THE UNIVERSITY OF HULL

The Synthesis and Properties of Achiral and Chiral Bent-core Liquid Crystals

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in the University of Hull

by

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Summary of Thesis Submitted for the Degree of PhD

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on

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The area of liquid crystals has received substantial research effort over the last century, particularly when the beneficial applications such as Liquid Crystal Displays (LCDs) were realised and developed. For the majority of this time, it has been considered that a linear molecular shape is required in order to generate a mesomorphic phase. It was therefore of particular interest and excitement when, in 1996, it was shown that a 'banana-shaped' molecular architecture could exhibit a new class of liquid crystalline phase. Additionally it was found that these new mesophases exhibited chiral domains, leading to electrooptical switching properties, despite the constituent molecules being achiral. Unsurprisingly, these observations have led to a vast frontier of research in the area of 'banana-shaped' and 'bent-core' systems over the past decade and many interesting properties relating to such systems have been reported.

The work contained within this thesis investigates two areas of bent-core liquid crystals. Firstly, the introduction of fluoro-substituents to the bent-core of an achiral banana-shaped system has been assessed, in terms of both position, and number of substituents. The resultant mesomorphic properties of these compounds have shown that there is a very delicate boundary between banana, and 'conventional' mesomorphism, relating to subtle changes in molecular structure. Appropriately positioned fluoro-substituents upon the bent-core generate a more linear conformation, facilitating the generation of nematic phases. Possible reasoning for this observation has been discussed.

Secondly, the effect of introducing a bent-core to a conventional calamitic structure, and the addition of fluoro-substituents, has been examined. Whilst a variation of this nature to the majority of calamitic molecular structures would have a severely detrimental effect upon the resultant mesophase morphology, it has been shown that this is not always the case and indeed the addition of fluoro-substituents is shown to enhance the mesomorphic stability of the smectic A phase.

Publications and Presentations

The following publications and conference presentations have included work contained within this thesis:

- K.M. Fergusson, M. Hird, "A Helical Liquid-crystal Phase generated by a Chiral Ester with a Bent-core Molecular Architecture", *Advanced Materials*, **2007**, *19*, 211-214

- J. Kirchoff, L.S. Hirst, K.M. Fergusson, M. Hird, "Low Electric-field Induced Switching in the B_1 Bent-core Liquid Crystal Phase", *Applied Physics Letters*, **2007**, *90*, 161905

- K.M. Fergusson, M. Hird, "Novel Chiral Bent-core Esters Exhibiting Interesting Mesomorphism", *oral presentation at the 19th Annual Conference of the British Liquid Crystal Society* (University of Exeter) **2005**, O27

- K.M. Fergusson, M. Hird, "Synthesis and Mesomorphic Properties of Novel Unsymmetrical Banana-shaped Esters", *poster presentation at the 19th Annual Conference of the British Liquid Crystal Society* (University of Exeter) **2005**, P19

- K.M. Fergusson, M. Hird, "Novel Chiral Bent-core Esters Exhibiting Interesting Mesomorphism", *oral presentation at the Young Researchers Workshop* (University of Hull) **2005**

- K.M. Fergusson, M. Hird, "Synthesis and Mesomorphic Properties of Novel Unsymmetrical Banana-shaped Esters", *poster presentation at the Young Researchers Workshop* (University of Hull) **2005**

- K.M. Fergusson, M. Hird, "Novel Chiral Bent-core Esters Exhibiting Interesting Mesomorphism", *oral presentation at the 10th International Conference on Ferroelectric Liquid Crystals* (Stare Jablonki, Poland) **2005**, O17

- K.M. Fergusson, M. Hird, "Synthesis and Mesomorphic Properties of Novel Unsymmetrical Banana-shaped Esters", *poster presentation at the 10th International Conference on Ferroelectric Liquid Crystals* (Stare Jablonki, Poland) **2005**, B3

- K.M. Fergusson, M. Hird "Banana-shaped Esters Incorporating Fluoro-substituents at the Bent-core: Interesting Synthetic Strategies and Mesomorphic Properties", *poster presentation at the 20th Annual Conference of the British Liquid Crystal Society* (University of York) **2006**, P17

- K.M. Fergusson, "Banana and Hockey Stick-shaped Esters Exhibiting Interesting Mesomorphism", *3rd year PhD colloquia* (University of Hull) **2006**

- K.M. Fergusson, M. Hird, "Novel Fluorinated Bent-core Esters: Interesting Synthetic Strategies and Mesomorphic Properties", *oral presentation at the 22nd Annual Conference of the British Liquid Crystal Society* (University of East Anglia) **2008**, O14

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My gratitude extends to all members, past and present, of the liquid crystal research group at the University of Hull, in particular Dr S.J. Cowling (electrooptical measurements), Dr L. Cseh, Dr J. Gąsowska, Prof. J.W. Goodby, Dr V. Görtz (electrooptical measurements), Dr D. Lacey, Dr R.A. Lewis, Dr R.A. McDonald, Mr P.J. Stackhouse, Dr A.I. Stipetic, Mr I. Radini, Dr C. Wilson, and Dr D. Wilson for many helpful and interesting discussions. Special thanks go to Mrs J. Haley for advice and assistance with many analytical techniques. I would like to extend these thanks to Miss H.E. Metcalf, Mr D.C. Matthews and Mr R. Mandle for their undertaking of undergraduate projects within my research area. It has been a very enjoyable and interesting time as part of the research group and I am grateful to everybody for making it so. Additionally I would like to thank Miss J. Kirchoff and Dr L.S. Hirst at Florida State University for their collaboration during the research programme.

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This thesis also represents the culmination of twenty years of education, throughout which I have had the unconditioned support of my family, for which I will be eternally grateful. In particular I would like to purvey my extreme gratitude to my Mother and Father who have selflessly provided many years of help and advice, both academically and financially.

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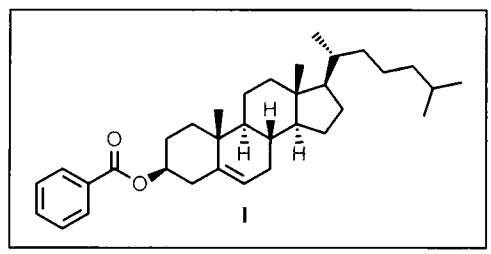
To every one of you, THANK YOU

Contents

1. Introduction

1.1 Historical Aspects of Liquid Crystals

From a historical point of view, there exist three states of matter, namely 'solid', 'liquid' and 'gas'. However, the observations of Friedrich Reinitzer in 1888[1,2] unveiled an insight into what would subsequently be termed a 'fourth state of matter'. Working as a botanist in Austria, Reinitzer was studying the melting point of cholesteryl benzoate (compound I), and discovered that upon heating the compound, a cloudy, translucent liquid was obtained at 145.5 °C, which remained until a temperature of 178.5 °C was reached, when the cloudy appearance vanished. This unusual behaviour lead Reinitzer to describe the compound as possessing two melting points[2]. In 1889 Reinitzer contacted Otto Lehmann[3], an experienced crystallographer of the time, who is credited with the development of the polarisation microscope, which has played an important role in the discovery and development of liquid crystals[4]. After studying cholesteryl benzoate, Lehman concluded that the 'cloudy appearance' exhibited double refraction, characterisic of a crystal[3]. However, as the substance exhibited characteristics of both the liquid state, and the crystalline state, Lehmann described it as 'fliessende Krystalle' (flowing crystals), and hence the term 'liquid crystal' was born[3,5].



I

As knowledge and experience of these liquid crystalline systems was acquired, it was subsequently suggested by Friedel that the term 'liquid crystal' did not truly describe the nature of this new state of matter, as although the phases did exhibit characteristics of both the liquid state and the crystalline state, they were genuinely neither[5] and instead constituted a fourth state of matter. It was therefore proposed that the new state of matter should be termed a 'mesophase', derived from the Greek word 'mesos', meaning between, or intermediate[5]. The term 'mesophase' and other related words remain prevalent in current liquid crystalline research and publications, but the original term 'liquid crystal' has not been lost either and indeed is generally used as the main title for all liquid crystalline research. The

fact that this original nomenclature has not been replaced is testament to the excitement and interest generated from the contrasting words of 'liquid' and 'crystal'[6] – how can a substance be both a 'liquid' and a 'crystal'?

Despite the interest being generated from these early observations of an additional state of matter, liquid crystalline research was not prevalent at the beginning of the twentieth century, as few accepted the phenomenon and no potential applications had been envisaged. Indeed it was not until a publication by Friedel in 1922[7] that the subject of liquid crystals gained acceptance throughout the wider scientific community[6]. The outbreak of the two world wars obviously put a hold on the advancement of liquid crystalline research. Although research work continued, it was not unil the 1960s and 1970s that research interest in the area would become more prevalent. The first meetings of the now biannual International Liquid Crystal Conferences (ILCC) in 1965 and 1968 resulted in a number of potential applications of liquid crystals being discussed[6], and therefore the quest to discover and synthesise appropriate liquid crystalline compounds was initiated, resulting in a rapid expansion in the number of liquid crystalline related work and publications[6, 8]. The increased interest in liquid crystals also resulted in many different areas being uncovered and established. Figure 1.1 shows the various main categories included within the generalised title of 'liquid crystalline' research at present.

