

Chapter 3

Synthesis and mesomorphic properties of

- (i) **4-*n*-Octyloxyphenyl-3'-(4-(4-*n*-alkoxybenzoyloxy)benzoyloxy)-biphenyl-4-carboxylates, (compounds 3.A.1 to 3.A.4)**

- (ii) **4-*n*-Nonanoyloxyphenyl-3'-(4-(4-*n*-alkoxybenzoyloxy)benzoyloxy)-biphenyl-4-carboxylates, (compounds 3.B.1 to 3.B.4)**

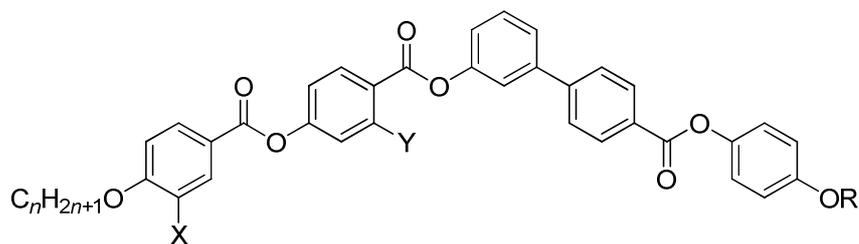
- (iii) **4-*n*-Octyloxycarbonylphenyl-3'-(4-(4-*n*-alkoxybenzoyloxy)-benzoyloxy)biphenyl-4-carboxylates, (compounds 3.C.1 to 3.C.4)**

- (iv) **4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-alkoxy-benzoyloxy)benzoyloxy)biphenyl-4-carboxylates, (compounds 3.D.1 to 3.D.14)**

3.1: Introduction

Among all the mesophase textures exhibited by compounds composed of bent-core molecules, the textures of B₇ phase are beautiful and fascinating. As mentioned in chapter 1, the B₇ phase was first reported by Weissflog *et al.* [1, 2] in derivatives of 2-nitroresorcinol and are known to exhibit helical superstructures. One of the characteristic textures is the filamentary growth patterns and interestingly these textures are also seen in a number of other systems [3-9] not derived from 2-nitroresorcinol. The symbol B₇ was assigned to all those systems which exhibited the filamentary growth patterns. The original B₇ phase [1] does not respond to an applied electric field but many other systems did respond and were characterized as ferroelectric [5, 6] as also antiferroelectric [7] in a different system. Moreover, the XRD data for the mesophases where the B₇ symbol was assigned were all different. A number of compounds derived from 2-cyanoresorcinol were reported [10, 11] by Reddy and Sadashiva and many of these showed textures and XRD data similar to that shown by 2-nitroresorcinol derivatives. Subsequently, a number of other compounds derived from either a 2-nitro- or a 2-cyanoresorcinol moiety containing terminal *n*-alkyl or *n*-alkoxy chain and exhibiting the B₇ phase were reported [12,13]. Although the confusion regarding the nomenclature of the B₇ phase remained for a few years, Coleman *et al.* [14] carried out an in-depth analysis of the B₇ phase using synchrotron X-ray and micro-beam X-ray diffraction studies, freeze fracture electron microscopy etc. and proposed a modulated-undulated layer structure based on splay of polarization. The proposed structure has been depicted in Chapter 1. Thus, a number of variants of B₇ phase are known now and this classification is based on the differences found in the XRD data and electro-optical measurements. A detailed analysis of these are found in a few review articles [15, 16].

In this chapter, the use of a new moiety viz. 3-hydroxybiphenyl 4-carboxylic acid has provided a number of compounds exhibiting this fascinating B₇ phase. In order to study the structure-property relationships, slight modification in the molecular structure has been made and thus four derivatives in each of the three parts of homologous series, **3.A**, **3.B** and **3.C** and a larger series **3.D** consisting of fourteen compounds have been synthesized. The synthesized and investigated compounds have the chemical structure shown in structure 3.



X = H, Y = H, R = -OC ₈ H ₁₇	n = 8, 10, 15, 18	Series 3.A
X = H, Y = H, R = -OCOC ₈ H ₁₇	n = 8, 10, 15, 18	Series 3.B
X = H, Y = H, R = -COOC ₈ H ₁₇	n = 8, 10, 15, 18	Series 3.C
X = F, Y = F, R = -OC ₈ H ₁₇	n = 5, 6, 7,..... 16, 18, 20	Series 3.D

Structure 3

3.2: Synthesis

The five ring unsymmetrical bent-core compounds belonging to the four different series viz. series **3.A**, **3.B**, **3.C** and **3.D** were synthesized by adopting four different pathways as shown in schemes **3.2**, **3.3**, **3.4** and **3.5** respectively. 4-Benzyloxyphenol, *n*-octylbromide, *n*-nonanoic acid, *n*-octanol and methyl 3-hydroxybiphenyl-4-carboxylate were obtained from commercial sources and used without further purification. 4-*n*-Octyloxyphenol, **3.A.b** was synthesized from 4-benzyloxyphenol in two steps as described in the literature [17] and given in scheme **3.1**. The synthesis of 3-benzyloxybiphenyl-4-carboxylic acid, **3.c** was described in chapter 2. 4-Benzyloxyphenol, **3.a** was esterified with *n*-nonanoic acid using one equivalent of *N,N'*-dicyclohexylcarbodiimide (DCC) and a catalytic amount of DMAP in dichloromethane followed by hydrogenolysis using 5% Pd-C catalyst in an atmosphere of hydrogen to obtain 4-hydroxyphenyl-*n*-nonanoate, **3.B.b** and the synthetic route followed is shown in scheme **3.1**. Similarly, 4-benzyloxybenzoic acid, **3.b** was condensed with *n*-octanol to yield **3.A.a** and cleavage of benzyl group by means of 5% Pd-C catalyst in an atmosphere of hydrogen provided *n*-octyl-4-hydroxybenzoate, **3.C.b**. Esterification of 3-benzyloxybiphenyl-4-carboxylic acid, **3.c** with appropriate phenols gave compounds **3.A.b**, **3.B.b** and **3.C.b** which on deprotection of

benzyl group yielded **3.A.d**, **3.B.d** and **3.C.d** respectively. 4-Benzyloxybenzoic acid, **3.b** was synthesized following a procedure described in the literature [18].

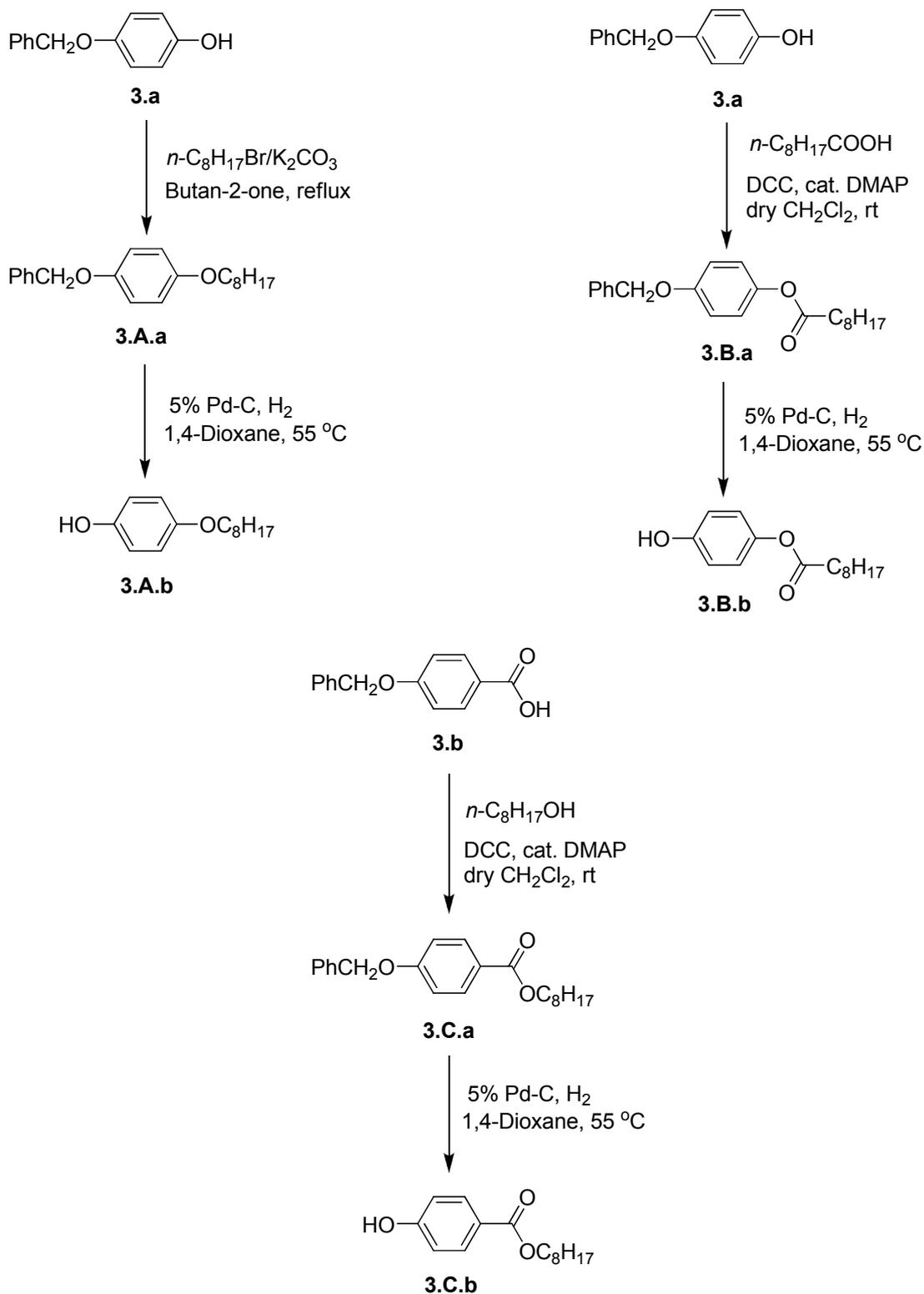
The unsymmetrical five-ring BC compounds belonging to series **3.A**, **3.B** and **3.C** were prepared by condensing three-ring phenols **3.A.d**, **3.B.d** and **3.C.d** with corresponding two-ring acids, **3.d** as shown in schemes **3.2**, **3.3** and **3.4** respectively. Similarly, the lateral fluorine containing compounds of series **3.D** were synthesized using sequential esterification and hydrogenolysis procedures as outlined in scheme **3.4**. 2-Fluoro-4-benzyloxybenzoic acid, **3.e** was esterified with three-ring phenol **3.A.d** using DCC and a catalytic amount of DMAP in dichloromethane. The deprotection of benzyl group by means of 5% Pd-C in an atmosphere of hydrogen yielded four-ring BC compound **3.D.b**. This phenol was treated with corresponding 3-fluoro-4-*n*-alkoxybenzoic acid to obtain desired BC compounds of series **3.D**. 2-Fluoro-4-benzyloxybenzoic acid [19], 3-fluoro-4-*n*-alkoxybenzoic acids [20] and 4-*n*-alkoxybenzoic acids [21] were synthesized following procedures described in the literature. All the compounds were purified by column chromatography on silica gel and repeated crystallization using analytical grade solvents.

3.3: Results and discussion

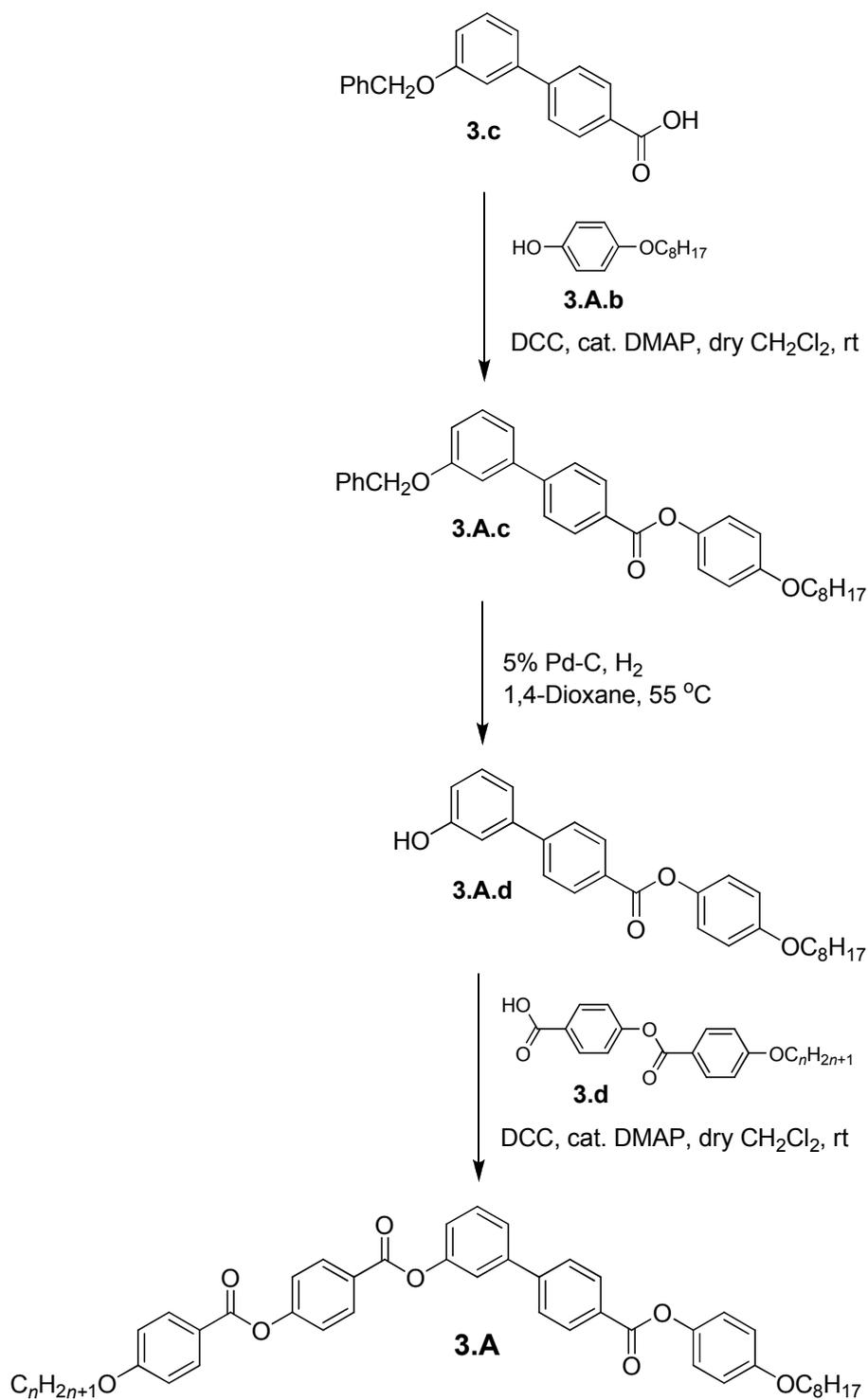
3.3.1: Mesomorphic properties

The transition temperatures and the associated enthalpy values obtained for four new homologous series of compounds **3.A**, **3.B**, **3.C** and **3.D** are summarized in tables **3.1**, **3.2**, **3.3** and **3.4** respectively. As can be seen all investigated compounds are mesomorphic in nature.

