 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.722-7.717 (d, 1H,  $^4J$ 1.96Hz, Ar-H), 7.704-7.699 (d, 1H,  $^4J$ 1.96Hz, Ar-H), 7.48-7.46 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.01-6.98 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 4.07-4.04 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-4.00 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.277-2.274 (d, 2H,  $^3J$ 1.08Hz, =C(CH<sub>3</sub>)), 1.85-1.78 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 26H, 13 x -CH<sub>2</sub>-), 0.92-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**2-[(E-4-n-Octyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.D.6**

Yield, 71%; m.p. 101.0°C;  $\nu_{\text{max}}$ : 3101, 2922, 2853, 1744, 1734, 1732, 1605, 1240, 1055 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 8.25-8.21 (t, 1H,  $^3J$ 8.68Hz, Ar-H), 8.18-8.15 (d, 2H,  $^3J$ 8.84Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.8Hz, Ar-H), 7.91 (s, 1H, =C(H)), 7.723-7.717 (d, 1H,  $^4J$ 1.96Hz, Ar-H), 7.704-7.699 (d, 1H,  $^4J$ 1.96Hz, Ar-H), 7.48-7.46 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.00-6.98 (d, 2H,  $^3J$ 8.84Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.8Hz, Ar-H), 4.08-4.04 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-4.00 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.274 (d, 2H,  $^3J$ 1.0Hz, =C(CH<sub>3</sub>)), 1.86-1.78 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.48-1.27 (m, 28H, 14 x -CH<sub>2</sub>-), 0.90-0.87 (m, 6H, 2 x -CH<sub>3</sub>).

**2-[(E-4-n-Nonyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.D.7**

Yield, 80%; m.p. 99.0°C;  $\nu_{\text{max}}$ : 3101, 2922, 2853, 1744, 1734, 1732, 1605, 1256, 1069 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 8.25-8.21 (t, 1H,  $^3J$ 8.68Hz, Ar-H), 8.18-8.15 (d, 2H,  $^3J$ 8.84Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.90 (s, 1H, =C(H)), 7.726-7.721 (d, 1H,  $^4J$ 1.72Hz, Ar-H), 7.708-7.703 (d, 1H,  $^4J$ 1.72Hz, Ar-H), 7.48-7.46 (d, 2H,  $^3J$ 8.68Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.00-6.98 (d, 2H,  $^3J$ 8.84Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 4.08-4.04 (t, 2H,  $^3J$ 6.48Hz, Ar-O-CH<sub>2</sub>-), 4.03-4.00 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.274 (d, 2H,  $^3J$ 1.0Hz, =C(CH<sub>3</sub>)), 1.86-1.78 (m, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.28 (m, 30H, 15 x -CH<sub>2</sub>-), 0.91-0.88 (m, 6H, 2 x -CH<sub>3</sub>).

**2-[(E-4-n-Decyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.D.8**

Yield, 76%; m.p. 99.0°C;  $\nu_{\text{max}}$ : 3101, 2922, 2853, 1744, 1734, 1605, 1256, 1069 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 8.25-8.21 (t, 1H,  $^3J$ 8.56Hz, Ar-H), 8.18-8.15 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 7.90 (s, 1H, =C(H)), 7.726-7.721 (d, 1H,  $^4J$ 1.92Hz, Ar-H), 7.708-7.703 (d, 1H,  $^4J$ 1.92Hz, Ar-H), 7.48-7.46 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.00-6.98 (d, 2H,  $^3J$ 8.92Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 4.08-4.04 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 4.03-4.00 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.274 (d, 2H,  $^3J$ 1.08Hz, =C(CH<sub>3</sub>)), 1.86-1.78 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.28 (m, 32H, 16 x -CH<sub>2</sub>-), 0.91-0.88 (m, 6H, 2 x -CH<sub>3</sub>).