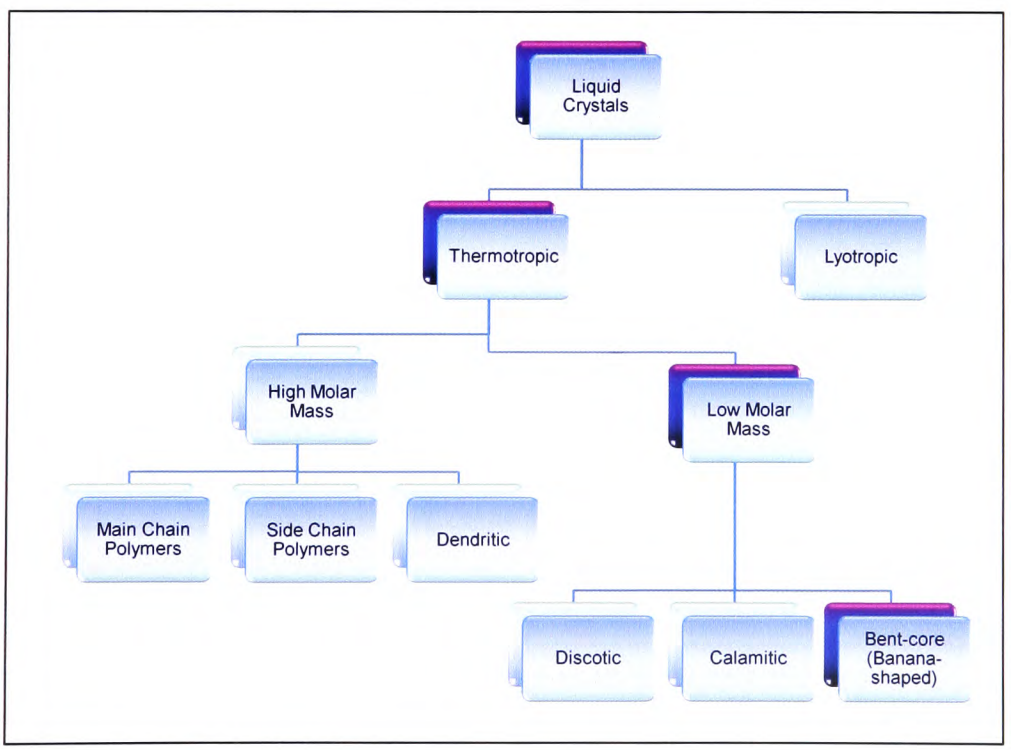
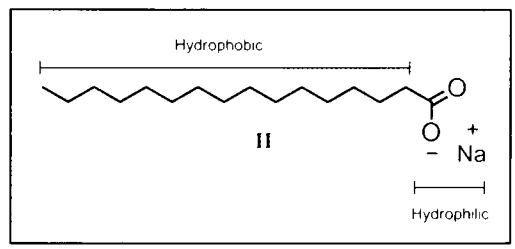


Figure 1.1. The main categories of liquid crystals.

As shown in figure 1.1, the field of liquid crystals can be broadly divided into two main categories, 'lyotropic' and 'thermotropic'. 'Lyotropic' liquid crystals are comprised of an amphiphilic molecule, where one part is hydrophilic and one part is hydrophobic, such as compound **II**[9]. Upon interaction between the compound and an appropriate solvent (usually water) at a certain concentration, the molecules arrange into spheres, rods or discs, called micelles[9-13], and it is upon this basis that lyotropic liquid crystals are prevalent in every day life. Examples include soap and detergents, whilst not so obvious examples include the structural conformation of biological phospholipid membranes[9, 10, 14].



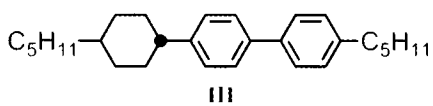
Lyotropic liquid crystals are not included within the work presented within this thesis, and therefore will not be covered in any further detail.

'Thermotropic' is the term given to liquid crystals which exhibit their mesogenic properties as a result of the application of heat to the compound, such as in the case of compound I, where a temperature of 146.5 °C was required to melt the compound into its mesomorphic state. As shown in figure 1.1, thermotropic liquid crystals can be further broken down into 'high molar mass' (which includes polymeric and dendritic systems), and 'low molar mass'. The field of 'low molar mass' liquid crystals is again divided into categories, relating to the molecular shape. The work contained within this thesis is concerned with thermotropic, low molar mass liquid crystals and therefore the remainder of this introduction will focus upon the relevant aspects of thermotropic liquid crystals and their associated properties, in particular calamitic and bent-core (banana-shaped) systems.

1.2 Properties of Thermotropic Liquid Crystals

After the initial observations of Reinitzer and Lehmann, other compounds exhibiting liquid crystalline properties began to be found, inevitably leading to debate regarding the structure-property relationships governing the generation of liquid crystalline phases[15, 16]. In 1907 Vorländer reported that "... the crystalline-liquid state results from a molecular structure which is as linear as possible"[8,15]. This theory held true for many years and therefore many

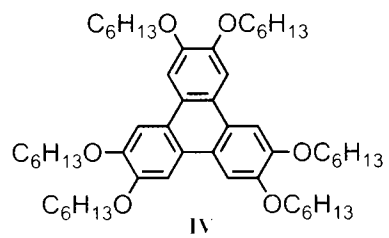
liquid crystalline compounds were reported which all shared a similar rod-like molecular shape (compound **III**[17] is shown as an example of a rod-like structure). This general description soon acquired the name 'calamitic'[8,18], derived from the Greek word for 'reed'[8].



III

Cr 13.0 SmA 164.0 N 166.0 I

However, it is no longer the case that a molecule must be rod-like in structure in order to generate liquid crystalline phases. Despite predictions that it should be possible to generate thermotropic liquid crystalline phases from disc-like molecules[15,19], it was not until the work of Chandrasekhar in 1977[20] that the theories were proved correct, and compounds such as **IV**[15,20,21] exhibited columnar liquid crystal phases.



IV

Cr 68 Col_h[a] 97 I

Compounds with other molecular shapes have also been shown to exhibit a variety of liquid crystalline phases, such as 'wedge-shaped'[22], 'T-shaped'[23] and 'banana-shaped' (bent-core), of which the latter will be covered in further detail later in this introductory section. With the aims of this thesis in mind, the remainder of this introduction will focus upon thermotropic calamitic and bent-core liquid crystals.

Before moving on into the most relevant aspects of liquid crystals to this thesis, the highly important work of Professor George Gray CBE must be reviewed. In the 1970s, working at the University of Hull, Gray and his team synthesised the cyanobiphenyls[6,24], the most familiar compound being 4-cyano-4'-pentylbiphenyl (**V**), also known as '5CB' or 'K15'.

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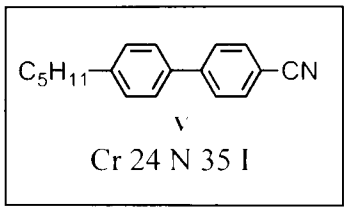
[a] Col_h = Columnar phase, with hexagonal packing of the columns within the mesophase



Materials such as 5CB show 'positive dielectric anisotropy', meaning that the polarisation generated by the cyano group is directed along the long molecular axis, rendering the molecule particularly suited to the electrooptical properties required in order to make a successful twisted nematic liquid crystal display (TNLCD) device. The materials synthesised by Gray also satisfied the other requirement of a display device, as they were stable and did not undergo degradation. Gray's work provided the catalyst for the generation of many display devices and this has continued to the present day, as LCDs are dominating the display market and raplidly replacing traditional cathode ray tube (CRT) displays[25].

1.3 Liquid Crystal Phases

It is a common perception that there exists three states of matter, namely 'solid', 'liquid', and 'gas'. This phenomenon is depicted in figure 1.2, and shows the various degrees of order within the three states. The crystalline (solid) state has long range ordering of the constituent molecules over three dimensions. When heat is applied to the crystalline solid, the thermal motions and vibrations between the molecules eventually become so great that both positional and orientational order is lost. This transition is defined as the melting point and the result is the disordered, isotropic liquid. Further heating results in greater thermal motion and vibrations of the constituents molecules and a second transition into the gaseous state occurs, where the molecules become even more disordered compared to the liquid state and fewer molecules will be found within a given unit area.

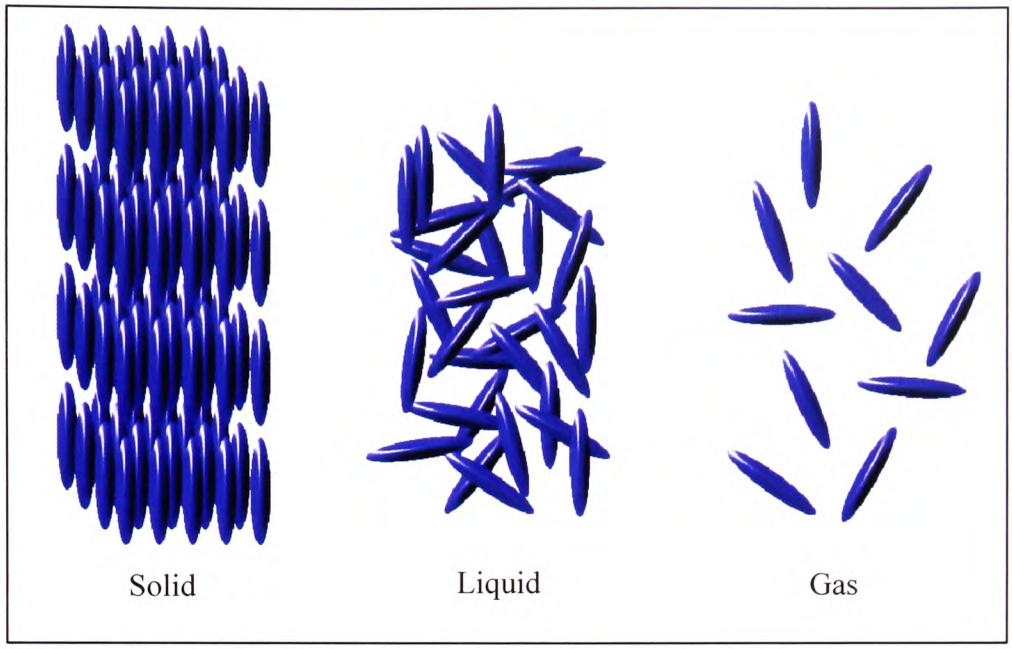


Figure 1.2. The three states of matter, 'Solid', 'Liquid' and 'Gas'.