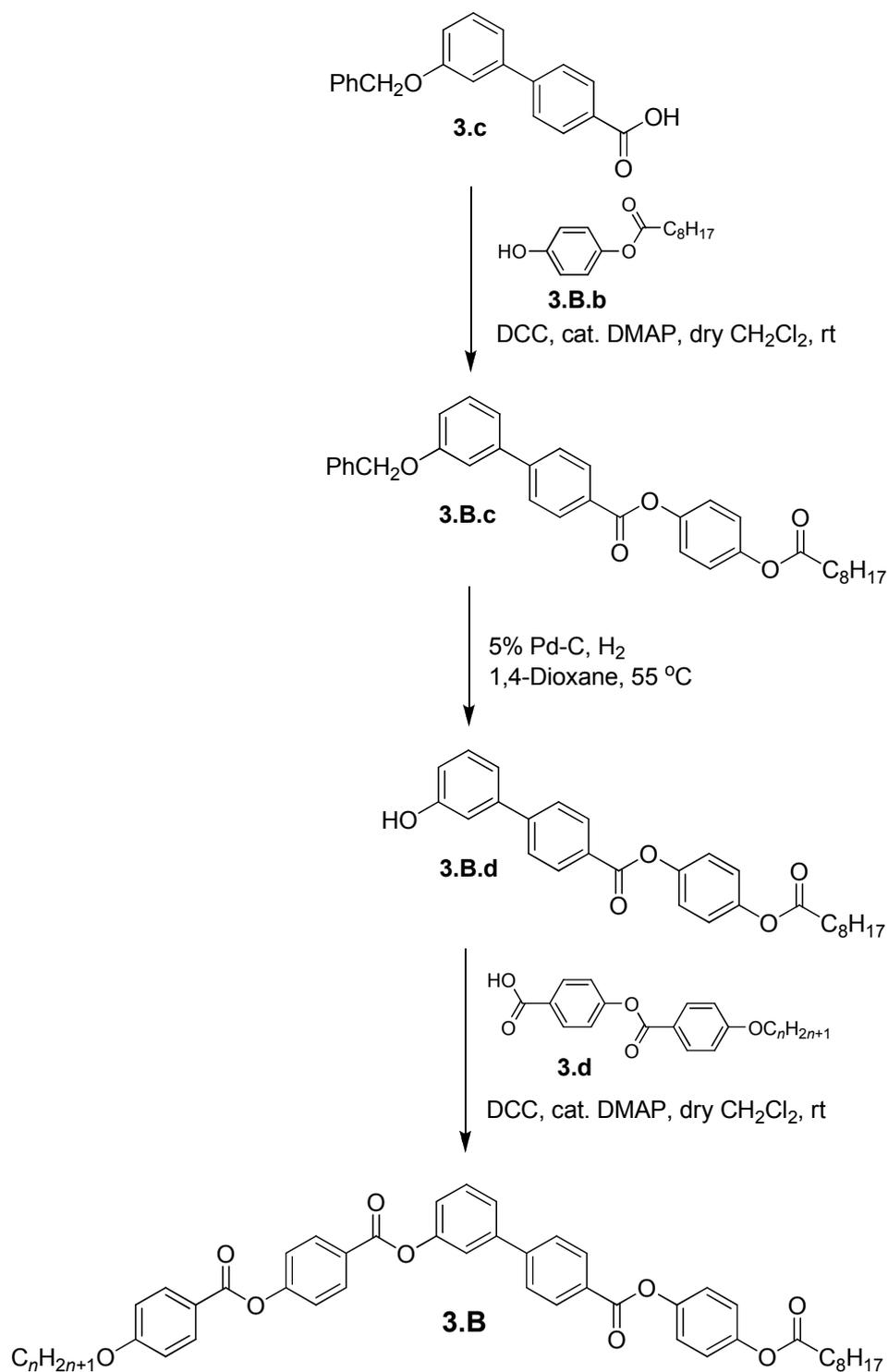
As can be seen in table **3.1**, all the four compounds exhibit a metastable mesophase. Compounds **3.A.1** and **3.A.2** exhibit mosaic texture that are typically observed for a B₁ phase which has a columnar structure with a rectangular lattice. The optical texture obtained for compound **3.A.1** is shown in figure **3.1.a**. This structure has been confirmed using XRD data which is described later. Hence, this mesophase has been characterized as a Col_r phase. Remarkably, when the terminal chain length is increased to *n*-pentadecyloxy- and *n*-octadecyloxy- the mesophase structure completely changes. When a sample of compound **3.A.3**



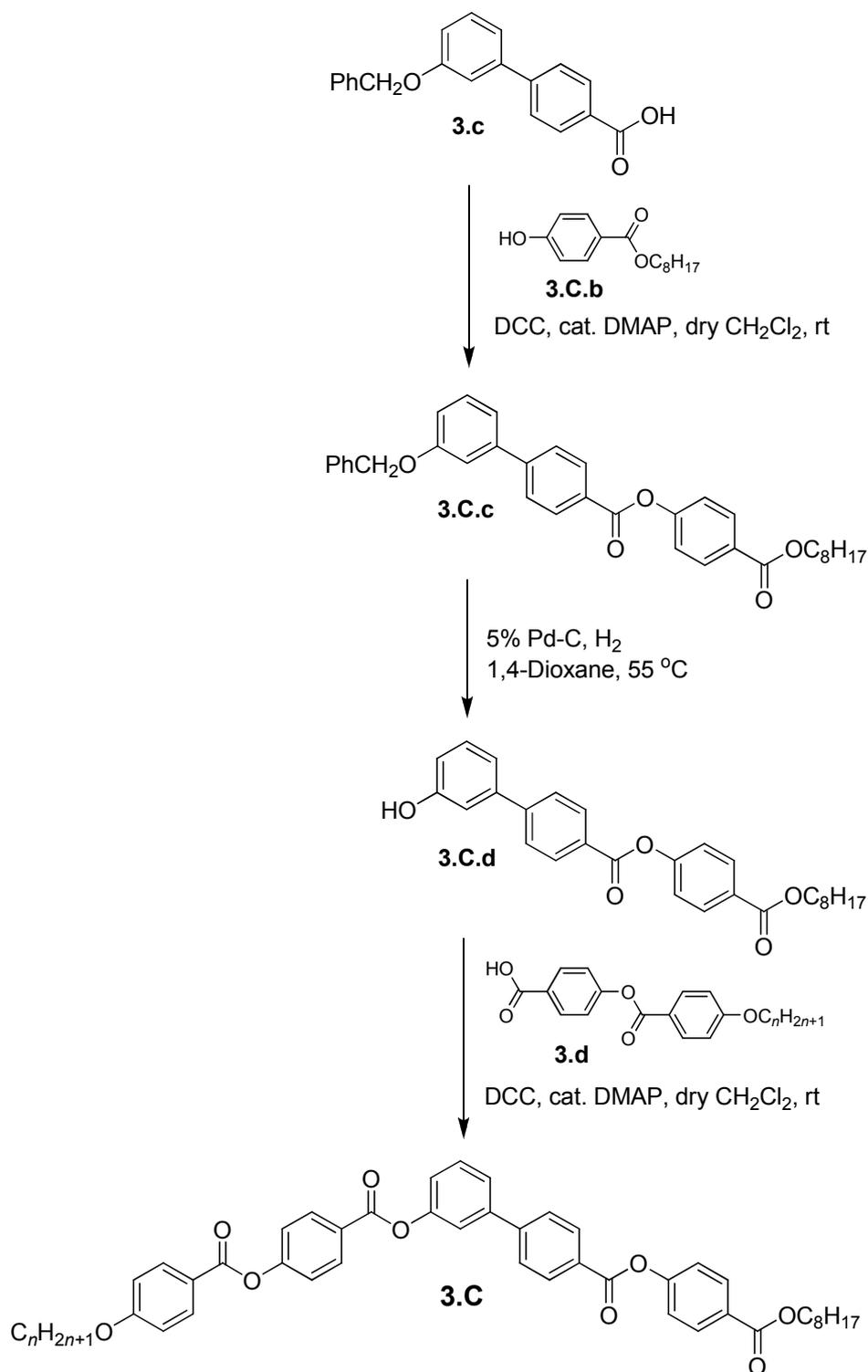
Scheme 3.1: Synthetic pathway followed for the preparation of key intermediates



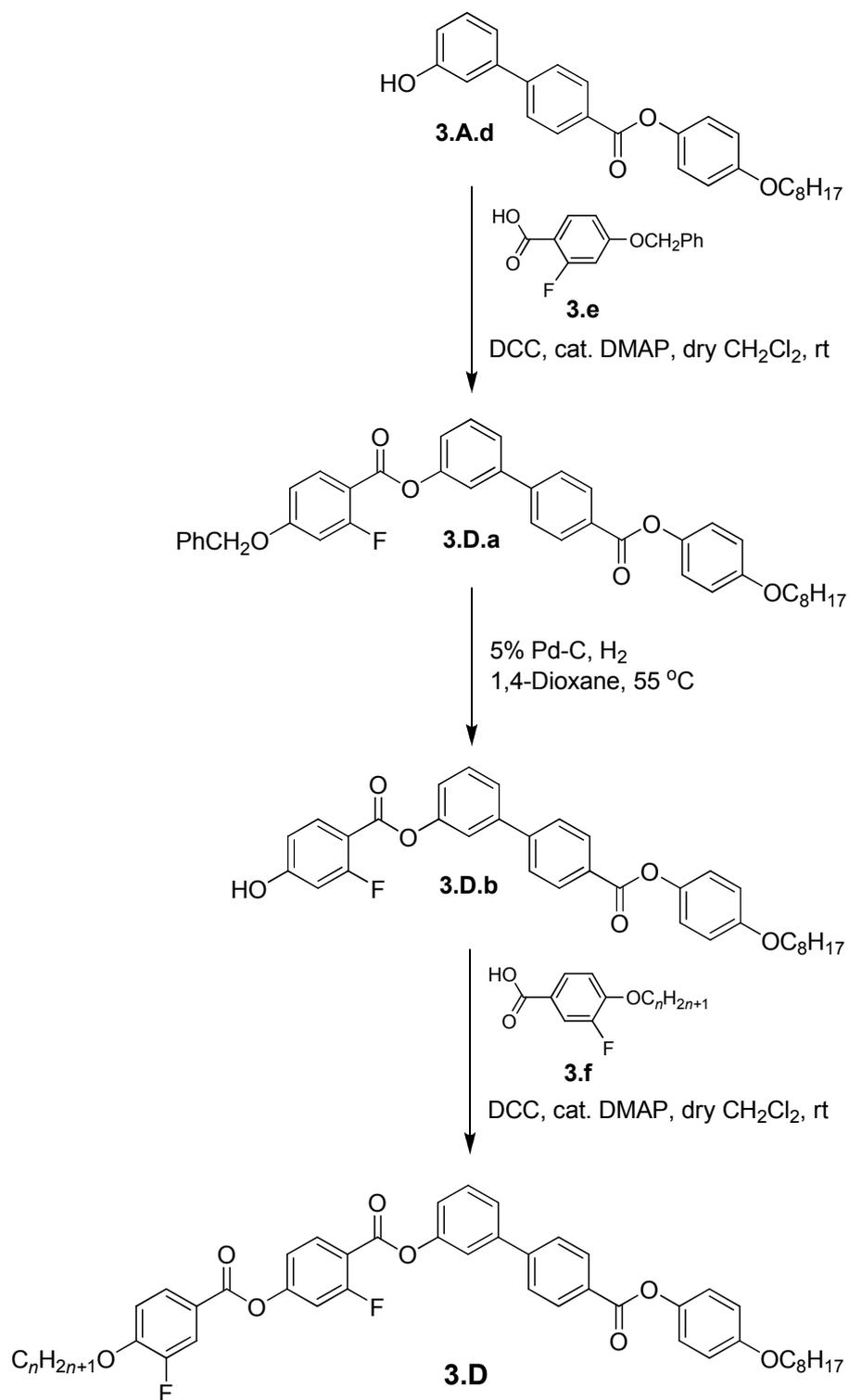
Scheme 3.2: Synthetic route followed for the preparation of BC compounds of series 3.A.



Scheme 3.3: Synthetic pathway employed for the preparation of BC compounds of series 3.B



Scheme 3.4: Synthetic pathway followed to prepare BC compounds of series 3.C



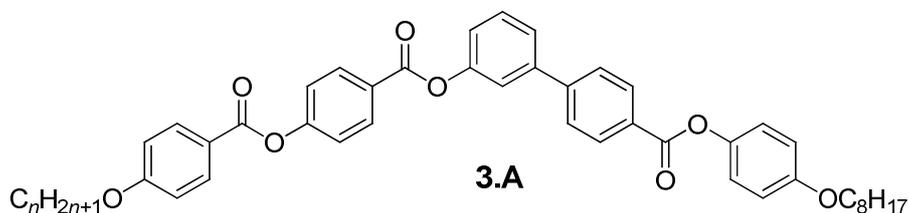
Scheme 3.5: Synthetic pathway followed for the preparation of BC compounds of series 3.D

sandwiched between two glass plates and slowly cooled from the isotropic state, helical texture develops and this resembles a B₇ phase. The optical texture obtained for compound **3.A.3** is shown in figure **3.1.b**. Confirmation of the mesophase structure by XRD was not possible as the samples crystallize rapidly. Since the mesophases of these two compounds switch electro-optically and show antiferroelectric characteristics, they have been assigned the symbol B_{7A}.