**2-[(E-4-n-Undecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-n-dodecyloxybenzoyloxy-4-benzoate), 6.D.9**

Yield, 77%; m.p. 105.0°C;  $\nu_{\text{max}}$ : 3107, 2920, 2853, 1744, 1734, 1605, 1256, 1069 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.35-8.32 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 8.24-8.20 (t, 1H,  $^3J$ 8.64Hz, Ar-H), 8.17-8.15 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.96-7.94 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 7.90 (s, 1H, =C(H)), 7.726-7.721 (d, 1H,  $^4J$ 1.84Hz, Ar-H), 7.708-7.703 (d, 1H,  $^4J$ 1.84Hz, Ar-H), 7.48-7.46 (d, 2H,  $^3J$ 8.72Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.01-6.98 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 6.97-6.95 (d, 2H,  $^3J$ 8.88Hz, Ar-H), 4.08-4.04 (t, 2H,  $^3J$ 6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-4.00 (t, 2H,  $^3J$ 6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.273 (d, 2H,  $^3J$ 1.04Hz, =C(CH<sub>3</sub>)), 1.86-1.78 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.28 (m, 34H, 17 x -CH<sub>2</sub>-), 0.91-0.88 (m, 6H, 2 x -CH<sub>3</sub>).

**2-[*(E*-4-*n*-Dodecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-*n*-dodecyloxybenzoyloxy-4-benzoate),**6.D.10****

Yield, 74%; m.p. 109.0°C;  $\nu_{\text{max}}$ : 3107, 2920, 2851, 1744, 1734, 1732, 1605, 1256, 1069 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.34-8.32 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 8.24-8.20 (t, 1H, <sup>3</sup>J8.68Hz, Ar-H), 8.18-8.15 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 7.96-7.94 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 7.90 (s, 1H, =C(H)), 7.726-7.721 (d, 1H, <sup>4</sup>J1.72Hz, Ar-H), 7.708-7.703 (d, 1H, <sup>4</sup>J1.72Hz, Ar-H), 7.48-7.46 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.01-6.98 (d, 2H, <sup>3</sup>J8.92Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.8Hz, Ar-H), 4.08-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-4.00 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.273 (d, 2H, <sup>3</sup>J1.04Hz, =C(CH<sub>3</sub>)), 1.86-1.78 (m, 4H, 2 × Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.28 (m, 36H, 18 x -CH<sub>2</sub>-), 0.90-0.88 (m, 6H, 2 x -CH<sub>3</sub>).

**2-[*(E*-4-*n*-Tetradecyloxy- $\alpha$ -methylcinnamoyloxy)-2-fluoro-4-benzoyloxy]naphthylene-7-(4-*n*-dodecyloxybenzoyloxy-4-benzoate),**6.D.11****

Yield, 77%; m.p. 104.0°C;  $\nu_{\text{max}}$ : 3102, 2918, 2851, 1744, 1734, 1605, 1256, 1069 cm<sup>-1</sup>;  $\delta_{\text{H}}$ : 8.34-8.32 (d, 2H, <sup>3</sup>J8.68Hz, Ar-H), 8.24-8.20 (t, 1H, <sup>3</sup>J8.68Hz, Ar-H), 8.18-8.15 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 7.96-7.94 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 7.90 (s, 1H, =C(H)), 7.726-7.722 (d, 1H, <sup>4</sup>J1.88Hz, Ar-H), 7.708-7.703 (d, 1H, <sup>4</sup>J1.88Hz, Ar-H), 7.48-7.46 (d, 2H, <sup>3</sup>J8.72Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.17-7.14 (m, 2H, Ar-H), 7.01-6.98 (d, 2H, <sup>3</sup>J8.88Hz, Ar-H), 6.97-6.95 (d, 2H, <sup>3</sup>J8.84Hz, Ar-H), 4.08-4.04 (t, 2H, <sup>3</sup>J6.52Hz, Ar-O-CH<sub>2</sub>-), 4.03-4.00 (t, 2H, <sup>3</sup>J6.56Hz, Ar-O-CH<sub>2</sub>-), 2.276-2.273 (d, 2H, <sup>3</sup>J0.96Hz, =C(CH<sub>3</sub>)), 1.86-1.78 (m, 4H, 2 x Ar-O-CH<sub>2</sub>-CH<sub>2</sub>-), 1.49-1.28 (m, 40H, 20 x -CH<sub>2</sub>-), 0.90-0.88 (m, 6H, 2 x -CH<sub>3</sub>).