However, this pattern of transitions is not universal for all materials. Compounds such as carbon dioxide do not pass through a liquid state, instead 'subliming' from the solid, directly to the gaseous state. In the case of a thermotropic liquid crystalline compound, heating the crystalline solid to its melting point can result in a transition into a liquid crystalline phase, as shown in figure 1.3 (shown as a schematic representation of a calamitic, rod-like compound). As can be seen in figure 1.3, the crystalline solid has long range order, due to the strong intermolecular forces of attraction holding the molecules together. If the compound is non-mesomorphic, then at its melting point, a transition into the isotropic liquid will occur (T1), and upon cooling again, the compound will re-crystallise to reform a crystalline solid, although this will occur at a lower temperature (<T1) than that of the melting point, due to supercooling. A smectic liquid crystal phase is formed if the mesogenic solid is heated and the thermal vibrations are sufficient to break the terminal forces of attraction, whereas the lateral attractions are stronger, which hold the molecules in a layered structure (T2). T4 represents the transition from a smectic phase to a nematic phase, as a result of the lateral attractive forces also being broken, resulting in a statistically parallel arrangement of the molecules[9]. Further heating of the nematic phase leads to a transition into the isotropic liquid (T6), termed the 'clearing point'. However, not all liquid crystalline compounds follow the same mesophase morphology. A mesogenic compound may undergo a transition into a nematic phase when melting from the crystalline solid (T3), or the compound may 'clear' into the isotropic liquid directly from a smectic phase (T5).

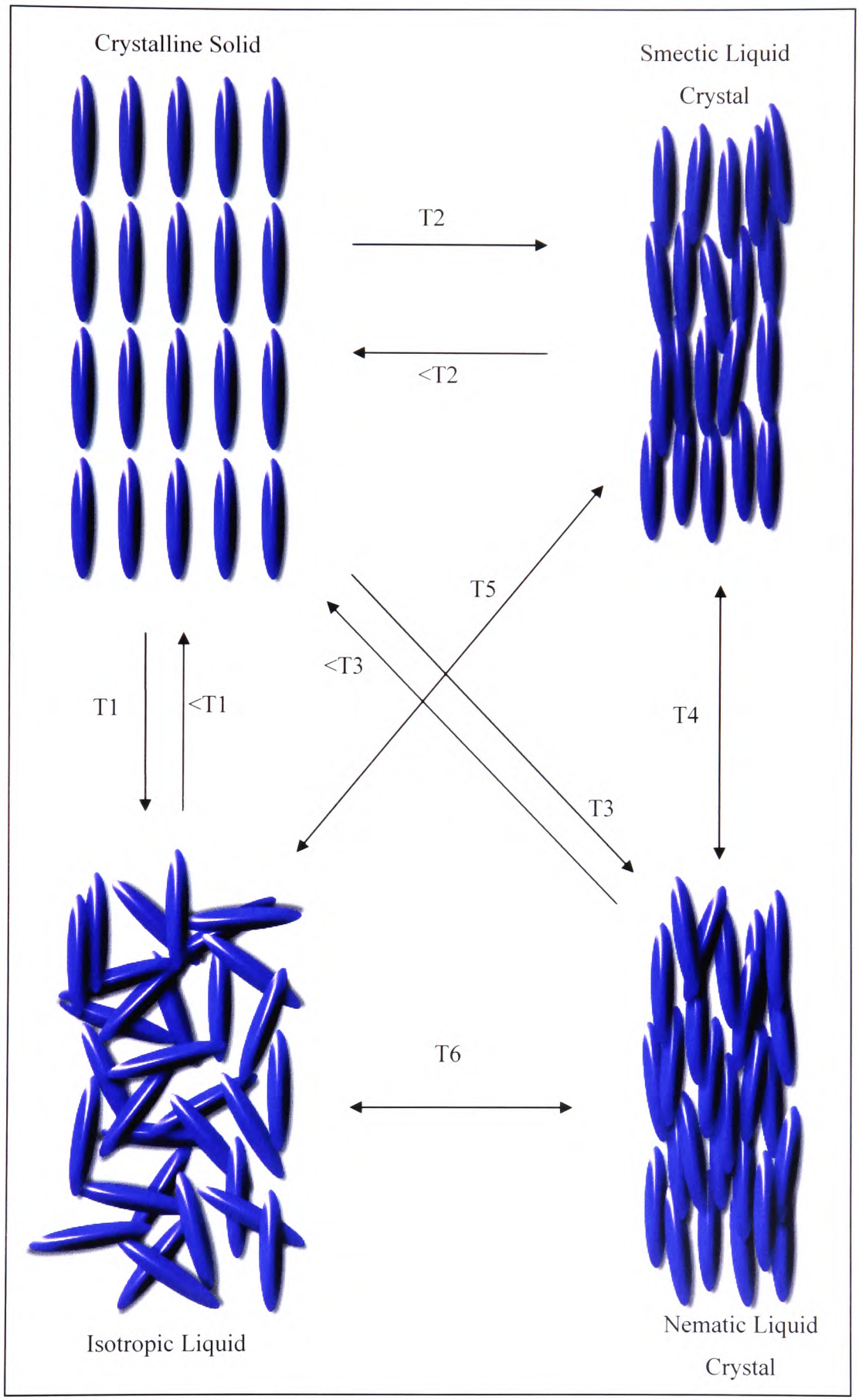


Figure 1.3. Possible melting sequences.

A liquid crystalline phase that is exhibited above the melting point of the material is termed 'enantiotropic'[13], as has been described above. However, a mesomorphic phase exhibited below the melting point of a material, due to supercooling, and before the material recrystallises, is termed 'monotropic'[13]. In figure 1.3, this would be as a result of the crystalline solid undergoing the transition T1 into the isotropic liquid and then upon cooling the isotropic liquid, undergoing a transition into either a nematic phase (<T6), or a smectic phase (<T5), before recrystallising to re-afford the crystalline solid. It should be noted that figure 1.3 shows idealised 'snap-shots' of the molecules within each phase and should be remembered that the molecules possess properties of the liquid state, meaning that they are constantly rotating and altering orientation, although as an average they are oriented in the manner depicted. Due to the fact that the nematic phase does not possess any intermolecular attractions, and its structure is as a result of the molecules being oriented, on average, with their director (ň) pointing in the same direction, the phase is therefore the most fluid of the liquid crystalline phases. Whilst there is only one possible arrangement of the constituent molecules within the nematic phase, the smectic phase is 'polymorphic', as there are numerous variations of phase structure. Figure 1.4 clearly shows the various smectic phases that have been identified and classified. Of note within the figure is the sub-division of the smectic phases into two general classes, the liquid crystal smectic phases, and the crystal smectics. The crystal smectics are not liquid crystalline in nature, as they possess order over three dimensions. However, the molecules are disordered compared to that of a true crystalline solid, and therefore the crystal phases are described as mesophases, but not liquid crystalline phases[9]. The second classification placed upon smectic liquid crystals is the 'orthogonal' or 'tilted' nature of the phase. The smectic A phase (SmA), as can be seen in figure 1.4, consists of layers of molecules orthogonal to each other, with the director of the molecule being normal to the layer. If the molecules within a SmA phase undergo a transition into a smectic C (SmC) phase, the molecules are then tilted with respect to the layer normal, with the magnitutue of tilt defined as the tilt angle (θ), which is temperature dependent. Within the tilted SmC phase, there are also two possibilities, that of the synclinic phase where the direction of tilt is equal throughout the layers, and that of the anticlinic phase where the direction of tilt is reversed from layer to layer. As can be seen in figure 1.4, there are numerous other variations upon the phase structure, but these will not be discussed as they are not of relavence with regard to this thesis. It should be noted that a number of the so-called 'banana phases' share similar phase structures and properties to those of the smectic phases and will be discussed in section 1.5.

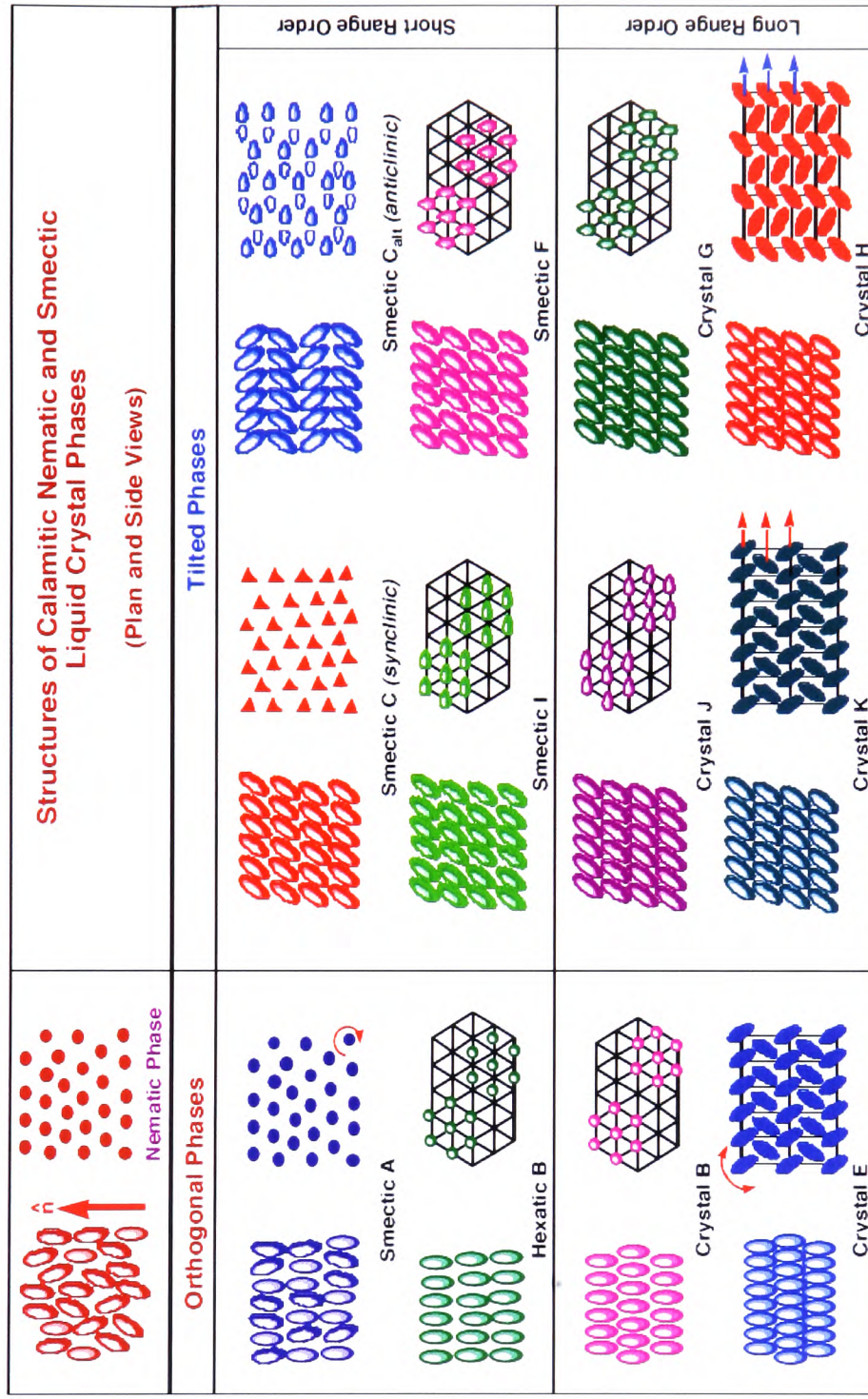


Figure 1.4. Structures of the nematic and smectic phases, adapted from reference[26].