The transition temperatures and the associated enthalpy values for the four compounds belonging to series **3.B** are summarized in table **3.2**. The difference between compounds of series **3.A** and **3.B** is that the former has a terminal *n*-alkoxy chain while the latter has a *n*-alkanoate chain. The types of mesophases occurring in the two series are similar. However, in series **3.B**, they are enantiotropic. Compounds **3.B.1** and **3.B.2** exhibit textures that are typically seen for a Col_r phase and those obtained for compound **3.B.1** are shown in figure **3.2.a**. Incidentally, the structure of the mesophase was confirmed as Col_r by XRD measurements. Compounds **3.B.3** and **3.B.4** showed helical textures similar to those observed for compound **3.A.3** and a typical texture for the B_{7'} phase is shown in figure **3.2.b**. Since these mesophases are enantiotropic, XRD measurements could be made which indicated a simple layer structure. The mesophases also switch electro-optically and hence they have been characterized as a B_{7'} phase. It is also appropriate to mention here that this type of mesophase was observed previously [22, 23].

The transition temperatures together with the associated enthalpy values obtained for the four compounds of series **3.C** are summarized in table **3.3**. Interestingly, the mesophases of compounds **3.C.1** and **3.C.2** are metastable while those of **3.C.3** and **3.C.4** are enantiotropic. The optical textures and the XRD data obtained for first two compounds indicate that the mesophase is indeed a columnar phase with a rectangular lattice and the mesophase does not respond to an applied electric field. Hence, they have been characterized as a Col_r or a B₁ phase. The mesophase structure of the higher homologues **3.C.3** and **3.C.4** could also be fitted to a rectangular columnar structure on the basis of XRD data. When a thin film of sample of compound **3.C.4** was filled in a cell treated for planar alignment and cooled slowly from the isotropic phase, a texture developed and the same is shown in figure **3.3**. Electro-optical studies indicated this phase to be polar in nature with antiferroelectric characteristics. Hence, this phase has been assigned the symbol Col_rP_A.

Table 3.1: Transition temperatures (°C) and the associated enthalpy values ($\Delta H/\text{kJ mol}^{-1}$) (in italics) for compounds of series 3.A^a



Compound	<i>n</i>	Cr	Col _r	B _{7A}	I
3.A.1	8	• 136.5 <i>89.0</i>	(• 126.0) <i>31.8</i>	-	•
3.A.2	10	• 139.5 <i>95.1</i>	(• 125.5) <i>30.8</i>	-	•
3.A.3	15	• 133.5 <i>83.7</i>	-	(• 124.5) <i>26.6</i>	•
3.A.4	18	• 130.5 <i>93.6</i>	-	(• 122.5) <i>23.9</i>	•

^aAbbreviations: Cr: crystalline phase; B_{7A}: B₇ phase with antiferroelectric behaviour; Col_r: columnar phase with a rectangular lattice; I: isotropic phase; (): phase is monotropic; •: phase exists; -: phase does not exist.

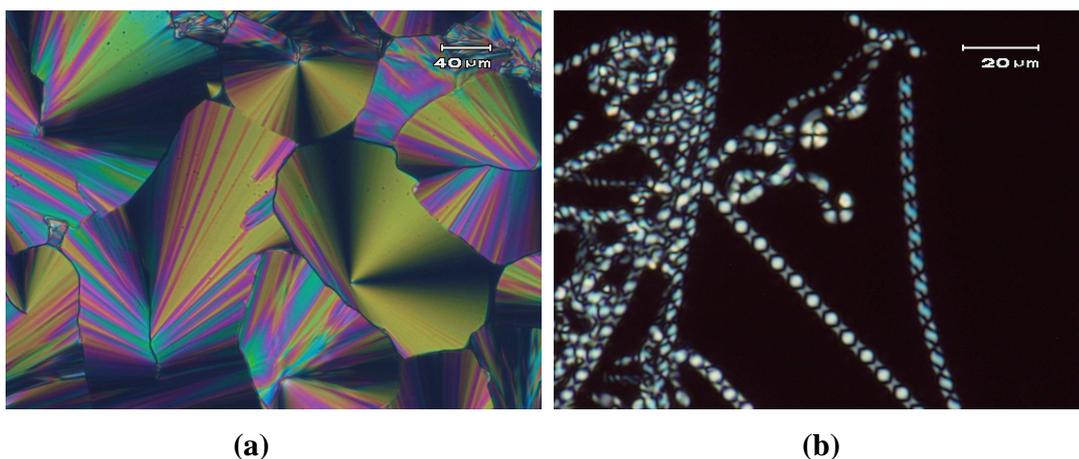
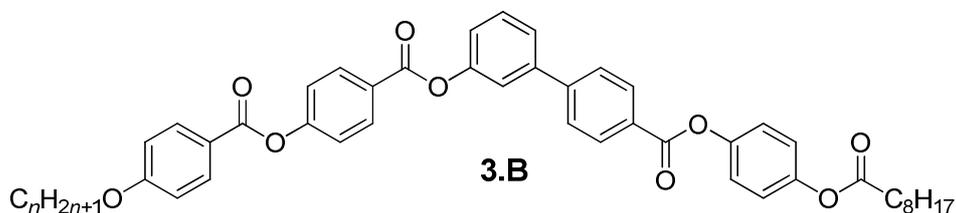


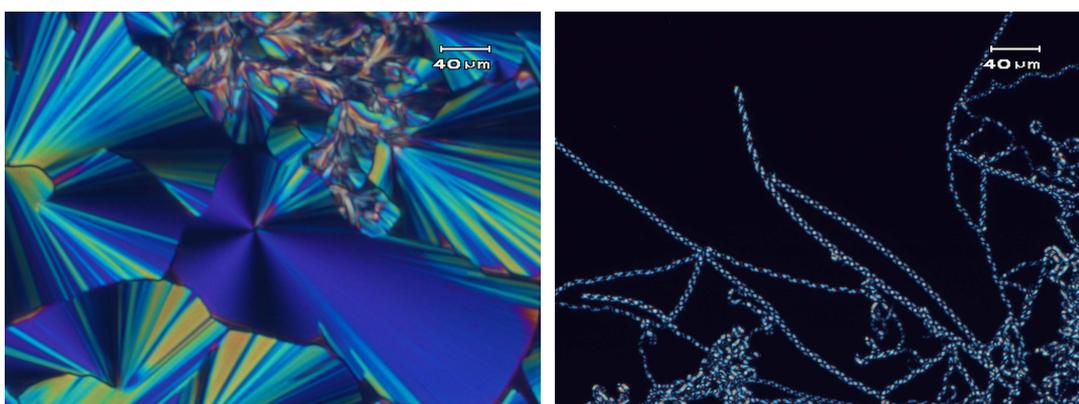
Figure 3.1: Optical texture obtained for Col_r and B_{7A} phases of compounds 3.A.1 and 3.A.3 at (a) and (b) T = 123 °C respectively between glass plates.

Table 3.2: Transition temperatures (°C) and the associated enthalpy values ($\Delta H/\text{kJ mol}^{-1}$) (in italics) for compounds of series 3.B^a



Compound	<i>n</i>	Cr	Col _r	B ₇ '	I
3.B.1	8	• 115.0 <i>40.8</i>	• 135.0 <i>30.6</i>	-	•
3.B.2	10	• 116.5 <i>37.0</i>	• 136.5 <i>26.7</i>	-	•
3.B.3	15	• 116.5 <i>45.6</i>	-	• 134.0 <i>24.5</i>	•
3.B.4	18	• 111.5 <i>60.6</i>	-	• 134.5 <i>23.9</i>	•

^aSee **Table 3.1**: B₇': variant of B₇ phase with antiferroelectric properties.

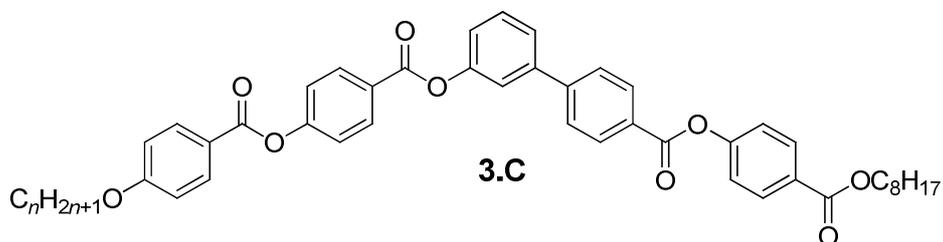


(a)

(b)

Figure 3.2: Optical textures obtained for Col_r phase of compound 3.B.1 (a) T = 127 °C and (b) B₇' phase of compound 3.B.3 at T = 132 °C between glass plates without any treatment.

Table 3.3: Transition temperatures (°C) and the associated enthalpy values ($\Delta H/\text{kJ mol}^{-1}$) (in italics) for compounds of series 3.C^a



Compound	<i>n</i>	Cr	Col _r	Col _r P _A	I
3.C.1	8	• 123.5 <i>74.7</i>	(• 120.5) <i>25.6</i>	-	•
3.C.2	10	• 125.0 <i>77.0</i>	(• 122.5) <i>25.5</i>	-	•
3.C.3	15	• 117.5 <i>42.6</i>	-	• 125.0 <i>21.2</i>	•
3.C.4	18	• 112.5 <i>63.1</i>	-	• 123.5 <i>19.9</i>	•

^aSee Table 3.1

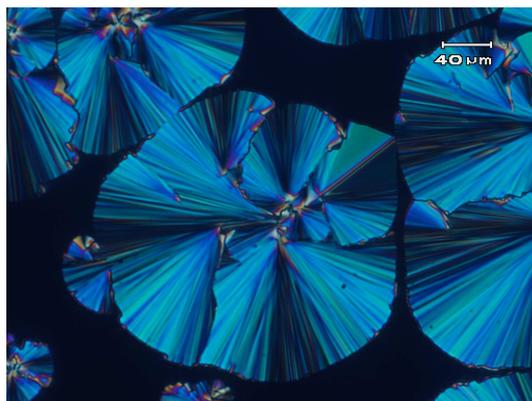
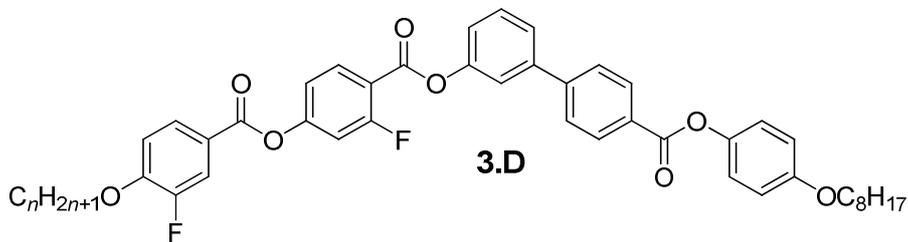


Figure 3.3: Optical texture obtained for Col_rP_A phase of compound 3.C.4 in a cell treated for planar alignment showing circular domain with banana-leaf at T = 120 °C.

Remarkably, when a fluorine substituent was introduced *ortho* to the terminal *n*-alkoxy chain and *ortho* to the carbonyl group of the middle phenyl ring, the mesophases became largely enantiotropic with fairly wide thermal ranges. A homologous series containing fourteen compounds was thus synthesized and these belong to series **3.D**. The transition temperatures and the associated enthalpy values obtained for these compounds are summarized in table **3.4**. The unsubstituted parent compounds belong to series **3.A**. The influence of the fluorine substituents can be gauged by comparing the transition temperatures of compounds of **3.A.4** and **3.D.13**. Although the clearing points are similar, the melting point has got reduced by 23 ° and hence the mesophase is enantiotropic. The lower homologues **3.D.1** to **3.D.4** show optical textures and XRD data similar to those of **3.B.1** and hence the mesophase exhibited by these has been characterized as a columnar phase with a rectangular lattice (Col_r). The remaining homologues **3.D.5** to **3.D.14** showed the same type of mesophase. When a thin film of sample of compound **3.D.5** was filled in a cell treated for planar alignment and cooled slowly from isotropic phase, fascinating textures similar to that obtained for a B₇ were seen. A typical texture obtained for this phase is shown in figure **3.4.a**. The other variants of the texture obtained for compound **3.D.13** are shown in figures **3.4.b** and **3.4.c**. On the basis of XRD data obtained and electro-optical studies (described later), the mesophase exhibited by compounds **3.D.5** to **3.D.14** are the same and has been characterized as a B_{7A} phase. A DSC thermogram obtained for compound **3.D.13** is given in figure **3.5**. The enthalpy for the clearing temperature is quite high and varies from about 21 to 29 kJ mol⁻¹ and are comparable to those obtained for a B₇ phase in various other systems.

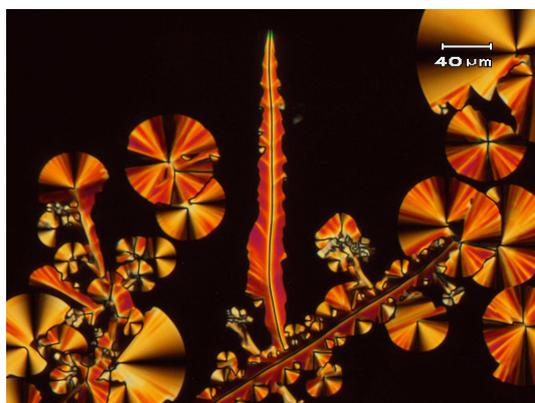
A plot of the transition temperature as a function of the number of carbon atoms in the terminal chain for compounds belonging to series **3.D** is given in figure **3.6**. A rising curve for the Col_r clearing temperature and almost a flat curve for the B_{7A} to isotropic phase can be seen.

Table 3.4: Transition temperatures (°C) and the associated enthalpy values ($\Delta H/\text{kJ mol}^{-1}$) (in italics) for compounds of series 3.D^a

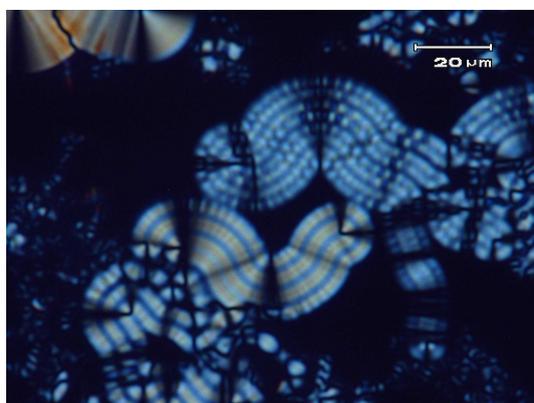


Compound	<i>n</i>	Cr	Col _r	B _{7A}	I	
3.D.1	5	•	124.0 <i>100.0</i>	(• 115.5) 28.8	-	•
3.D.2	6	•	118.0 <i>59.9</i>	• 121.0 29.4	-	•
3.D.3	7	•	108.5 <i>47.8</i>	• 122.0 28.9	-	•
3.D.4	8	•	109.0 <i>47.6</i>	• 122.5 29.3	-	•
3.D.5	9	•	111.0 <i>48.1</i>	-	• 122.5 28.6	•
3.D.6	10	•	112.0 <i>47.6</i>	-	• 122.5 28.0	•
3.D.7	11	•	110.5 <i>45.3</i>	-	• 122.5 26.3	•
3.D.8	12	•	112.0 <i>48.6</i>	-	• 123.0 26.6	•
3.D.9	13	•	113.0 <i>47.7</i>	-	• 123.0 25.6	•
3.D.10	14	•	112.5 <i>48.0</i>	-	• 123.0 25.2	•
3.D.11	15	•	111.5 <i>48.0</i>	-	• 123.0 24.5	•
3.D.12	16	•	109.5 <i>50.8</i>	-	• 123.0 23.7	•
3.D.13	18	•	107.5 <i>60.2</i>	-	• 123.0 22.3	•
3.D.14	20	•	105.3 <i>57.5</i>	-	• 123.0 20.9	•

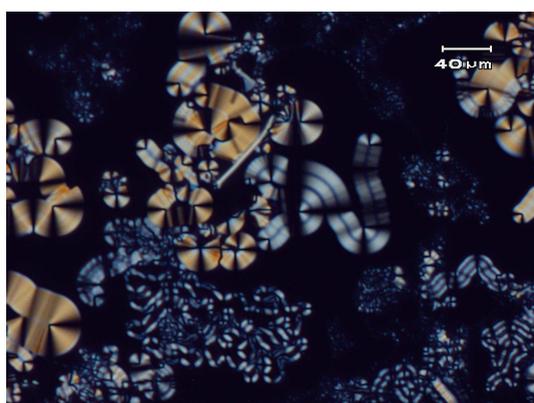
^aSee Table 3.1:



(a)



(b)



(c)

Figure 3.4: Optical textures obtained for B_{7A} phase of compound 3.D.5 at (a) T = 108 °C; compound 3.D.13 at (b) T = 119 °C and (c) T = 119 °C different region of same compound in a cell treated for planar alignment.

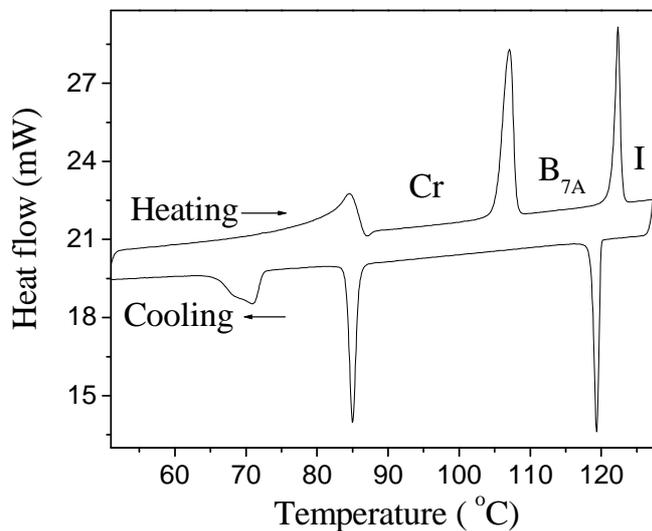


Figure 3.5: A DSC thermogram obtained for compound 3.D.13 showing B_{7A} phase.

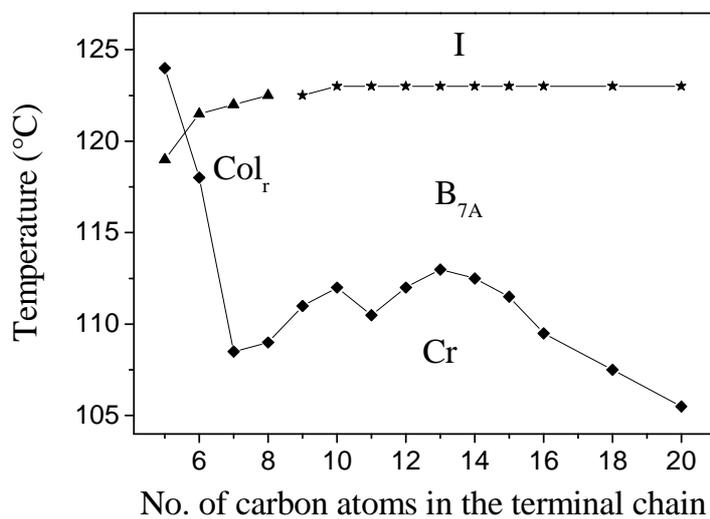


Figure 3.6: A plot of transition temperature as a function of number of carbon atoms in the terminal *n*-alkoxy chain for compounds of series 3.D.

3.3.2: X-Ray diffraction measurements

The structure of the mesophases of compounds belonging to series **3.A**, **3.B**, **3.C** and **3.D** were investigated by XRD measurements. For example, a powder sample of compound **3.A.1** was filled in the isotropic state in Lindemann capillary having a diameter 0.7 mm and the ends were sealed carefully. The sample was cooled to mesophase and on irradiation, gave three sharp reflections in the small angle region with d-spacings of 37.94 Å, 25.97 Å and 19.31 Å which could be indexed to 11, 20 and 22 plane of a columnar rectangular lattice with lattice parameters $a = 51.94$ Å and $b = 55.55$ Å. In addition, a diffuse wide angle reflection at about 4.66 Å was obtained indicating a liquid-like order of the phase. The XRD intensity profile obtained for the mesophase of this compound is shown in figure **3.7.a**. On the basis of XRD data, this phase has been characterized as a Col_r phase. Similar XRD measurements were carried out for the other compounds as well.

Mesophases of compounds **3.B.1** and **3.B.2** showed reflections seen for a columnar rectangular phase and the d-spacings obtained are given in table **3.5**. The higher homologues **3.B.3** and **3.B.4** gave a simple layered order in the small angle region which are in the ratio of 1 : ½ : ⅓. The d-spacings obtained in the mesophase for these compounds are also given in table **3.5**. The XRD intensity profile obtained for compound **3.B.3** is shown in figure **3.7.b**.

Similarly, X-ray diffraction measurements were carried out on the mesophase of compounds of series **3.C**. All the compounds exhibited Col_r phase which could be indexed to a centered rectangular lattice and the data obtained are given in table **3.5**. On the basis of XRD and electro-optical studies, the mesophase of compounds **3.C.1** and **3.C.2** has been characterized as Col_r phase whereas the mesophase of compounds **3.C.3** and **3.C.4** has been characterized as a Col_rP_A mesophase. The XRD intensity profile obtained for the mesophase of compound **3.C.4** is shown in figure **3.8.a**. Here, only the prominent peaks were taken and indexed to a columnar rectangular lattice. However, high resolution X-ray measurements on the mesophase may provide a better picture of the structure of this mesophase. Similarly, it is necessary to carry out high resolution XRD measurements for compounds **3.D.5** to **3.D.14** of series **3.D**. The XRD intensity profile obtained for compound **3.D.13** is shown in figure **3.8.b**. As can be seen, the peaks in the small angle region are not well resolved. It is difficult to determine the exact

structure of the mesophase with this available data. However, from the available data, it has been possible to fit the data to an oblique lattice for most of the compounds while a rectangular lattice was found for some of the compounds. Since exact structure could not be determined with certainty, the mesophase of these compounds **3.D.5** to **3.D.14** has been assigned the general symbol B_{7A} on the basis of textural observations and electro-optical studies.

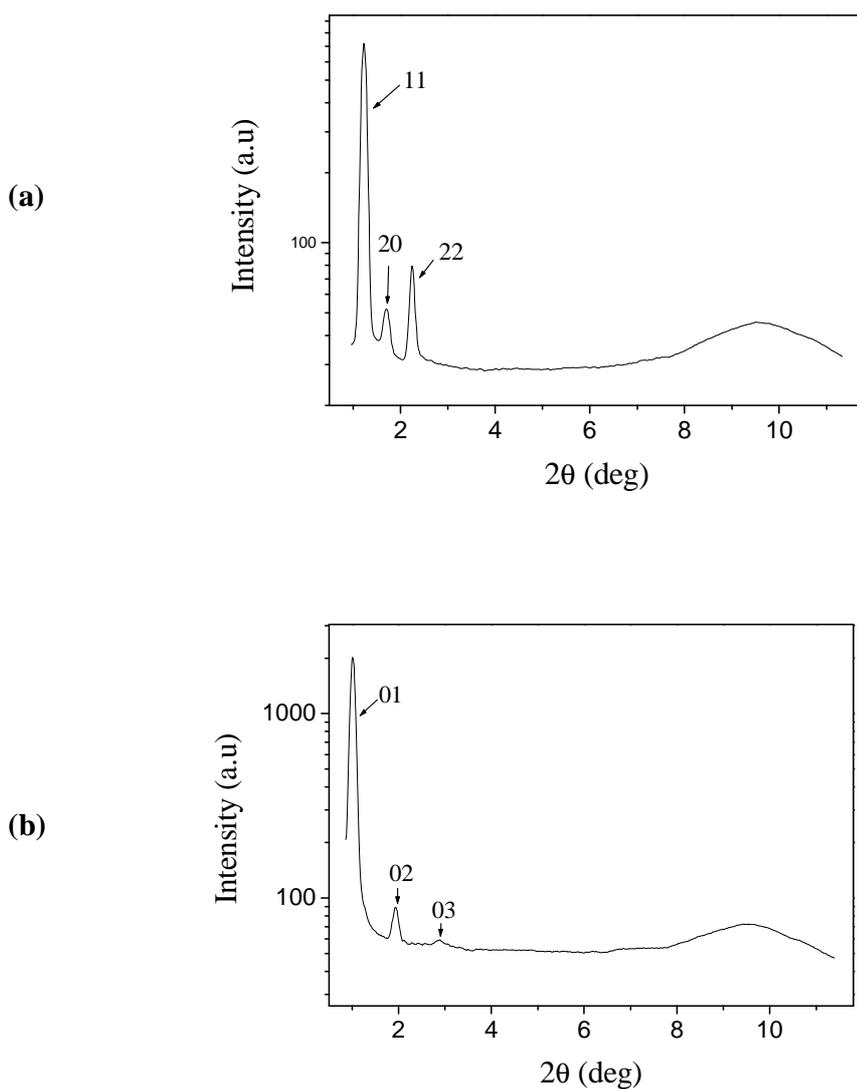
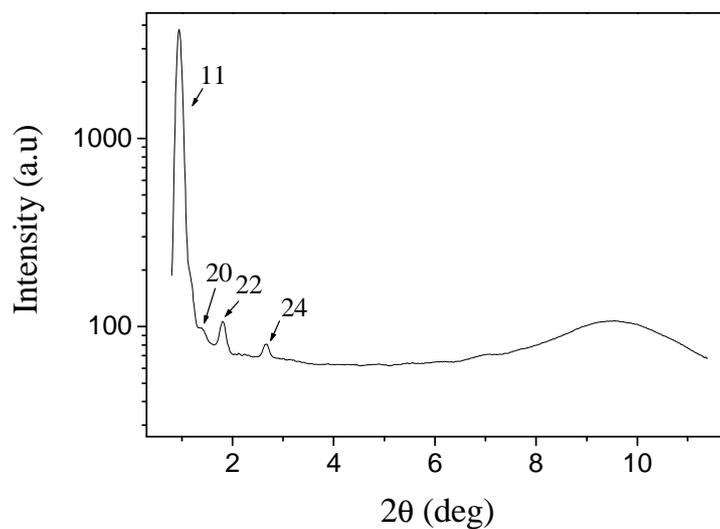
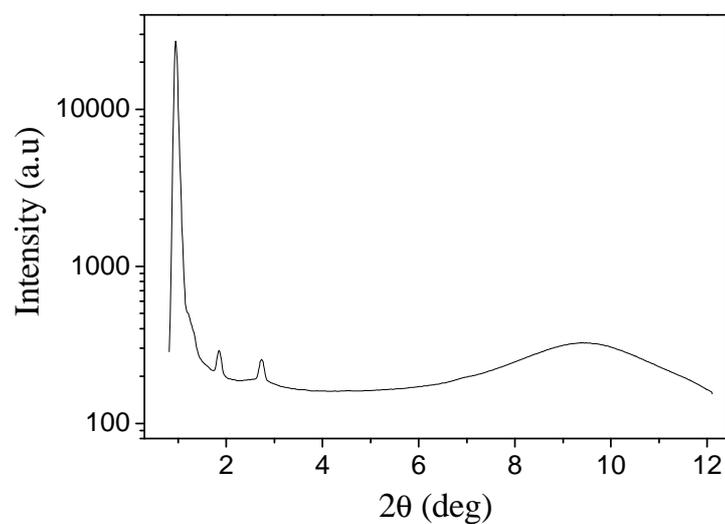


Figure 3.7: The XRD intensity profiles obtained for Col_r phase of compound **3.A.1** (a) at $T = 122\text{ }^\circ\text{C}$ and (b) B_7' phase of compound **3.B.3** at $T = 125\text{ }^\circ\text{C}$.



(a)



(b)

Figure 3.8: The XRD intensity profiles obtained for Col_rP_A phase of compound 3.C.4 (a) at T = 115 °C and (b) B_{7A} phase of compound 3.D.13 at T = 115 °C.