1.4 Chirality

The definition of a 'chiral' object is the ability to exist as two 'handed' forms. The simplest example of this is the left and right hands of the human body, which are mirror images of each other. As a result, the two images (hands) are non-superposable, meaning that it is not possible for the two images to coincide throughout their whole extent when placed on top of each other[27-29]. Chirality also plays an important role in organic chemistry, due to the stereochemistry associated with the tetrahedral arrangement of an sp^3-hybridised carbon. A chiral centre arises when the four groups attached to the tetrahedral carbon unit are different, resulting in two possible stereoisomers, which are mirror images of each other and similarly to the analogy of two hands, are not superposable on each other. A good example and a common chiral unit employed in the synthesis of liquid crystals is 2-octanol[9], which as shown in figure 1.5, can be spatially arranged in two ways about the chiral centre, generating two enantiomers, termed (*S*)-2-octanol and (*R*)-2-octanol.

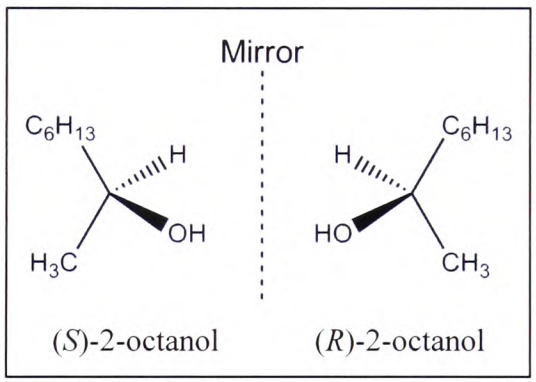


Figure 1.5. Stereoisomers of 2-octanol.

The two enantiomers of a chiral compound have opposing effects on the rotation of plane polarised light; one will rotate plane polarised light in one direction, whereas the other enantiomer will rotate the plane polarised light to the same magnitude but in the opposite direction[9,29]. If the two enantiomers are mixed in a 1:1 ratio, a racemic mixture is formed, which causes no rotation of plane polarised light. The configuration of the stereo centres in chiral compounds is of significant importance particularly in the case of biologically active compounds such as pharmaceuticals. Possibly the most recognised example of this is the tragic effect of thalidomide, a drug prescribed to pregnant women in the late 1950's to combat morning sickness. The commercial drug sold was a racemic mixture and it was subsequently found out that whilst one of the isomers had the desired properties, the

remaining enantiomer was teratogenic, resulting in the birth of thousands of children with deformities[30].

1.4.1 Implications of Chirality for Liquid Crystals

The issue of chirality within organic molecules obviously has extreme importance with regards to biological processes, for example drug activity. It is therefore not a surprise that incorporating a chiral moiety into a liquid crystalline molecular structure also results in some very interesting mesophases and associated properties[31]. Incoporating a chiral moiety into a liquid crystalline phase can be achieved in one of two ways; firstly, the addition of a chiral centre to a compound; secondly, the addition of a chiral dopant to an otherwise achiral host material[32], which produces a liquid crystalline mixture.

1.4.1.1 The Chiral Nematic Phase

In the case of a nematic phase, the incorporation of a chiral unit causes a twist of the director, resulting in a helical structure throughout the bulk material[9, 32, 33], as shown in figure 1.6. It should be noted that the figure is a simplified image to illustrate the nature of the helix within the phase, and that the chiral nematic phase does not actually consist of 'layers' as depicted. The pitch length is the distance required to rotate the molecular direction through 360° and is dependent upon both the nature of the liquid crystalline material present, and temperature[9]. High temperatures cause the director of the molecule to rotate at a greater angle, therefore reducing the pitch length, causing a tighter pitch. In contrast, cooling the sample has the opposing effect, causing an increase of the pitch length. If the pitch length of the material is within the region of the wavelength of visible light, then a selective reflection occurs and the colour observed is dependent upon the pitch length. It is now known that the optical behaviour of cholesteryl benzoate observed by Reinitzer was in fact due to a chiral nematic phase[9], and the colours he described as the sample cooled are as a result of the selective reflection of light and changing pitch length. As this phenomenon was first observed in compounds based upon cholesterol, the phase was described as a 'cholesteric phase', a term that remains interchangeable with 'chiral nematic' today, although it is not limited to cholesterol-based molecular architectures[9]. The special optical properties were soon exploited and incorporated into applications. These applications will be discussed in section 1.6.

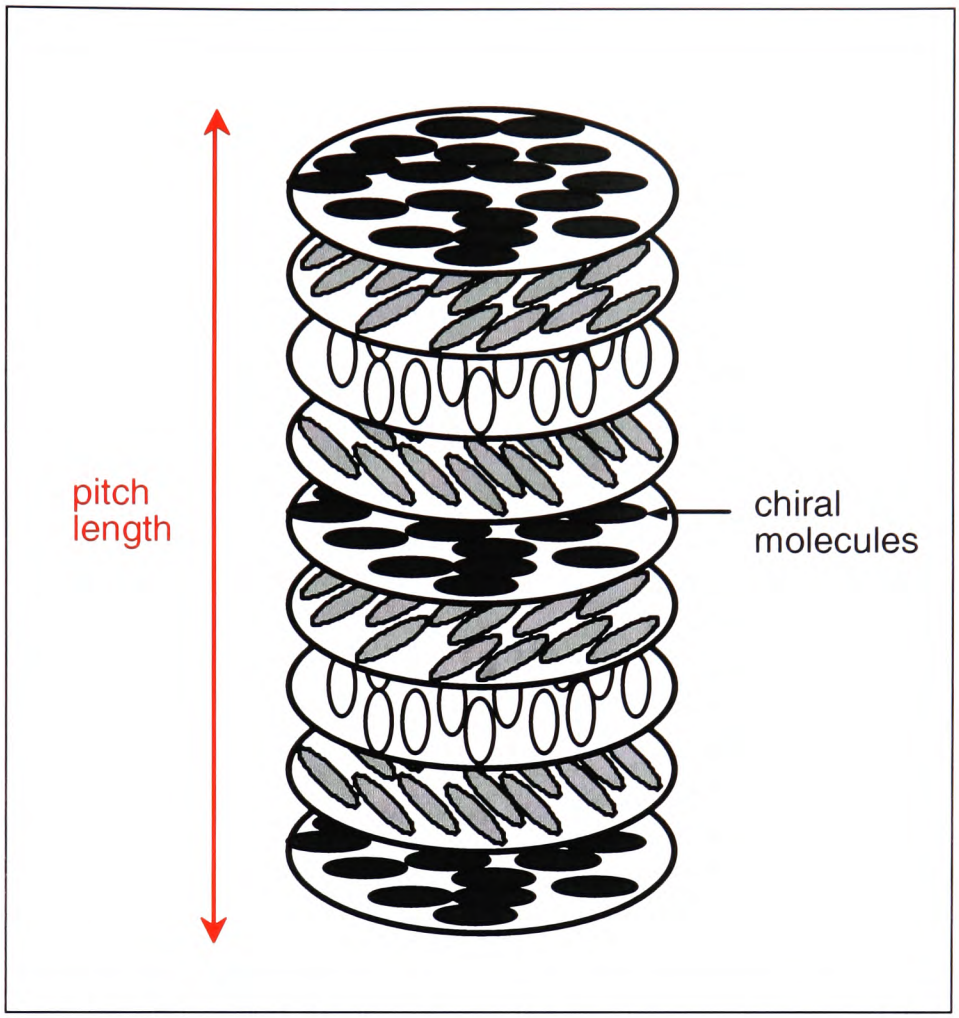


Figure 1.6. Helical structure of the chiral nematic phase.

1.4.1.2 The Chiral Smectic C Phase and Subphases

As was shown in figure 1.4, the molecules within a SmA phase lie orthogonal to the layer normal. This is also the case if a chiral moiety is incorporated into the molecular structure. However, in the case of a tilted SmC phase, the inclusion of a chiral moiety within the molecular structure dramatically affects the symmetry of the phase and therefore also its properties. The symmetry of the achiral SmC phase is shown in figure 1.7 and consists of a two-fold axis normal to the direction of tilt, a mirror plane, and a centre of symmetry. Thus, the phase is assigned the point group 'C_{2h}'[31, 34-36].