Table 3.5: d-spacings obtained by XRD measurements and calculated lattice parameters of the mesophases of compounds of series 3.A, 3.B and 3.C

Compound	d-spacings/Å(Miller indices)	Lattice parameters/Å		Phase type	T/°C
		a	b		
3.A.1	37.94(11), 25.97(20), 19.31(22)	51.94	55.55	Col _r	122
3.B.1	39.59(11), 28.95(20), 20.09(22)	57.9	54.25	Col _r	125
3.B.2	42(11), 33.07(20), 25.57(12), 21.26(22)	66.14	54.36	Col _r	125
3.B.3	45.0(01), 22.5(02), 15.3(03)	-	-	SmCP _A	125
3.B.4	48.0(01), 24.0(02), 16.3(03)	-	-	SmCP _A	125
3.C.1	41.4(11), 30.86(20), 20.22(22)	61.72	55.82	Col _r	115
3.C.2	42.88(11), 31.76(20), 20.99(22)	63.52	58.12	Col _r	118
3.C.3	46.8(11), 32.07(20), 23.39(22), 15.7(40)	64.14	68.43	Col _r P _A	115
3.C.4	48.72(11), 31.76(20), 24.41(22), 16.7(24)	63.52	75.92	Col _r P _A	115

3.3.3: Electro-optical studies

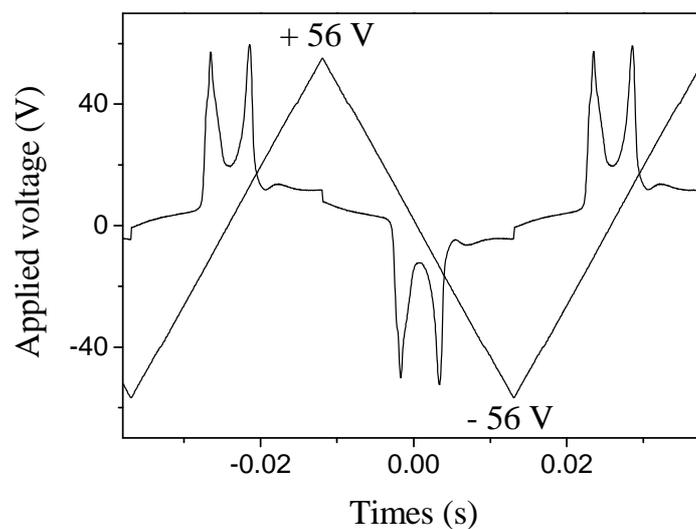
In order to examine the polar nature of the mesophase, electro-optical studies were carried out on the mesophases using the standard triangular-wave field method. As an example, a sample of compound **3.B.4** was filled in a commercial cell (EHC, Japan) having a thickness 6 μm with and its inner surfaces treated for planar alignment. Then, the sample was slowly cooled to mesophase and a triangular-wave field was applied. Above a threshold voltage, two peaks

per half period of the applied field were seen in the current response trace. On applying an appropriate voltage of 112 V_{pp} and a frequency of 20 Hz, symmetrical peaks current response trace was obtained and the same is shown in figure **3.9.a**. The optical textures obtained during switching under the field and on termination of the field are also shown in figures **3.9.b** and **3.9.c** respectively. The two peaks in the half-cycle indicate a antiferroelectric ground state. The polarization value was calculated to be 385 nC cm⁻². Hence, the mesophase has been assigned the symbol B₇' to indicate that this is a switchable B₇ phase.

Similar experiments were carried out for the compounds of series **3.C** and **3.D** as well and current response traces obtained for the same are shown in figures **3.10** and **3.11** respectively. Compound **3.C.4** did not show two well resolved current peaks but the antiferroelectric nature of the mesophase could be established. Thus, the mesophase was characterized as Col_rP_A phase. In the case of compounds **3.A.3** and **3.A.4** of series **3.A**, we were not able to record the current response trace as the sample crystallizes rapidly.

3.4: Summary

Several compounds belonging to four different homologous series and derived from 3-hydroxybiphenyl-4-carboxylic acid have been synthesized and their mesomorphic properties were investigated. The compounds indicate that slight modification in the chemical structure has a bearing on the type of mesophase obtained. A non-switchable columnar phase with a rectangular lattice, a smectic C phase with antiferroelectric properties and showing helical textures and columnar phase with antiferroelectric properties with variants of fascinating optical textures have been obtained. Although, the symbol B_{7A} has been assigned to the mesophases of the higher homologues of series **3.D**, high resolution XRD data are necessary to conclusively establish their structures. These represent the first examples of B_{7A} phase obtained from unsymmetrical 3-hydroxybiphenyl-4-carboxylic acid moiety.



(a)

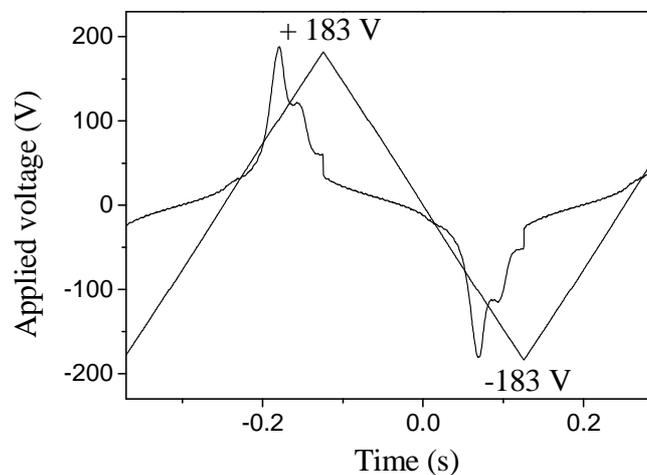


(b)



(c)

Figure 3.9: (a) Switching current response trace obtained for compound 3.B.4 in the B_7' phase at $T = 125\text{ }^\circ\text{C}$ on applying a triangular-wave field, at 112 V_{pp} , 20 Hz ; $P_S \approx 385\text{ nC cm}^{-2}$; cell thickness, $6\text{ }\mu\text{m}$. Optical textures obtained (b) under the electric field and (c) without the electric field.



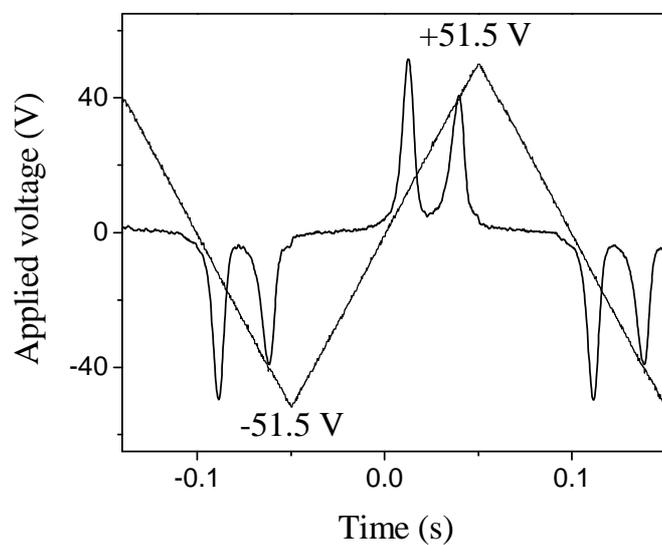
(a)



(b)

(c)

Figure 3.10: (a) Switching current response trace obtained for compound 3.C.4 in the $Col_P A$ phase at $T = 115\text{ }^\circ\text{C}$ on applying a triangular-wave field, at 366 V_{pp} , 2 Hz ; $P_S \approx 345\text{ nC cm}^{-2}$; cell thickness, $6\text{ }\mu\text{m}$. Optical textures obtained (b) under the electric field and (c) without the field.



(a)



(b)



(c)

Figure 3.11: (a) Switching current response trace obtained for compound 3.D.13 in the B_{7A} phase at $T = 114\text{ }^\circ\text{C}$ on applying a triangular-wave field, at 103 V_{pp} , 5 Hz ; $P_S \approx 492\text{ nC cm}^{-2}$; cell thickness, $4\text{ }\mu\text{m}$. Optical textures obtained (b) under the electric field and (c) without the field.

Experimental

4-*n*-Octyloxyphenol, 3.A.b

This was prepared following a procedure described in the literature [17]. mp 62-63 °C.

4-Benzyloxyphenyl *n*-nonanoate, 3.B.a

4-Benzyloxyphenol, **3.a** (4 g, 20 mmol), *n*-nonanoic acid (3.16 g, 20 mmol) and a catalytic amount of DMAP in dichloromethane (50 mL) was stirred for 10 min at room temperature. To this stirred mixture, DCC (4.53 g, 22 mmol) was added and stirring continued for a further 2 h. The precipitated *N,N'*-dicyclohexylurea was filtered off and washed thoroughly with chloroform. The filtrate was concentrated to obtain a material, which was passed through a column of silica gel using a mixture of chloroform and hexane as an eluant. The product obtained from the column was further purified by crystallization using *n*-hexane. Yield: 5.44 g (80%); mp 68-70 °C; IR (nujol) ν_{\max} : 2953, 2824, 2852, 1749, 1718, 1606, 1508, 1456, 1377, 1342 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 7.43- 7.28 (m, 7H, Ar-H), 6.97 (d, $J = 8.40$ Hz, 2H, Ar-H), 5.04 (s, 2H, Ar-O-CH₂-Ar-), 2.52 (t, $J = 7.52$ Hz, 2H, Ar-OCO-CH₂-), 1.77-1.69 (quin, $J = 7.32$ Hz, 2H, Ar-OCO-CH₂-CH₂-), 1.49-1.03 (m, 10H, -(CH₂)₅-), 0.97 (t, $J = 6.44$ Hz, 3H, -CH₃); Elemental analysis: C₂₂H₂₈O₃ requires C 77.61, H 8.29; found C 78.0, H 8.62%.

4-Hydroxyphenyl *n*-nonanoate, 3.B.b

Compound **3.B.a**, (4 g) in 1,4-dioxane (50 mL) and 5% Pd-C (0.8 g) were stirred in an atmosphere of hydrogen at 55 °C until the reaction was complete which was monitored by thin layer chromatography using Merck 60 silica gel plates. The reaction mixture was filtered hot and the solvent was evaporated to obtain the product, which was crystallized using a mixture of *n*-hexane and 1,4-dioxane. Yield: 2.52 g (86%); mp 70-72.5 °C; IR (nujol) ν_{\max} : 3198, 2955, 2922, 2852, 1751, 1747, 1600, 1465, 1377, 1342 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 6.88 (d, $J = 8.82$ Hz, 2H, Ar-H), 6.72 (d, $J = 8.92$ Hz, 2H, Ar-H), 5.63 (s, 1H, Ar-OH, exchangeable with D₂O), 2.53 (t, $J = 7.48$ Hz, 2H, Ar-OCO-CH₂-), 1.77-1.7 (quin, $J = 7.28$ Hz, 2H, Ar-OCO-CH₂-CH₂-), 1.4-1.28 (m, 14H, -(CH₂)₇-), 0.88 (t, $J = 6.56$ Hz, 3H, -CH₃); Elemental analysis: C₁₅H₂₂O₃ requires C 71.97, H 8.86; found C 71.77, H 9.2%.

4-Benzyloxybenzoic acid, 3.b

This compound was prepared following a procedure described in the literature [18].

***n*-Octyl-(4-benzyloxy)benzoate, 3.C.a**

n-Octyl-(4-benzyloxy)benzoate, **3.C.a** was synthesized following a procedure described for the preparation of compound **3.B.a** using 4-benzyloxybenzoic acid, **3.b** and *n*-octanol as starting material. Yield: (88%); liq; IR (nujol) ν_{\max} : 2929, 2854, 1720, 1714, 1606, 1606, 1581, 1510, 1454, 1421, 1384 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.99 (d, $J = 8.92$ Hz, 2H, Ar-H), 7.43-7.35 (m, 5H, Ar-H), 6.99 (d, $J = 8.9$ Hz, 2H, Ar-H), 5.12 (s, 2H, Ar-O-CH₂-Ar-), 4.27 (t, $J = 6.64$ Hz, 2H, Ar-COO-CH₂-), 1.76-1.7 (quin, $J = 6.64$ Hz, 2H, Ar-COO-CH₂-CH₂-), 1.42-1.25 (m, 14H, -(CH₂)₇-), 0.87 (t, $J = 6.64$ Hz, 3H, -CH₃); Elemental analysis: C₂₂H₂₈O₃ requires C 77.61, H 8.29; found C 77.85, H 8.6%.

***n*-Octyl-4-hydroxybenzoate, 3.C.b**

This compound was synthesized following a procedure described for the preparation of compound **3.B.b** using *n*-octyl-(4-benzyloxy)benzoate, **3.C.a** as starting material. Yield 2.64 g (90%), mp 50-52 °C; IR (nujol) ν_{\max} : 3389, 3063, 2953, 2922, 2854, 2725, 2661, 1680, 1604, 1587, 1510, 1456, 1377, 1350 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.95 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.89 (d, $J = 8.8$ Hz, 2H, Ar-H), 4.29 (t, $J = 6.8$ Hz, 2H, Ar-COO-CH₂-), 1.78-1.71 (quin, $J = 6.8$ Hz, 2H, Ar-COO-CH₂-CH₂-), 1.44-1.27 (m, 14H, -(CH₂)₇-), 0.87 (t, $J = 6.8$ Hz, 3H, -CH₃); Elemental analysis: C₁₅H₂₂O₃ requires C 71.97, H 8.86; found C 72.24, H 9.15%.

3-Benzyloxybiphenyl-4-carboxylic acid, 3.c

The synthesis of 3-benzyloxybiphenyl-4-carboxylic acid, **3.c** was already described in chapter 2.

4-*n*-Octyloxyphenyl-3-benzyloxybiphenyl-4-carboxylate, 3.A.c

This was synthesized following a procedure described for the preparation of compound **3.B.a** using 3-benzyloxybiphenyl-4-carboxylic acid, **3.c** and 4-*n*-octyloxyphenol, **3.A.b** as starting material. Yield: (75%); mp 89-90.5 °C; IR (nujol) ν_{\max} : 2953, 2922, 2852, 2710, 2669, 1743, 1591, 1508, 1456, 1396, 1375 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.24 (d, $J = 8.48$ Hz,

2H, Ar-H), 7.7 (d, $J = 8.54$ Hz, 2H, Ar-H), 7.48-7.34 (m, 5H, Ar-H), 7.12 (d, $J = 9.01$ Hz, 2H, Ar-H), 7.03 (d, $J = 6.26$ Hz, 1H, Ar-H), 6.93 (d, $J = 9.05$ Hz, 2H, Ar-H), 5.14 (s, 2H, Ar-O-CH₂-Ar-), 3.96 (t, $J = 6.54$ Hz, 2H, Ar-O-CH₂-), 1.82-1.79 (quin, $J = 6.75$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.5-1.27 (m, 10H, -(CH₂)₅-), 0.89 (t, $J = 6.64$ Hz, 3H, -CH₃); Elemental analysis: C₃₄H₃₆O₄ requires C 80.28, H 7.13; found C 79.92, H 7.22%.