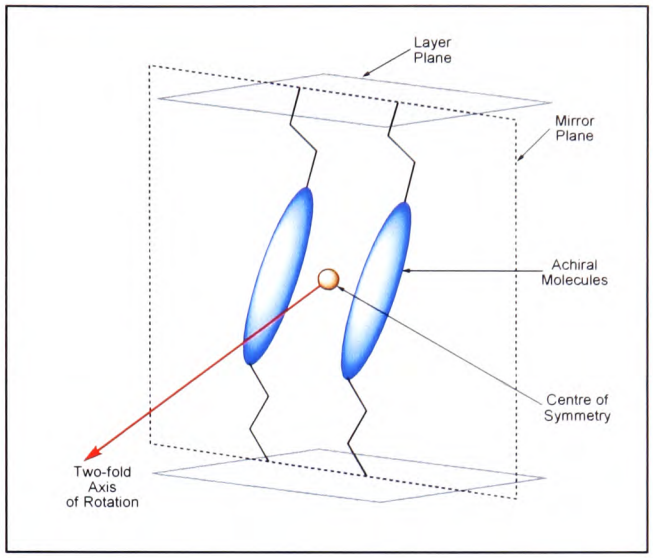


Figure 1.7. C_{2h} Symmetry of the achiral SmC phase. For clarity, one layer is shown.

Introducing a chiral unit to a SmC phase causes a reduction in the symmetry of the phase, due to the preferential packing of the chiral units within each layer, as a result of the chiral molecules packing more efficiently when groups are pointing in the same direction, thus representing a C_2 symmetry argument[31, 34-37]. The reduced symmetry of the phase also generates a dipole acting along the two-fold axis, termed the 'spontaneous polarisation' (Ps), as shown in figure 1.8.

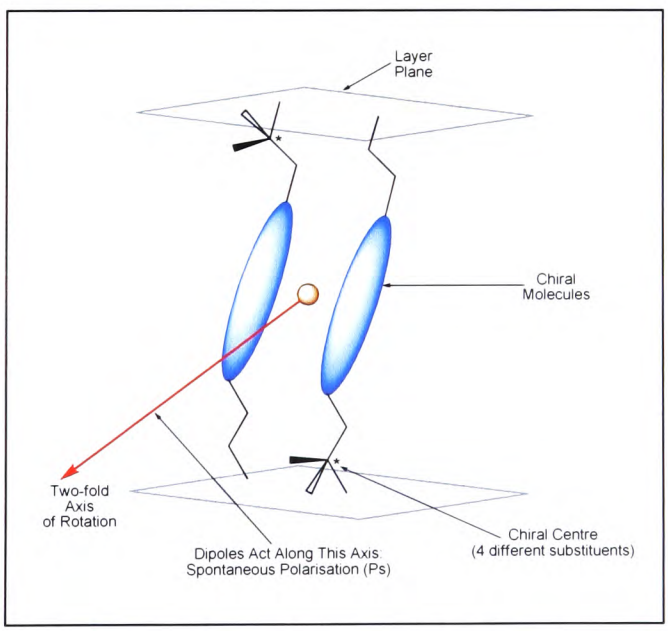


Figure 1.8. C_2 Symmetry of the chiral SmC* phase. For clarity, one layer is shown.

Figure 1.8 shows the consequences of the reduced symmetry upon a single layer of the SmC* phase, and the preferred orientation of the molecules due to the chiral units. When this concept is extended into the bulk phase, a helical structural arrangement results, similarly to that of the chiral nematic. Due to the tilted, layered nature of the molecules within the smectic layers, it is inherently a more complex structure[38], and a chiral smectic C phase arises (denoted by SmC*). As can be seen in figure 1.9, in the SmC* phase, the direction of tilt rotates gradually from layer to layer, which also causes the direction of the polarisation (shown by the letter '**P**' in figure 1.9) to rotate. Whilst each layer within the phase has a polarisation direction, this is cancelled out throughout the bulk of the phase due to the rotation throughout the helix. Figure 1.9 illustrates one complete rotation of the director, which corresponds to the pitch length of the material. The overall polarisation is equal to zero, leading the phase to be classed as 'helielectric', rather than 'ferroelectric'[9]. The tilt angle of the SmC* phase is temperature dependent, resulting in the largest tilt angle being generated at lower temperatures.

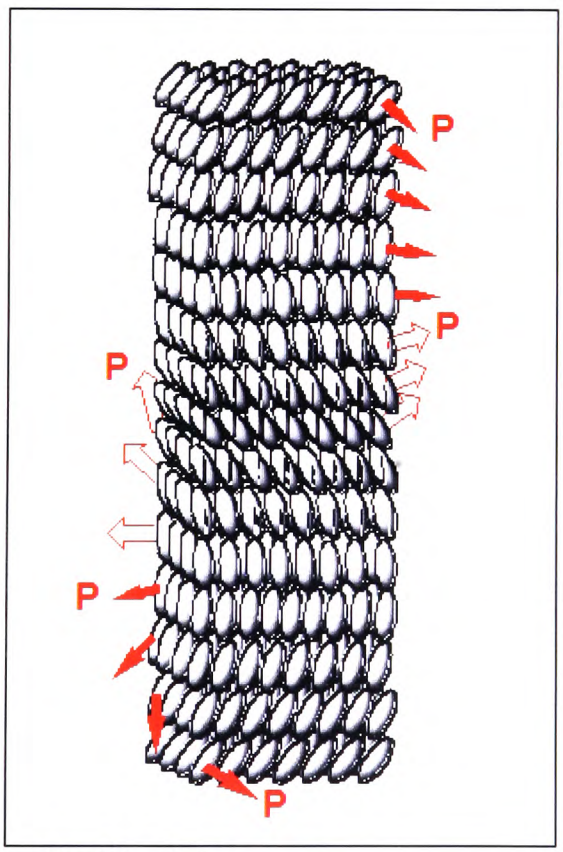


Figure 1.9. Structure of the chiral SmC phase.

Therefore, the helical nature of the SmC* phase also exhibits optical properties similarly to the chiral nematic phase. In contrast to the chiral nematic phase, the temperature has an opposite effect on the pitch length. As the temperature is reduced, the tilt angle of the SmC* phase increases, which therefore causes the pitch of the helix to tighten, reducing the pitch length. Increasing the temperature has the opposite effect, resulting in an enlarged pitch length[9, 31].

1.4.1.2.1 Ferro-, Antiferro- and Ferri-electric Phases

Whilst the overall polarisation of the SmC* phase is zero in its unwound state (figure 1.9), each layer has a polarisation associated with it due to the reduced symmetry (shown in figure 1.8), and is therefore ferroelectric. However, by unwinding the helix, it is possible to generate a truly polarised phase, as a result of the polarisation of each layer no longer being cancelled out as the direction of polarisation rotates.

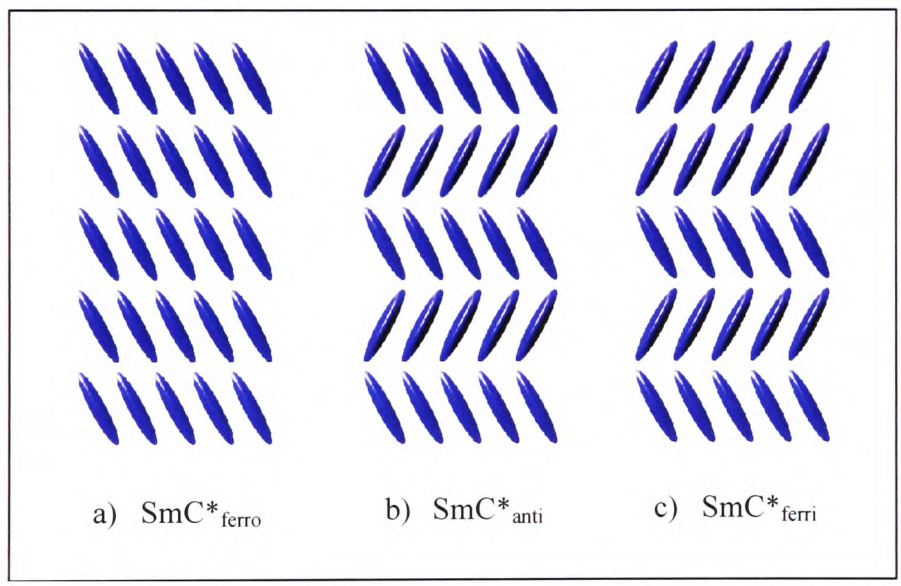
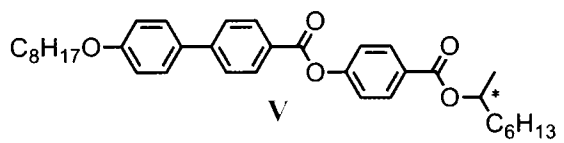


Figure 1.10. Structures of the SmC^*_{ferro}, SmC^*_{anti}, and SmC^*_{ferri} subphases, in unwound states.

Figure 1.10a shows the structure of the ferroelectric phase (SmC^*_{ferro}), where the tilt direction of the molecules within the layers is equal throughout the layers, therefore generating an overall polarisation[9, 35]. The antiferroelectric phase (figure 1.10b) arises when the direction of tilt alternates from layer to layer, resulting in zero polarisation, due to the polarisation of each layer being cancelled out by the next, where the tilt is in the opposing direction[35, 39]. The final subphase is the ferrielectric phase (figure 1.10c), which is to some degree an intermediate between the ferro- and anti-ferroelectric phases[35]. The direction of tilt within the ferrielectric

phase alternates between the layers, but not to an equal extent (as is with the antiferroelectric phase), and therefore there is a greater proportion of layers with the tilt direction in one orientation, therefore providing an overall polarisation. Whilst it is possible to determine each of these subphases by optical microscopy, it can be extremely difficult and relies upon substantial experience. Electrooptical measurements can also be used to characterise / confirm each of these phases, as the differing arrangements give rise to differing responses when an electric current is applied[35, 40]. A typical example of a calamitic structure generating the SmC* phase(s) is compound V, the classical material 1-methylheptyl 4-(4'-octyloxybiphenyl-4-carbonyloxy)benzoate (MHPOBC)[9, 41, 42]. MHPOBC has been the subject of many research activities and publications due to its interesting mesophase morphology, which exhibits not only the SmC* phase, but the three sub-phases of the SmC* phase, namely ferro-, antiferro- and ferri-electric. In addition to these phases, the compound also exhibits the SmC^*_{α} phase, which is found as an intermediate phase between the SmA* and SmC*, although its structure is not fully understood[43].