4-*n*-Octyloxyphenyl-3-hydroxybiphenyl-4-carboxylate, 3.A.d

This was synthesized following a procedure described for the preparation of compound 3.B.b using compound 3.A.c. Yield: (91%); mp 130-131.5 °C; IR (nujol) ν_{\max} : 3402, 2953, 2923, 2852, 2710, 2669, 1742, 1598, 1506, 1461, 1400, 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.25 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.69 (d, $J = 8.18$ Hz, 2H, Ar-H), 7.35 (t, $J = 7.83$ Hz, 1H, Ar-H), 7.22 (d, $J = 7.72$ Hz, 1H, Ar-H), 7.13 (d, $J = 9.02$ Hz, 3H, Ar-H), 6.93 (d, $J = 9$ Hz, 2H, Ar-H), 6.87 (d, $J_1 = 2.43$ Hz, $J_2 = 5.6$ Hz, 1H, Ar-H), 5.06 (s, 1H, Ar-OH, exchangeable with D₂O), 3.96 (t, $J = 6.6$ Hz, 2H, Ar-O-CH₂-), 1.82-1.75 (quin, $J = 7.01$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.46-1.29 (m, 10H, -(CH₂)₅-), 0.89 (t, $J = 6.64$ Hz, 3H, -CH₃); Elemental analysis: C₂₇H₃₀O₄ requires C 77.48, H 7.21; found C 77.66, H 7.47%.

4-*n*-Alkoxybenzoyloxy-4-benzoic acid, 3.d

The synthesis of two-ring carboxylic acids, 3.d has been described in chapter 2.

2-Fluoro-4-benzyloxybenzoic acid, 3.e

This compound was synthesized according to a procedure described in the literature [19].

4-*n*-Octyloxyphenyl-3'-(4-benzyloxy-2-fluorobenzoyloxy)biphenyl-4-carboxylate, 3.D.a

This was synthesized following a procedure described for the preparation of compound 3.B.a using compound 3.A.d and 4-benzyloxy-2-fluorobenzoic acid, 3.e. Yield: (86%); mp 102-103 °C; IR (nujol) ν_{\max} : 2951, 2922, 2852, 2710, 2667, 1720, 1712, 1620, 1606, 1504, 1461, 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.25 (d, $J = 8.31$ Hz, 2H, Ar-H), 8.09 (t, $J = 8.58$ Hz, 2H, Ar-H), 7.73 (d, $J = 8.32$ Hz, 2H, Ar-H), 7.54-7.51 (m, 3H, Ar-H), 7.43-7.37 (m, 4H, Ar-H), 7.28 (t, $J = 7.83$ Hz, 1H, Ar-H), 7.13 (d, $J = 8.95$ Hz, 2H, Ar-H), 6.93 (d, $J = 9$ Hz, 2H, Ar-H), 6.87 (dd, $J_1 = 2.16$ Hz, $J_2 = 6.65$ Hz, 1H, Ar-H), 6.78 (dd, $J_1 = 2.23$ Hz, $J_2 = 8.8$ Hz, 1H, Ar-H),

5.15 (s, 2H, Ar-O-CH₂-Ar-), 3.96 (t, $J = 6.51$ Hz, 2H, Ar-O-CH₂-), 1.81-1.75 (quin, $J = 7.77$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.48-1.29 (m, 10H, -(CH₂)₅-), 0.89 (t, $J = 6.94$ Hz, 3H, -CH₃); Elemental analysis: C₄₁H₃₉FO₆ requires C 76.12, H 6.08; found C 75.88, H 6.33%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-hydroxybenzoyloxy)biphenyl-4-carboxylate, 3.D.b

This was synthesized following a procedure described for the preparation of compound 3.B.b using compound 3.A.d and 4-benzyloxy-2-fluorobenzoic acid, 3.e. Yield: (91%); mp 141-143 °C; IR (nujol) ν_{\max} : 3379, 2952, 2923, 2852, 2710, 2671, 1732, 1716, 1697, 1635, 1591, 1558, 1541, 1508, 1456, 1375 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.25 (d, $J = 8.36$ Hz, 2H, Ar-H), 8.05 (t, $J = 8.5$ Hz, 2H, Ar-H), 7.73 (d, $J = 8.32$ Hz, 2H, Ar-H), 7.55-7.51 (m, 3H, Ar-H), 7.26 (t, $J = 7.72$ Hz, 1H, Ar-H), 7.13 (d, $J = 9$ Hz, 2H, Ar-H), 6.93 (d, $J = 9$ Hz, 2H, Ar-H), 6.72 (dd, $J_1 = 2.2$ Hz, $J_2 = 8.67$ Hz, 1H, Ar-H), 6.65 (dd, $J_1 = 2.4$ Hz, $J_2 = 9.8$ Hz, 1H, Ar-H), 5.93 (s, 1H, Ar-OH, exchangeable with D₂O), 1.8-1.77 (quin, $J = 6.92$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.46-1.29 (m, 10H, -(CH₂)₅-), 0.89 (t, $J = 7$ Hz, 3H, -CH₃); Elemental analysis: C₃₄H₃₃FO₆ requires C 73.35, H 5.98; found C 73.01, H 5.75%.

3-Fluoro-4-*n*-alkoxybenzoic acid, 3.f

These acids were synthesized according to a procedure described in the literature [20].

4-*n*-Nonanoyloxyphenyl-3-benzyloxybiphenyl-4-carboxylate, 3.B.c

This was synthesized following a procedure described for the preparation of compound 3.B.a using 3-benzyloxybiphenyl-4-carboxylic acid, 3.c and 4-hydroxyphenyl *n*-nonanoate, 3.B.b as starting materials. Yield: (76%); mp 94.5-95.5 °C; IR (nujol) ν_{\max} : 2953, 2922, 2852, 2727, 2665, 1766, 1728, 1606, 1587, 1564, 1500, 1462, 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.24 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.71 (d, $J = 8.44$ Hz, 2H, Ar-H), 7.47 (d, $J = 7.45$ Hz, 2H, Ar-H), 7.42-7.34 (m, 5H, Ar-H), 7.23 (d, $J = 5.4$ Hz, 3H, Ar-H), 7.15 (d, $J = 6.76$ Hz, 2H, Ar-H), 7.03 (dd, $J_1 = 1.21$ Hz, $J_2 = 5.72$ Hz, 1H, Ar-H), 5.15 (s, 2H, Ar-O-CH₂-Ar-); 2.56 (t, $J = 7.52$ Hz, 2H, Ar-OCO-CH₂-), 1.8-1.72 (quin, $J = 7.36$ Hz, 2H, Ar-OCO-CH₂-CH₂-), 1.44-1.25 (m, 10H, -(CH₂)₅-), 0.89 (t, $J = 6.9$ Hz, 3H, -CH₃); Elemental analysis: C₃₅H₃₆O₅ requires C 78.33, H 6.75; found C 78, H 6.78%.

4-*n*-Nonanoyloxyphenyl-3-hydroxybiphenyl-4-carboxylate, 3.B.d

This was synthesized following a procedure described for the preparation of compound **3.B.b** using 3-benzyloxybiphenyl-4-carboxylic acid, **3.c**. Yield: (77%); mp 122-123.5 °C; IR (nujol) ν_{\max} : 3406, 2955, 2922, 2852, 2727, 2665, 1734, 1716, 1604, 1599, 1564, 1521, 1462, 1404, 1375 cm^{-1} ; ^1H NMR (400 MHz, CD_3COCD_3) δ : 8.48 (s, 1H, Ar-OH, exchangeable with D_2O), 8.21 (d, $J = 8.24$ Hz, 2H, Ar-H), 7.81 (d, $J = 8.49$ Hz, 2H, Ar-H), 7.33-7.3 (m, 3H, Ar-H), 7.2 (d, $J = 9$ Hz, 4H, Ar-H), 6.9 (dd, $J_1 = 1.56$ Hz, $J_2 = 5.8$ Hz, 1H, Ar-H), 2.57 (t, $J = 7.45$ Hz, 2H, Ar-OCO-CH₂-), 1.74-1.67 (quin, $J = 7.25$ Hz, 2H, Ar-OCO-CH₂-CH₂-), 1.42-1.28 (m, 10H, -(CH₂)₅-), 0.86 (t, $J = 6.77$ Hz, 3H, -CH₃); Elemental analysis: C₂₈H₃₀O₅ requires C 75.31, H 6.76; found C 75.61, H 6.95%.

4-*n*-Octyloxycarbonylphenyl-3-benzyloxybiphenyl-4-carboxylate, 3.C.c

This was synthesized following a procedure described for the preparation of compound **3.B.a** using 3-benzyloxybiphenyl-4-carboxylic acid, **3.c** and 4-*n*-octyloxyphenol, **3.A.b** as starting materials. Yield: (88%); mp 106-107.5 °C; IR (nujol) ν_{\max} : 2949, 2920, 2914, 2901, 2850, 2727, 2663, 1737, 1705, 1604, 1591, 1456, 1377 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.25 (d, $J = 6.7$ Hz, 2H, Ar-H), 8.13 (d, $J = 6.62$ Hz, 2H, Ar-H), 7.71 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.47 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.4 (t, $J = 6.8$ Hz, 3H, Ar-H), 7.35 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.32 (d, $J = 8.31$ Hz, 2H, Ar-H), 7.275-7.269 (m, 2H, Ar-H), 7.04 (dd, $J_1 = 1.1$ Hz, $J_2 = 6$ Hz, 1H, Ar-H), 5.15 (s, 2H, Ar-O-CH₂-Ar-), 4.33 (t, $J = 6.68$ Hz, 2H, Ar-O-CH₂-), 1.79-1.75 (quin, $J = 8.43$ Hz, 2H, Ar-COO-CH₂-CH₂-), 1.45-1.29 (m, 10H, -(CH₂)₅-), 0.9 (t, $J = 6.76$ Hz, 3H, -CH₃); Elemental analysis: C₃₅H₃₆O₅ requires C 78.33, H 6.75; found C 78.69, H 7.12%.

4-*n*-Octyloxycarbonylphenyl-3-hydroxybiphenyl-4-carboxylate, 3.C.d

This was synthesized following a procedure described for the preparation of compound **3.B.b** using 3-benzyloxybiphenyl-4-carboxylic acid, **3.c**. Yield: (91%); mp 119.5-121.5 °C; IR (nujol) ν_{\max} : 3338, 2955, 2920, 2852, 2727, 2665, 1737, 1730, 1680, 1599, 1568, 1460, 1454, 1406, 1377 cm^{-1} ; ^1H NMR (400 MHz, CD_3COCD_3) δ : 8.49 (s, 1H, Ar-OH, exchangeable with D_2O), 8.23 (d, $J = 8.6$ Hz, 2H, Ar-H), 8.11 (d, $J = 6.42$ Hz, 2H, Ar-H), 7.83 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.45 (d, $J = 8.78$ Hz, 2H, Ar-H), 7.32 (t, $J = 5.7$ Hz, 1H, Ar-H), 7.35 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.21 (d, $J = 8.98$ Hz, 2H, Ar-H), 6.9 (dd, $J_1 = 1.5$ Hz, $J_2 = 6.1$ Hz, 1H, Ar-H), 4.31 (t,

$J = 7.4$ Hz, 2H, Ar-COO-CH₂-), 1.79-1.75 (quin, $J = 7.11$ Hz, 2H, Ar-COO-CH₂-CH₂-), 1.48-1.28 (m, 10H, -(CH₂)₅-), 0.85 (t, $J = 6.99$ Hz, 3H, -CH₃); Elemental analysis: C₂₈H₃₀O₅ requires C 75.31, H 6.76; found C 75.69, H 6.54%.

4-*n*-Octyloxyphenyl-3'-(4-(4-*n*-octyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate,

3.A.1

A mixture of three-ring phenol, **3.A.d** (0.100 g, 0.239 mmol), 4-*n*-octyloxybenzoyloxy-4-benzoic acid, **3.d** (0.97 g, 0.263 mmol) and a catalytic amount of DMAP were stirred in anhydrous dichloromethane for 10 min. To this, DCC (0.59 g, 0.287 mmol) was added and stirred for a further 12 h. The precipitated *N,N'*-dicyclohexylurea was filtered off and washed with excess of chloroform. Removal of solvent from the filtrate provided a white material, which was chromatographed on silica gel using chloroform as eluent. The solvent was removed from the eluate, to obtain target compound **3.A.1** which was crystallized using a mixture of chloroform and acetonitrile. Yield: 0.143 g (78%); mp 136.8 °C; IR (KBr) ν_{\max} : 3076, 3051, 2955, 2926, 2854, 1747, 1735, 1730, 1604, 1504, 1467, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.3 (d, $J = 8.77$ Hz, 2H, Ar-H), 8.26 (d, $J = 8.53$ Hz, 2H, Ar-H), 8.16 (d, $J = 8.92$ Hz, 2H, Ar-H), 7.74 (d, $J = 8.49$ Hz, 2H, Ar-H), 7.57-7.51 (m, 3H, Ar-H), 7.39 (d, $J = 8.77$ Hz, 2H, Ar-H), 7.27 (t, $J = 7.1$ Hz, 1H, Ar-H), 7.13 (d, $J = 6.76$ Hz, 2H, Ar-H), 6.99 (d, $J = 8.97$ Hz, 2H, Ar-H), 6.93 (d, $J = 9.04$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.52$ Hz, 2H, Ar-O-CH₂), 1.85-1.75 (quin, $J = 6.57$ Hz, 4H, 2 × Ar-O-CH₂-CH₂-), 1.48-1.3 (m, 20H, -(CH₂)₅- + -(CH₂)₅-), 0.89 (t, $J = 7.16$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₄₉H₅₄O₈ requires C 76.34, H 7.06; found C 76.7, H 6.58%.

4-*n*-Octyloxyphenyl-3'-(4-(4-*n*-decyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate,

3.A.2

This and other target compounds described in this chapter were synthesized following a procedure described for the preparation of compound **3.A.1**. Yield: (81%); mp 139.3 °C; IR (KBr) ν_{\max} : 3076, 3052, 2953, 2924, 2852, 1749, 1728, 1604, 1504, 1465, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.3 (d, $J = 8.75$ Hz, 2H, Ar-H), 8.26 (d, $J = 8.53$ Hz, 2H, Ar-H), 8.15 (d, $J = 8.92$ Hz, 2H, Ar-H), 7.74 (d, $J = 8.51$ Hz, 2H, Ar-H), 7.57-7.51 (m, 3H, Ar-H), 7.39 (d, $J = 8.77$ Hz, 2H, Ar-H), 7.27 (t, $J = 7.1$ Hz, 1H, Ar-H), 7.13 (d, $J = 6.76$ Hz, 2H, Ar-H), 6.98 (d,

$J = 8.94$ Hz, 2H, Ar-H), 6.93 (d, $J = 9.01$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.48$ Hz, 2H, Ar-O-CH₂-), 1.85-1.77 (quin, $J = 6.62$ Hz, 4H, 2 × Ar-O-CH₂-CH₂-), 1.48-1.29 (m, 24H, -(CH₂)₅- + -(CH₂)₇-), 0.88 (t, $J = 7.23$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₁H₅₈O₈ requires C 76.67, H 7.34; found C 76.80, H 7.43%.

4-*n*-Octyloxyphenyl-3'-(4-(4-*n*-pentadecyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.A.3

Yield: (84%); mp 133.4 °C; IR (KBr) ν_{\max} : 3075, 3051, 2955, 2926, 2854, 1747, 1733, 1604, 1504, 1463, 1396 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.3 (d, $J = 8.8$ Hz, 2H, Ar-H), 8.26 (d, $J = 8.65$ Hz, 2H, Ar-H), 8.15 (d, $J = 8.94$ Hz, 2H, Ar-H), 7.74 (d, $J = 8.55$ Hz, 2H, Ar-H), 7.57-7.51 (m, 3H, Ar-H), 7.39 (d, $J = 8.82$ Hz, 2H, Ar-H), 7.28 (t, $J = 7.1$ Hz, 1H, Ar-H), 7.13 (d, $J = 6.76$ Hz, 2H, Ar-H), 6.98 (d, $J = 8.95$ Hz, 2H, Ar-H), 6.94 (d, $J = 9.12$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.54$ Hz, 2H, Ar-O-CH₂-), 1.85-1.75 (quin, $J = 6.7$ Hz, 4H, 2 × Ar-O-CH₂-CH₂-), 1.53-1.26 (m, 34H, -(CH₂)₅- + -(CH₂)₁₂-), 0.88 (t, $J = 7.24$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₆H₆₆O₈ requires C 77.39, H 7.89; found C 77.79, H 8.27%.

4-*n*-Octyloxyphenyl-3'-(4-(4-*n*-octadecyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.A.4

Yield: (80%); mp 130.8 °C; IR (KBr) ν_{\max} : 3074, 3053, 2954, 2926, 2854, 1745, 1737, 1606, 1504, 1467, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.3 (d, $J = 8.69$ Hz, 2H, Ar-H), 8.26 (d, $J = 8.51$ Hz, 2H, Ar-H), 8.15 (d, $J = 8.92$ Hz, 2H, Ar-H), 7.74 (d, $J = 8.49$ Hz, 2H, Ar-H), 7.57-7.51 (m, 3H, Ar-H), 7.39 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.28 (t, $J = 7.34$ Hz, 1H, Ar-H), 7.13 (d, $J = 6.72$ Hz, 2H, Ar-H), 6.99 (d, $J = 8.97$ Hz, 2H, Ar-H), 6.93 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.58$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.52$ Hz, 2H, Ar-O-CH₂-), 1.86-1.75 (quin, $J = 6.62$ Hz, 4H, 2 × Ar-O-CH₂-CH₂-), 1.48-1.25 (m, 40H, -(CH₂)₅- + -(CH₂)₁₅-), 0.88 (t, $J = 7.3$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₉H₇₄O₈ requires C 77.77, H 8.18; found C 77.84, H 7.89%.

4-*n*-Nonanoyloxyphenyl-3'-(4-(4-*n*-octyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.B.1

Yield: (71%); mp 114.9 °C; IR (KBr) ν_{\max} : 3071, 3045, 2953, 2921, 2852, 1732, 1712, 1690, 1604, 1585, 1506, 1467, 1437, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, $J = 9.1$ Hz, 2H, Ar-H), 8.26 (d, $J = 8.47$ Hz, 2H, Ar-H), 8.15 (d, $J = 8.92$ Hz, 2H, Ar-H), 7.75 (d, $J = 6.89$ Hz, 2H, Ar-H), 7.57-7.52 (m, 3H, Ar-H), 7.39 (d, $J = 8.77$ Hz, 2H, Ar-H), 7.28 (t, $J = 6.88$ Hz, 2H, Ar-H), 7.24 (d, $J = 4.5$ Hz, 1H, Ar-H), 7.15 (d, $J = 9$ Hz, 2H, Ar-H), 6.99 (d, $J = 8.97$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 2.56 (t, $J = 7.44$ Hz, 2H, Ar-OCO-CH₂-), 1.85-1.74 (quin, $J = 7$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.78-1.72 (quin, $J = 7.36$ Hz, 2H, Ar-OCO-CH₂-CH₂-), 1.53-1.3 (m, 20H, -(CH₂)₅- + -(CH₂)₅-), 0.89 (t, $J = 6.73$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₀H₅₄O₉ requires C 75.16, H 6.8; found C 75.53, H 6.65%.

4-*n*-Nonanoyloxyphenyl-3'-(4-(4-*n*-decyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.B.2

Yield: (72%); mp 116.7 °C; IR (KBr) ν_{\max} : 3072, 3047, 2956, 2922, 2850, 1742, 1730, 1691, 1604, 1585, 1568, 1508, 1467, 1400, 1383 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, $J = 9.32$ Hz, 2H, Ar-H), 8.27 (d, $J = 8.42$ Hz, 2H, Ar-H), 8.16 (d, $J = 8.89$ Hz, 2H, Ar-H), 7.74 (d, $J = 6.88$ Hz, 2H, Ar-H), 7.58-7.52 (m, 3H, Ar-H), 7.39 (d, $J = 8.77$ Hz, 2H, Ar-H), 7.29 (t, $J = 6.86$ Hz, 2H, Ar-H), 7.24 (d, $J = 4.31$ Hz, 1H, Ar-H), 7.15 (d, $J = 8.9$ Hz, 2H, Ar-H), 6.99 (d, $J = 8.88$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.52$ Hz, 2H, Ar-O-CH₂-), 2.56 (t, $J = 7.41$ Hz, 2H, Ar-OCO-CH₂-), 1.86-1.8 (quin, $J = 7.3$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.79-1.72 (quin, $J = 7.34$ Hz, 2H, Ar-OCO-CH₂-CH₂-), 1.53-1.28 (m, 24H, -(CH₂)₅- + -(CH₂)₇-), 0.89 (t, $J = 6.71$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₂H₅₈O₉ requires C 75.52, H 7.06; found C 75.87, H 6.73%.

4-*n*-Nonanoyloxyphenyl-3'-(4-(4-*n*-pentadecyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.B.3

Yield: (75%); mp 116.5 °C; IR (KBr) ν_{\max} : 3071, 3041, 2955, 2922, 2851, 1751, 1734, 1691, 1604, 1585, 1508, 1467, 1438, 1383 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, $J = 9.1$ Hz, 2H, Ar-H), 8.26 (d, $J = 8.41$ Hz, 2H, Ar-H), 8.15 (d, $J = 8.91$ Hz, 2H, Ar-H), 7.75 (d, $J = 6.74$ Hz, 2H, Ar-H), 7.57-7.52 (m, 3H, Ar-H), 7.39 (d, $J = 8.74$ Hz, 2H, Ar-H), 7.28 (t, $J = 6.82$ Hz, 2H, Ar-H), 7.24 (d, $J = 4.21$ Hz, 1H, Ar-H), 7.15 (d, $J = 9$ Hz, 2H, Ar-H), 6.99 (d,

$J = 8.21$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 2.56 (t, $J = 7.38$ Hz, 2H, Ar-OCO-CH₂-), 1.85-1.74 (quin, $J = 7.1$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.78-1.72 (quin, $J = 7.27$ Hz, 2H, Ar-OCO-CH₂-CH₂-), 1.53-1.26 (m, 34H, -(CH₂)₅- + -(CH₂)₁₂-), 0.89 (t, $J = 6.69$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₇H₆₈O₉ requires C 76.31, H 7.63; found C 76.64, H 7.31%.

4-*n*-Nonanoyloxyphenyl-3'-(4-(4-*n*-octadecyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.B.4

Yield: (70%); mp 111.2 °C; IR (KBr) ν_{\max} : 3072, 3051, 2955, 2924, 2852, 1747, 1734, 1604, 1587, 1568, 1469, 1381 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, $J = 9.12$ Hz, 2H, Ar-H), 8.26 (d, $J = 8.38$ Hz, 2H, Ar-H), 8.15 (d, $J = 8.92$ Hz, 2H, Ar-H), 7.75 (d, $J = 6.86$ Hz, 2H, Ar-H), 7.57-7.52 (m, 3H, Ar-H), 7.39 (d, $J = 8.70$ Hz, 2H, Ar-H), 7.28 (t, $J = 6.84$ Hz, 2H, Ar-H), 7.24 (d, $J = 4.45$ Hz, 1H, Ar-H), 7.15 (d, $J = 9.04$ Hz, 2H, Ar-H), 6.99 (d, $J = 8.97$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.52$ Hz, 2H, Ar-O-CH₂-), 2.56 (t, $J = 7.38$ Hz, 2H, Ar-OCO-CH₂-), 1.85-1.74 (quin, $J = 7.15$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.38-1.32 (quin, $J = 7.33$ Hz, 2H, Ar-OCO-CH₂-CH₂-), 1.53-1.3 (m, 40H, -(CH₂)₅- + -(CH₂)₁₅-), 0.9 (t, $J = 6.71$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₆₀H₇₄O₉ requires C 76.73, H 7.93; found C 76.54, H 8.16%.

4-*n*-Octyloxycarbonylphenyl-3'-(4-(4-*n*-octyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.C.1

Yield: (76%); mp 123.2 °C; IR (KBr) ν_{\max} : 3107, 3074, 3049, 2954, 2922, 2852, 1745, 1732, 1714, 1591, 1566, 1467, 1410, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.30 (d, $J = 8.84$ Hz, 2H, Ar-H), 8.27 (d, $J = 8.52$ Hz, 2H, Ar-H), 8.14 (t, $J = 7.96$ Hz, 4H, Ar-H), 7.76 (d, $J = 8.56$ Hz, 2H, Ar-H), 7.57-7.53 (m, 3H, Ar-H), 7.39 (d, $J = 8.81$ Hz, 2H, Ar-H), 7.33 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.29 (t, $J = 6.85$ Hz, 1H, Ar-H), 6.99 (d, $J = 8.97$ Hz, 2H, Ar-H), 4.33 (t, $J = 6.69$ Hz, 2H, Ar-O-CH₂-), 4.05 (t, $J = 6.56$ Hz, 2H, Ar-COO-CH₂-), 1.83-1.77 (quin, $J = 7.9$ Hz, 4H, Ar-O-CH₂-CH₂- + Ar-COO-CH₂-CH₂-), 1.52-1.27 (m, 20H, -(CH₂)₅- + -(CH₂)₅-), 0.89 (t, $J = 7$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₀H₅₄O₉ requires C 75.16, H 6.80; found C 75.03, H 6.49%.

4-*n*-Octyloxycarbonylphenyl-3'-(4-(4-*n*-decyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.C.2

Yield: (75%); mp 125 °C; IR (KBr) ν_{\max} : 3107, 3076, 3049, 2955, 2920, 2852, 1747, 1728, 1712, 1589, 1566, 1467, 1410, 1398, 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, $J = 8.84$ Hz, 2H, Ar-H), 8.28 (d, $J = 8.56$ Hz, 2H, Ar-H), 8.15 (t, $J = 7.72$ Hz, 4H, Ar-H), 7.77 (d, $J = 8.56$ Hz, 2H, Ar-H), 7.58-7.53 (m, 3H, Ar-H), 7.4 (d, $J = 8.81$ Hz, 2H, Ar-H), 7.33 (d, $J = 8.64$ Hz, 2H, Ar-H), 7.3 (t, $J = 7.1$ Hz, 1H, Ar-H), 6.99 (d, $J = 9.12$ Hz, 2H, Ar-H), 4.33 (t, $J = 6.65$ Hz, 2H, Ar-O-CH₂-), 4.05 (t, $J = 6.62$ Hz, 2H, Ar-COO-CH₂-), 1.84-1.74 (quin, $J = 7.92$ Hz, 4H, Ar-O-CH₂-CH₂- + Ar-COO-CH₂-CH₂-), 1.54-1.28 (m, 24H, -(CH₂)₅- + -(CH₂)₇-), 0.89 (t, $J = 6.87$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₂H₅₈O₉ requires C 75.52, H 7.06; found C 75.28, H 7.12%.

4-*n*-Octyloxycarbonylphenyl-3'-(4-(4-*n*-pentadecyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.C.3

Yield: (72%); mp 117.5 °C; IR (KBr) ν_{\max} : 3105, 3074, 3046, 2955, 2920, 2854, 1745, 1733, 1708, 1604, 1587, 1566, 1467, 1410, 1379 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, $J = 8.8$ Hz, 2H, Ar-H), 8.27 (d, $J = 8.53$ Hz, 2H, Ar-H), 8.14 (t, $J = 7.92$ Hz, 4H, Ar-H), 7.76 (d, $J = 8.59$ Hz, 2H, Ar-H), 7.57-7.52 (m, 3H, Ar-H), 7.39 (d, $J = 8.79$ Hz, 2H, Ar-H), 7.32 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.29 (t, $J = 6.77$ Hz, 1H, Ar-H), 6.99 (d, $J = 8.91$ Hz, 2H, Ar-H), 4.33 (t, $J = 6.69$ Hz, 2H, Ar-O-CH₂-), 4.05 (t, $J = 6.58$ Hz, 2H, Ar-COO-CH₂-), 1.86-1.75 (quin, $J = 7.71$ Hz, 4H, Ar-O-CH₂-CH₂- + Ar-COO-CH₂-CH₂-), 1.51-1.27 (m, 34H, -(CH₂)₅- + -(CH₂)₁₂-), 0.88 (t, $J = 7.01$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₇H₆₈O₉ requires C 76.31, H 7.63; found C 76.41, H 7.3%.