V

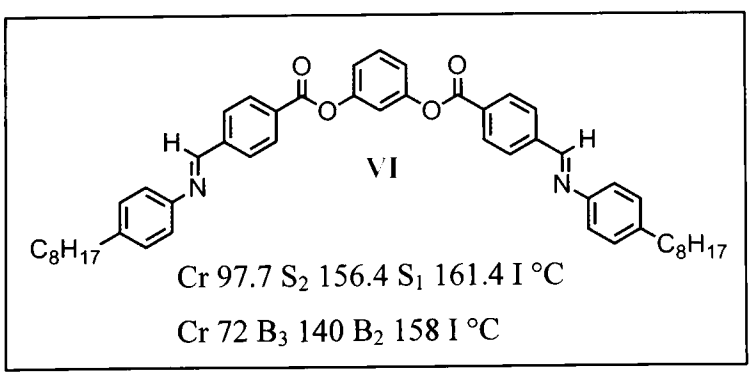
Cr 74.5 SmC^*_{anti} 118 SmC^*_{ferri} 119 SmC^*_{ferro} 121 SmC_{α} 122 SmA 156 I

When an electric field is applied to the SmC* phase, the Ps couples to the DC field, and produces two switched states[41], attainable *via* reversal of the DC current and results in the constituent molecules rotating around a 'cone'. This switching phenomenon generates the potential for device applications and will be discussed in section 1.6.

1.5 Bent-core Liquid Crystals

1.5.1 Phenomenon and Background

As has been previously referred to in section 1.2, the initial observations of liquid crystalline phases and behaviour resulted in the conclusion that in order for a compound to be mesomorphic, the molecular architecture must be of a linear, or very-near linear shape. Although the pioneering work of Chandrasekhar in the field of discotic liquid crystals dispelled this theory somewhat, the overall thinking related rod-like molecules to calamitic phases (ie. the nematic, and smectic phases), whereas, a discotic shape gave rise to discotic phases (ie. the discotic nematic and columnar phases). In the case of calamitic systems, it is still largely the case that a deviation from a linear structure will result in a reduction of mesophase stability and / or temperature range[44, 45]. In the early 1900s, Vorländer reported liquid crystalline behaviour (albeit of an unknown mesophase) in bent-core systems, however little interest was generated due to the growing knowledge that the generation of liquid crystalline phases was favoured by linear molecular architectures[44, 46] and it was not until Vorländer's compounds were re-investigated by Pelzl nearly one hundred years later that banana mesomorphism would be confirmed[46]. Matsunaga synthesised a number of banana-shaped structures in the early 1990s, reporting them as exhibiting smectic and nematic liquid crystalline properties, but unable to fully characterise the phases observed[44, 47]. However, it was not until 1996 and the work of Niori, that it was shown that a bent-core, banana-shaped molecular architecture (compound VI[44, 48, 49]) could generate a new class of mesophase[48, 50, 51], not miscible with conventional calamitic phases[49]. The unusual nature of the phases observed caused Niori to designate them as S_1 and S_2, although these would be later re-assigned B_2 and B_3, respectively, as will be discussed later in this section.



VI

Cr 97.7 S_2 156.4 S_1 161.4 I °C

Cr 72 B_3 140 B_2 158 I °C

Of particular interest was the fact that the banana-shaped molecules gave rise to chiral mesophases, despite the molecules themselves being achiral, generating ferroelectric switching as a result of the reduced symmetry[48]. It should be noted that an equal quantity of oppositely-handed domains exist within the bulk phase. These preliminary findings sparked a large interest in the area of bent-core systems and as a result there has been a large increase in the number of bent-core related work and publications, including several excellent reviews[44, 45, 49, 52, 53]. As a greater number of banana-shaped systems were synthesised, numerous 'banana phaes' were observed, and it was suggested at a workshop entitled 'Chirality by Achiral Molecules' held in Berlin (1997), that these phases should be decribed *via* the nomenclature B_1 through to B_8[44, 49, 50, 54-56] according to the order in which they were discovered.

1.5.2 Banana Phase Structure and Properties

Since the 'discovery' of banana phases in 1996, there have been eight phases identified as being 'banana phases', observed as a result of modifying the molecular structure. Although a detailed analysis of the complete range of banana mesomorphism is beyond the scope of this thesis, the following section will give an overview of each of the banana phases, explaining the main properties and / or characteristics. Further information regarding banana phases, and their interesting properties has been the subject of a number of excellent reviews by Pelzl[49], Hird[44], Ros[52], Takezoe[45] and Reddy[53].

B_1 Phase

The B_1 phase was first observed for shorter alkyl chain length members of banana-shaped systems, such as reported by Niori[48, 49], and is characterised by a mosaic-like optical texture. Since its discovery, the B_1 phase has been characterised as columnar in nature and can be further sub-divided into either tilted (Col_{ob}) or nontilted (Col_r)[53].

B_2 Phase

The higher temperature phase (S_1) presented by Takezoe at the 1996 International Liquid Crystal Conference was subsequently renamed the B_2 phase[50] and has subsequently become the most common phase observed, found in many homologous series[49]. The phase is closely related to the 'conventional' SmC phase, sharing a tilted, layered structure. The interesting switching properties and phase structure of the B_2 have received substantial interest and will be dicussed in further detail in section 1.5.2.1.

B_3 Phase

The B_3 phase is often found to be a lower temperature phase generated upon cooling the B_2 phase and is actually a crystal phase[49, 50, 57], possibly hexatic in nature[53]. Similarly to the crystal subphases of the smectic varieties (shown in figure 1.4), the B_3 phase is termed a mesophase, but is not liquid crystalline.

B_4 Phase

In addition to the B_3 phase, the B_4 phase is also a crystalline mesophase[50, 57] exhibiting a characteristic blue colour[50], due to the Rayleigh-like light scattering in the near UV region. Although the molecules are achiral, the phase incorporates a helical, chiral structure due to the twisting of the molecules, which is characterised by the two domains exhibiting opposite optical activity[49].

B_5 Phase

This phase is formed mostly upon cooling the B_2 phase and exhibits electrooptical switching which is comparable with the B_2 and B_8 phases[49, 50, 54, 58].

B_6 Phase

The B_6 phase exhibits a fan-shaped texture which is similar to a SmA phase, but with no homeotropic texture[49]. X-ray patterns have since enabled the phase to be classified as a tilted, intercalated smectic phase without in plane order[49].

B_7 Phase

Found primarily in nitro-substituted compounds[49, 50, 59], it has been suggested in the literature that there are a number of variants to the B_7 phase[60], as there have been compounds reported that exhibit B_7 phases with both ferroelectric[58, 60] and antiferroelectric[58, 61, 62] behaviour. Similar to the B_4 phase, the B_7 incorporates a helical structure[57] which gives rise to domains of opposite handedness[49]. The B_7 phase has received particular interest due to the unusual ribbon and spiral textures exhibited[53, 59, 63, 64].

B_8 Phase

This is regarded as being analogous to the bilayer smectic type phase and exhibits an antiferroelectric response, similar to the B_2 and B_5 phases[54].

1.5.2.1 Properties of the B_2 ($SmCP_A$) Phase

The B_2 phase has received substantial research interest in the area of banana-shaped liquid crystals, due to the frequency in which it is observed and the interesting nature of the phase structure, electrooptical properties and the similarity of the B_2 phase with the chiral SmC^* phase. As the B_2 phase has undergone further and more detailed investigation, the actual nature of the phase has been more thoroughly understood and the nomenclature has been updated accordingly. The B_2 phase can now be classified as the $SmCP_A$ and has the general structure as shown in figure 1.11 (only one layer has been shown for clarity and simplicity).

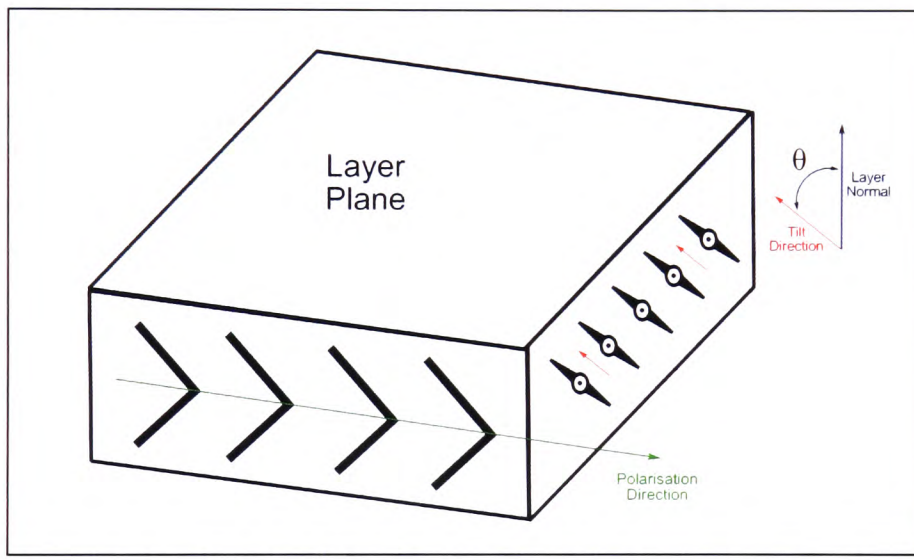


Figure 1.11. Single layer of the B_2 ($SmCP_A$) phase, showing the direction of polarisation, and tilt angle (θ). Adapted from Link et al.[65].

The nomenclature '$SmCP_A$' relates to the fact that for the ground-state configuration, the molecules within the layers of the phase are tilted relative to the layer normal (hence 'SmC'); the orientation of the molecules within the layer generates a polarisation (hence 'P'), directed parallel to the layer, as shown in figure 1.11. However, the structure of the bulk of the B_2 phase is more complicated and can be of two different ground state structures, which in turn give rise to two differing structures when an electric field is applied. The two ground-state structures of the B_2 phase are defined as 'SmC_SP_A', and 'SmC_AP_A', as shown in figure 1.12. At the top of the figure, the structure of the SmC_SP_A phase is shown, along with the two 'switched states' generated from the application of an electric field. As can be seen in figure 1.12, in the ground state SmC_SP_A structure (E = 0), the tilt direction from layer to layer is the same, therefore representing a 'synclinic' arrangement ('SmC_S').

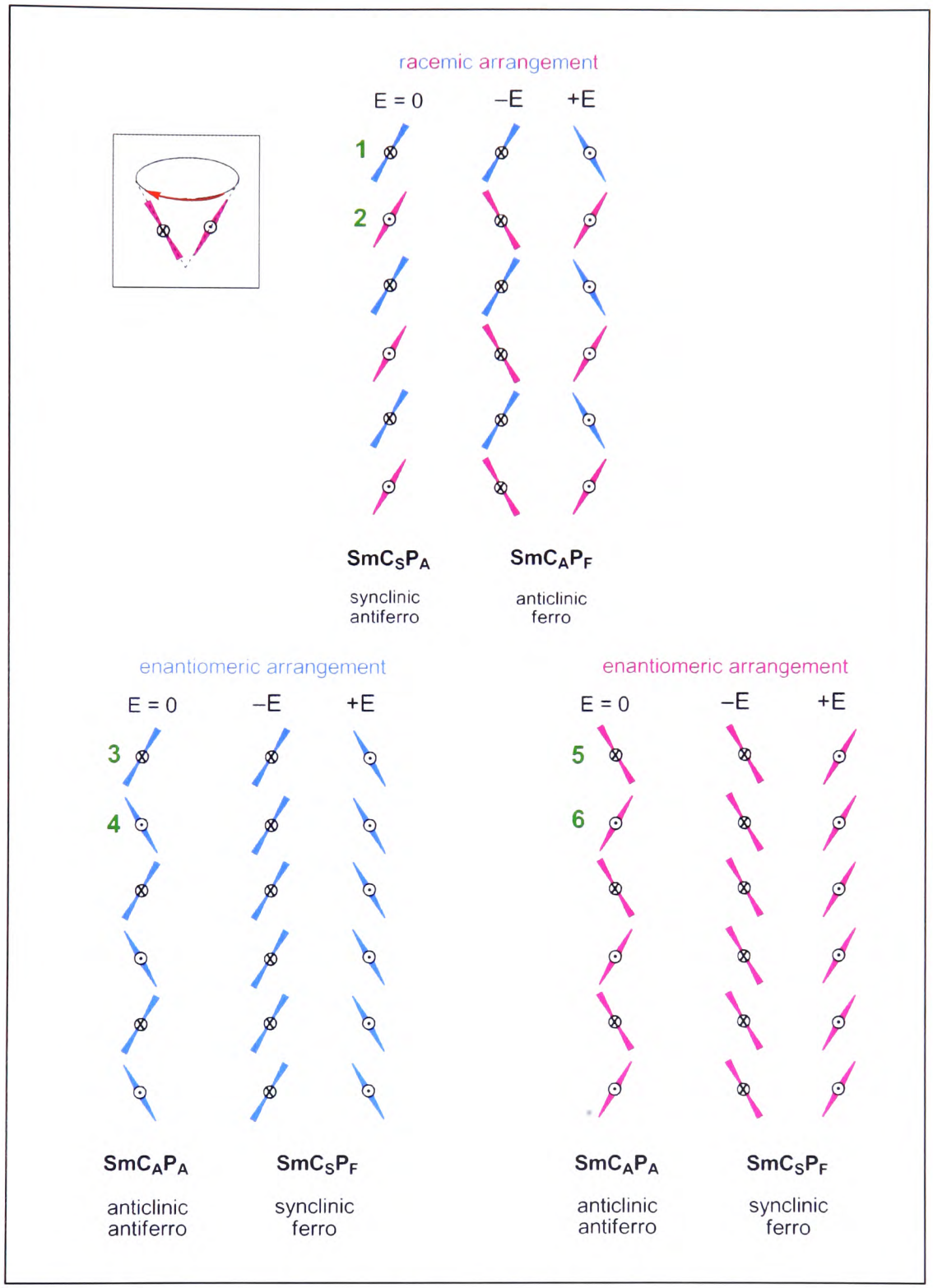


Figure 1.12. Arrangement of the molecules within the $SmCP_A$ phase. Adapted from Link et al.[65] and Hird[37].

The polarisation direction, however, reverses from layer to layer, depicted by the 'arms' of the bent-core constituent molecule either coming out of the plane of the paper (depicted by the blue molecules), or going into the plane of the paper (depicted by the purple molecules)

and therefore represents an 'antiferroelectric' structure (P_A). When an electric field is applied, the molecules orientate so that the Ps aligns with the electric field. For the SmC_SP_A phase shown in figure 1.12, application of '–E' results in no change for the blue molecules. However, the purple molecules undergo a rotation (as shown in the inset diagram of figure 1.12), in order for the Ps to align with the electric field, which also causes a reversal of tilt direction. The resultant structure formed when the electric field is applied is defined as 'SmC_AP_F', due to the alternating (anticlinic) tilt direction ('SmC_A') and the 'ferroelectric' ordering of the polarisation direction (P_F). The second ground state configuration of the $SmCP_A$, the SmC_AP_A phase, is shown in the lower half of figure 1.12 and corresponds to an anticlinic ordering of the tilt angle from layer to layer, and an antiferroelectric arrangement of the Ps of each layer. Once again, the application of an electric field causes the molecules to align and in this case results in a synclinic arrangement of tilt angle and ferroelectric ordering, which therefore corresponds to the nomenclature 'SmC_SP_F'. In the case of the SmC_AP_A and SmC_SP_F phase structures shown in figure 1.12, the purple molecules represent a mirror image of the corresponding blue molecules.

These considerations of the phase structure provide reasoning for the observation of macroscopic chirality in the B_2 phase, despite the molecules themselves being achiral[65]. As denoted in figure 1.12, the SmC_SP_A and SmC_AP_F structures represent racemic domains of the phase. This can be explained by considering and comparing molecules **1** and **2**. If molecule **1** undergoes a transformation (as depicted in the inset diagram of figure 1.12), the resultant orientation would have an equal polarisation to that of molecules **2**, but an opposite tilt. This is also the case if adjacent layers are considered in either of the switched states of the SmC_AP_F phase structure and therefore represents an alternating chirality from layer to layer, thus generating a racemic arrangement. The two enantiomeric arrangements shown for the SmC_AP_A (blue) and SmC_AP_A (purple) structures are responsible for the observation of chiral domains within the bulk phase and can be explained by consideration of molecules **3** and **4**. When molecule **3** undergoes a transformation (as depicted in the inset diagram of figure 1.12), then the resultant orientation will have an equal tilt and polarisation direction to that of compound **4**. However, if molecules **3** and **5** are considered, a transformation of molecule **3** would result in an equal tilt direction to compound **5**, but an opposing polarisation direction. This would also be the case if molecules **4** and **6** are considered, therefore giving rise to the observation of enantiomeric, or chiral domains.

1.5.3 Structure-Property Relationships of Bent-core Systems

1.5.3.1 Bent-core 'Calamitic-like' Systems

The rod-like nature of calamitic molecules is responsible for the anisotropic nature of the overall molecular shape, which gives rise to their liquid crystalline properties and subsequent use in applications such as display devices. Figure 1.13 shows a generalised structure for a calamitic structure, where the core units, A and B and the terminal chains, R and R' are linked together *via* various linking groups, X, Y, and Z.

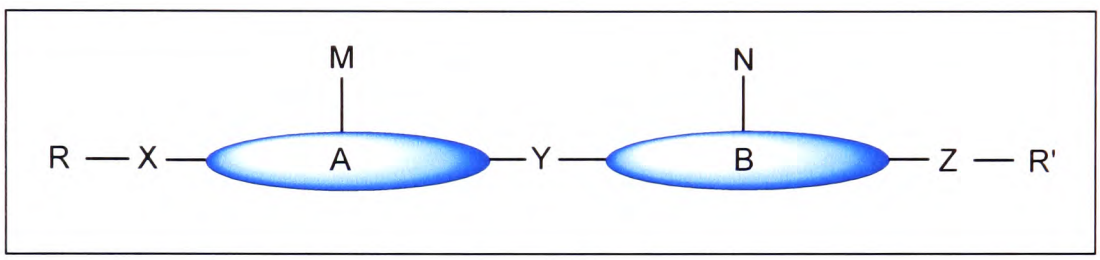
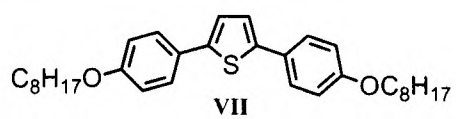


Figure 1.13. Generalised structure of a calamitic molecule.

It is usual to find that the core units of the molecules are of an aromatic or cyclic nature, as these provide a degree of rigidity to the molecule, without adding substantial breadth / width (both of which would have a detrimental effect upon liquid crystal phase generation). The linking groups can be identical, or each be of a different functionality, such as esters, ether, imine, carbon-carbon double / triple bonds, or even a simple single bond. Lateral substituents (M and N) are also employed in order to change the resultant mesophase morphologies and commonly employ small units such as the fluoro substituent, which does not cause a particularly large increase in breadth, but does confer high polarity[66], which is particularly important, for example, in ferroelectric applications where a lateral dipole is required.