4-*n*-Octyloxycarbonylphenyl-3'-(4-(4-*n*-octadecyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.C.4

Yield: (75%); mp 112.2 °C; IR (KBr) ν_{\max} : 3076, 3048, 2954, 2922, 2852, 1743, 1735, 1604, 1581, 1566, 1467, 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, $J = 8.82$ Hz, 2H, Ar-H), 8.27 (d, $J = 8.51$ Hz, 2H, Ar-H), 8.14 (t, $J = 7.92$ Hz, 4H, Ar-H), 7.76 (d, $J = 8.56$ Hz, 2H, Ar-H), 7.57-7.52 (m, 3H, Ar-H), 7.4 (d, $J = 8.81$ Hz, 2H, Ar-H), 7.32 (d, $J = 8.81$ Hz, 2H, Ar-H), 7.29 (t, $J = 6.79$ Hz, 1H, Ar-H), 6.99 (d, $J = 8.95$ Hz, 2H, Ar-H), 4.33 (t, $J = 6.67$ Hz, 2H,

Ar-O-CH₂-), 4.05 (t, $J = 6.6$ Hz, 2H, Ar-COO-CH₂-), 1.86-1.74 (quin, $J = 7.75$ Hz, 4H, Ar-O-CH₂-CH₂- + Ar-COO-CH₂-CH₂-), 1.51-1.27 (m, 40H, -(CH₂)₅- + -(CH₂)₁₅-), 0.89 (t, $J = 7.05$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₆₀H₇₄O₉ requires C 76.73, H 7.93; found C 76.87, H 8.19%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-pentyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.1

Yield: (77%); mp 124 °C; IR (KBr) ν_{\max} : 3072, 3044, 2956, 2918, 2852, 1742, 1604, 1586, 1566, 1467, 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.48$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.44$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.82$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 2.04$ Hz, $J_2 = 9.28$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.31$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.3$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.54$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.97$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.14 (t, $J = 6.52$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.42$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.26$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.83-1.76 (quin, $J = 6.88$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.52-1.25 (m, 14H, -(CH₂)₅- + -(CH₂)₂-), 0.9 (t, $J = 6.34$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₄₆H₄₆F₂O₈ requires C 72.23, H 6.05; found C 72.23, H 6.39%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-hexyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.2

Yield: (70%); mp 118 °C; IR (KBr) ν_{\max} : 3074, 2954, 2918, 2852, 1737, 1604, 1586, 1467, 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.15$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.41$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.76$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 2.06$ Hz, $J_2 = 8.88$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.21$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.21$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.21 (d, $J = 9.42$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.97$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.94 (d, $J = 8.92$ Hz, 2H, Ar-H), 4.14 (t, $J = 6.54$ Hz, 2H, Ar-O-CH₂-), 3.97 (t, $J = 6.5$ Hz, 2H, Ar-O-CH₂-), 1.92-1.85 (quin, $J = 7.25$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.83-1.76 (quin, $J = 6.97$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.52-1.28 (m, 16H, -(CH₂)₅- + -(CH₂)₃-), 0.9 (t, $J = 6.42$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₄₇H₄₈F₂O₈ requires C 72.48, H 6.2; found C 72.86, H 5.89%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-heptyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.3

Yield: (82%); mp 108.3 °C; IR (KBr) ν_{max} : 3082, 3066, 2956, 2924, 2848, 2652, 1737, 1614, 1587, 1504, 1467, 1437, 1423, 1398 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.26 (d, $J = 8.17$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.23$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.86$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 1.98$ Hz, $J_2 = 9.21$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.35$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.54$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.97$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.52$ Hz, 2H, Ar-O- $\underline{\text{CH}_2}$ -), 3.97 (t, $J = 6.48$ Hz, 2H, Ar-O- $\underline{\text{CH}_2}$ -), 1.91-1.84 (quin, $J = 7.1$ Hz, 2H, Ar-O- CH_2 - $\underline{\text{CH}_2}$ -), 1.83-1.75 (quin, $J = 6.86$ Hz, 2H, Ar-O- CH_2 - $\underline{\text{CH}_2}$ -), 1.54-1.25 (m, 18H, $-(\text{CH}_2)_5^- + -(\text{CH}_2)_4^-$), 0.89 (t, $J = 6.34$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{48}\text{H}_{50}\text{F}_2\text{O}_8$ requires C 72.70, H 6.36; found C 72.55, H 6.65%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-octyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.4

Yield: (70%); mp 108.7 °C; IR (KBr) ν_{max} : 3064, 2955, 2872, 2850, 2617, 1732, 1693, 1614, 1587, 1568, 1467, 1437, 1398 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.26 (d, $J = 8.35$ Hz, 2H, Ar-H), 8.23 (t, $J = 8.4$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.8$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 2.05$ Hz, $J_2 = 9.32$ Hz, 1H, Ar-H), 7.75 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.35$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.54$ Hz, 2H, Ar-H), 7.14 (d, $J = 8.63$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.56$ Hz, 2H, Ar-O- $\underline{\text{CH}_2}$ -), 3.96 (t, $J = 6.52$ Hz, 2H, Ar-O- $\underline{\text{CH}_2}$ -), 1.91-1.84 (quin, $J = 7.1$ Hz, 2H, Ar-O- CH_2 - $\underline{\text{CH}_2}$ -), 1.82-1.75 (quin, $J = 6.93$ Hz, 2H, Ar-O- CH_2 - $\underline{\text{CH}_2}$ -), 1.54-1.26 (m, 20H, $-(\text{CH}_2)_5^- + -(\text{CH}_2)_5^-$), 0.89 (t, $J = 6.32$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{49}\text{H}_{52}\text{F}_2\text{O}_8$ requires C 72.93, H 6.49; found C 73.17, H 6.2%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-nonyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.5

Yield: (81%); mp 110.8 °C; IR (KBr) ν_{max} : 3066, 2956, 2924, 2848, 2652, 1737, 1614, 1587, 1568, 1504, 1467, 1423, 1398 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 8.26 (d, $J = 8.24$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.4$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.63$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 2.02$

Hz, $J_2 = 9.42$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.35$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.54$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.97$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.21$ Hz, 1H, Ar-H), 6.94 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.45$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.5$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.11$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.82-1.76 (quin, $J = 6.91$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.25 (m, 22H, -(CH₂)₅- + -(CH₂)₆-), 0.89 (t, $J = 6.34$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₀H₅₄F₂O₈ requires C 73.15, H 6.62; found C 72.79, H 6.96%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-decyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.6

Yield: (79%); mp 111.8 °C; IR (KBr) ν_{\max} : 3072, 2955, 2924, 2852, 2690, 1732, 1614, 1587, 1568, 1504, 1467, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.16$ Hz, 2H, Ar-H), 8.21 (t, $J = 8.6$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.9$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 1.98$ Hz, $J_2 = 9.42$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.35$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.33$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.2 (d, $J = 9.54$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.76$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.94 (d, $J = 8.92$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.6$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.48$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.32$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, $J = 6.86$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.55-1.26 (m, 24H, -(CH₂)₅- + -(CH₂)₇-), 0.88 (t, $J = 6.45$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₁H₅₆F₂O₈ requires C 73.35, H 6.76; found C 73.13, H 6.45%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-undecyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.7

Yield: (78%); mp 110.2 °C; IR (KBr) ν_{\max} : 3066, 2956, 2918, 2848, 2652, 1732, 1614, 1587, 1568, 1504, 1467, 1437 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.25 (d, $J = 8.1$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.4$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.52$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 2.08$ Hz, $J_2 = 9.11$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.24$, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.4$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.62$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.32$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.6$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.1$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, $J = 6.86$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.26 (m, 26H, -(CH₂)₅- + -(CH₂)₈-), 0.88 (t,

$J = 6.36$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: C₅₂H₅₈F₂O₈ requires C 73.56, H 6.89; found C 73.22, H 7.15%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-dodecyloxybenzoyloxy)benzoyloxy) biphenyl-4-carboxylate, 3.D.8

Yield: (78%); mp 111.8 °C; IR (KBr) ν_{max} : 3076, 3066, 2948, 2926, 2848, 2618, 1735, 1614, 1586, 1506, 1467, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.42$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.4$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.82$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 1.98$ Hz, $J_2 = 8.93$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.5$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.54$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.97$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.6$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.32$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.25$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, $J = 7.01$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.26 (m, 28H, -(CH₂)₅- + -(CH₂)₉-), 0.89 (t, $J = 6.44$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: C₅₃H₆₀F₂O₈ requires C 73.76, H 7.01; found C 73.52, H 7.35%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-tridecyloxybenzoyloxy)benzoyloxy) biphenyl-4-carboxylate, 3.D.9

Yield: (83%); mp 112.9 °C; IR (KBr) ν_{max} : 3082, 3066, 2954, 2926, 2848, 2616, 1732, 1614, 1586, 1506, 1467, 1398 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.45$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.6$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.82$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 2.04$ Hz, $J_2 = 9.48$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.35$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.54$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.12$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.78$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.2$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.1$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.81-1.75 (quin, $J = 6.93$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.26 (m, 30H, -(CH₂)₅- + -(CH₂)₁₀-), 0.88 (t, $J = 6.34$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: C₅₄H₆₂F₂O₈ requires C 73.95, H 7.11; found C 73.61, H 7.4%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-tetradecyloxybenzoyloxy)benzoyloxy) biphenyl-4-carboxylate, 3.D.10

Yield: (79%); mp 112.5 °C; IR (KBr) ν_{\max} : 3064, 2955, 2918, 2872, 2850, 2617, 1728, 1693, 1614, 1587, 1506, 1467, 1437, 1423, 1398, 1329 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.25 (d, $J = 8.35$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.4$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.82$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 1.96$ Hz, $J_2 = 9.35$ Hz, 1H, Ar-H), 7.75 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.35$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.1$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.97$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.8$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.1$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.81-1.75 (quin, $J = 6.78$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.25 (m, 32H, -(CH₂)₅- + -(CH₂)₁₁-), 0.88 (t, $J = 6.4$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₅H₆₄F₂O₈ requires C 74.13, H 7.23; found C 73.83, H 7.28%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-pentadecyloxybenzoyloxy)benzoyloxy) biphenyl-4-carboxylate, 3.D.11

Yield: (75%); mp 111.6 °C; IR (KBr) ν_{\max} : 3082, 3066, 3039, 2956, 2924, 2918, 2848, 2690, 2652, 1737, 1730, 1614, 1587, 1568, 1504, 1467, 1437, 1423, 1398, 1379 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.1$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.32$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.8$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 1.94$ Hz, $J_2 = 9.24$ Hz, Ar-H), 7.75 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.35$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.38$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.48$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.95$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.78$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.64$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.54$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.1$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, $J = 6.93$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.26 (m, 34H, -(CH₂)₅- + -(CH₂)₁₂-), 0.89 (t, $J = 6.42$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₆H₆₆F₂O₈ requires C 74.3, H 7.33; found C 74.63, H 7.05%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-hexadecyloxybenzoyloxy)benzoyloxy) biphenyl-4-carboxylate, 3.D.12

Yield: (78%); mp 109.4 °C; IR (KBr) ν_{\max} : 3064, 3037, 2954, 2922, 2948, 2727, 2690, 2652, 1732, 1612, 1586, 1504, 1467, 1379 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.3$ Hz, 2H, Ar-H), 8.23 (t, $J = 8.21$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.6$ Hz, 1H, Ar-H), 7.87 (dd,

$J_1 = 1.98$ Hz, $J_2 = 9.17$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.24$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.48$ Hz, 1H, Ar-H), 7.2 (d, $J = 9.4$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.88$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.94 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.6$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.52$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.1$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, $J = 6.93$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.26 (m, 36H, -(CH₂)₅- + -(CH₂)₁₃-), 0.88 (t, $J = 6.34$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₇H₆₈F₂O₈ requires C 74.48, H 7.45; found C 74.15, H 7.16%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-octadecyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.13

Yield: (78%); mp 107.4 °C; IR (KBr) ν_{\max} : 3066, 3038, 2956, 2924, 2846, 2686, 2654, 1735, 1614, 1587, 1504, 1467, 1437, 1398, 1379, 1329 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.35$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.4$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.82$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 1.96$ Hz, $J_2 = 9.35$ Hz, 1H, Ar-H), 7.75 (d, $J = 8.36$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.35$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.35$ Hz, 1H, Ar-H), 7.19 (d, $J = 9.54$ Hz, 2H, Ar-H), 7.13 (d, $J = 8.97$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.31$ Hz, 1H, Ar-H), 6.93 (d, $J = 8.99$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.56$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.52$ Hz, 2H, Ar-O-CH₂-), 1.91-1.84 (quin, $J = 7.1$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.82-1.75 (quin, $J = 6.93$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.26 (m, 40H, -(CH₂)₅- + -(CH₂)₁₅-), 0.88 (t, $J = 6.34$ Hz, 6H, 2 × -CH₃); Elemental analysis: C₅₉H₇₂F₂O₈ requires C 74.81, H 7.65; found C 74.81, H 7.9%.

4-*n*-Octyloxyphenyl-3'-(2-fluoro-4-(3-fluoro-4-*n*-icosyloxybenzoyloxy)benzoyloxy)biphenyl-4-carboxylate, 3.D.14

Yield: (74%); mp 105.3 °C; IR (KBr) ν_{\max} : 3064, 3044, 2924, 2846, 2656, 1737, 1608, 1586, 1504, 1467, 1437, 1379 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (d, $J = 8.12$ Hz, 2H, Ar-H), 8.22 (t, $J = 8.8$ Hz, 1H, Ar-H), 7.96 (d, $J = 8.64$ Hz, 1H, Ar-H), 7.89 (dd, $J_1 = 2.1$ Hz, $J_2 = 9.1$ Hz, 1H, Ar-H), 7.74 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.55 (t, $J = 8.2$ Hz, 3H, Ar-H), 7.3 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.2 (d, $J = 9.4$ Hz, 2H, Ar-H), 7.13 (d, $J = 7.5$ Hz, 2H, Ar-H), 7.05 (t, $J = 8.6$ Hz, 1H, Ar-H), 6.94 (d, $J = 7.2$ Hz, 2H, Ar-H), 4.13 (t, $J = 6.3$ Hz, 2H, Ar-O-CH₂-), 3.96 (t, $J = 6.5$ Hz, 2H, Ar-O-CH₂-), 1.91-1.82 (quin, $J = 7$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.81-1.75 (quin, $J = 7.93$ Hz, 2H, Ar-O-CH₂-CH₂-), 1.54-1.26 (m, 44H, -(CH₂)₅- + -(CH₂)₁₇-), 0.87 (t,

$J = 6.36$ Hz, 6H, $2 \times -\text{CH}_3$); Elemental analysis: $\text{C}_{61}\text{H}_{76}\text{F}_2\text{O}_8$ requires C 75.13, H 7.84; found C 74.96, H 7.92%.

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