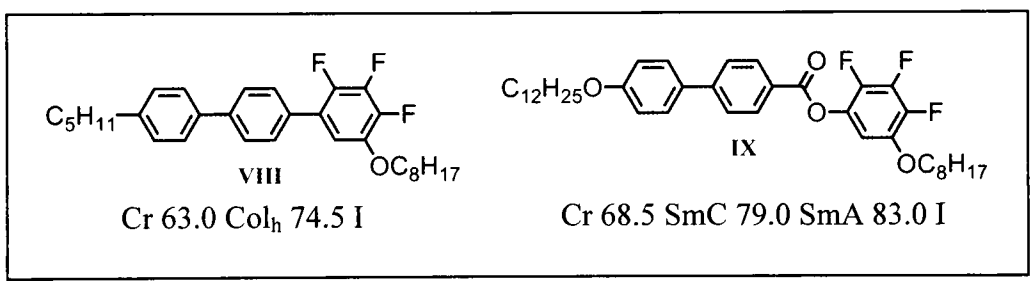
Before the advent of bent-core (banana-shaped) liquid crystals as is known today, it was found that the introduction of a minimal bend to a 'typical' calamitic structure did not have a catastrophic effect upon the mesophase stability. Compound **VII**[67] is such an example, where a five-membered heterocyclic ring, in this case a thiophene ring, generates a slight bend within the molecule (approximately 150°[66]).



VII

Cr 154 SmC 161 SmA 164 N 167 I

Despite the fact that compound **VII** incorporates a bent-core, and therefore detracts away from the stereotypical 'rod-like' molecular structure required for the generation of calamitic mesophases, a rich mesomorphism is observed, albeit relatively short-ranged due to the magnitude of the melting point. Other five-membered heterocyclic rings such as thiophene[68-71], selenophene[71, 72], thiazole, thiadiazole[73], and oxadiazole[74-76], have also been employed in a similar manner, so as to accommodate a bend within the molecular structure, whilst maintaining near-linearity, therefore generating calamitic mesophases[44]. Compounds **VIII** and **IX**, synthesised by Hird[55], incorporate a more significant bend within the molecule, due to the 1,3-disubstitution pattern of the 'core'. For these compounds, a bent-core was necessary to accommodate the trifluoro-substituents, intended to further explore the area of high dielectric biaxiality. As can be seen from the transition temperatures, the increased degree of bend (in comparison to five-membered rings such as compound **VII**) has not had the catastrophic effect that may be expected, and indeed some very interesting properties were exhibited.



Cr 63.0 Col_h 74.5 I

Cr 68.5 SmC 79.0 SmA 83.0 I

Compound **VIII** is particularly interesting, generating a columnar phase rather than an expected calamitic phase. When investigated further, the columnar phase of compound **VIII** also exhibited ferroelectric switching, indicating a reduction in symmetry of the mesophase. The phenomenon of reduced symmetry is also observed for structures such as compound **IX**, where domains of opposing handedness were observed within the SmC phase[55]. Whilst these bent-core compounds (**VIII** and **IX**) are not of a 'banana-shape' and instead constitute a more 'hockey-stick' shaped molecular architecture, the reduced symmetry of the mesophase(s) introduces a link to the 'banana phases' exhibited by molecular shapes of a true 'banana-shape'. This supports the knowledge that phases such as the B_2 ($SmCP_A$) phase closely resembles the SmC phase and therefore share similar properties.

1.5.3.2 Banana-shaped Systems

As has been discussed in section 1.5.1, liquid crystalline phases have been known in banana-shaped systems since the work of Vorländer at the beginning of the twentieth century, but it is only relatively recently that the interesting properties and mesophases associated with such molecular architectures has begun to be understood and investigated. This has resulted in a vast array of banana-shaped systems being synthesised, varying in the number of rings, the linking groups employed and a variety of substituents located at various points upon the molecule. Many of the banana-shaped systems synthesised have been of a common structure, as shown in figure 1.14. Molecules with five phenyl rings are very common, although banana-shaped systems with additional rings have been reported. Symmetrical banana-shaped systems are also very commonly found, due to their relative ease of synthesis[37, 44]. Similarly to the calamitic systems described previously, the linking groups are often esters, ethers, imine or carbon-carbon bonds, along with alkyl or alkyloxy terminal chains.

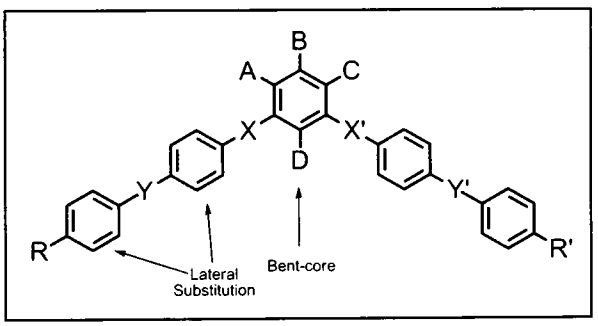
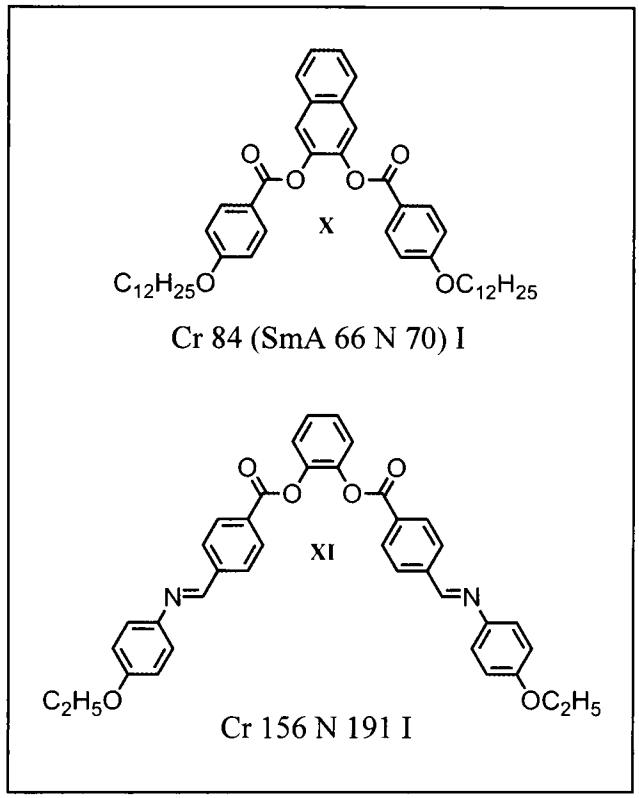


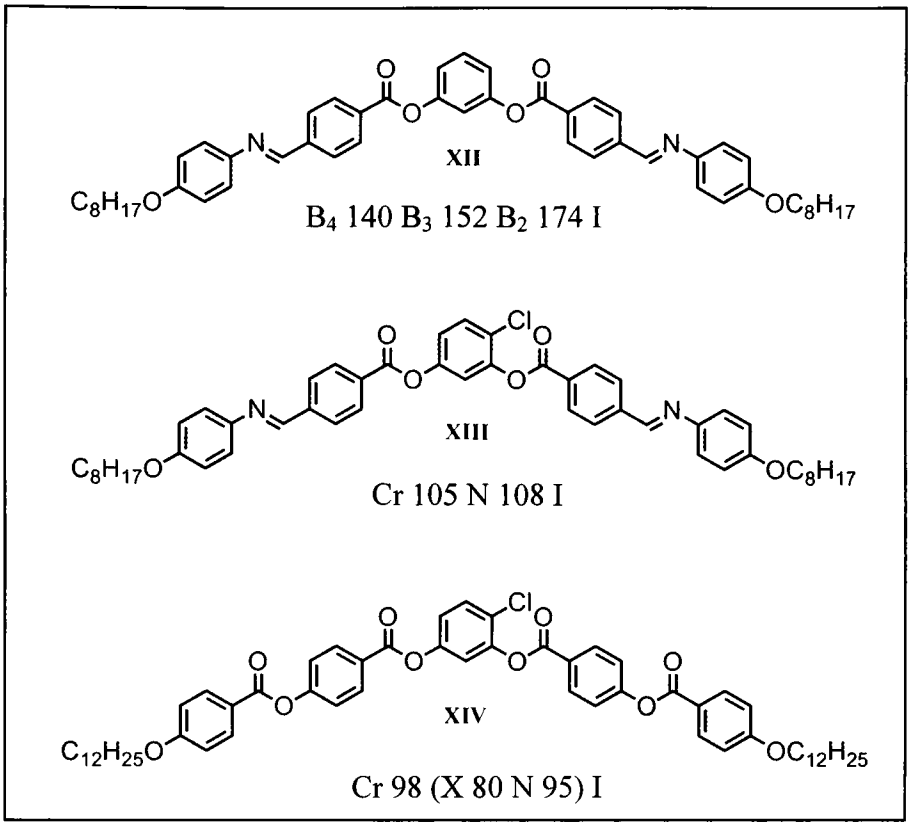
Figure 1.14. Generalised structure of a banana-shaped molecule.

The introduction of small substituents, such as halogen, methyl, methoxy and nitro units, to the bent-core (A, B, C and D in figure 1.14), or 'arms' (shown by arrows in figure 1.14) of such molecules results in the generation of the novel mesophases now described by the nomenclature B_1-B_8[49]. Whilst initial investigations into the effect of various substitution on banana-shaped molecules was aimed at surveying the new and exciting 'B-phases', at more accessible temperatures[49], it has also been shown that selection of an appropriate molecular architecture can result in the generation of a calamitic mesophase, from a 'banana-shaped' molecule. Compounds X and XI are such examples, where the 1,2-disubstitution pattern of the bent-core generates a greater degree of bend compared to the 1,3-disubstituted systems previously discussed. It can therefore be envisaged that as the angle of bend at the bent-core

becomes more acute, the 'arms' of the molecule become closer together. Therefore the overall molecular shape resembles that of a calamitic rod-like molecule.



Perhaps of more interest is the observation of a calamitic phase in a 'true' banana-shaped structure (compounds **XIII** and **XIV**), as reported by Akutagawa[47] and Pelzl[77]. It is interesting to note the rich banana mesomorphism exhibited by compound **XII**, the un-substituted analogue of compound **XIII**. The addition of the single chloro-substituent at position 4 of the bent-core in compound **XIII** causes a complete loss of banana mesomorphism and instead facilitates the generation of a 'conventional' calamitic phase, in the form of a nematic. Compound **XIV** is of a similar construction to compound **XIII** and also exhibits a nematic phase, in addition to an uncharacterised lower temperature phase (designated 'X'), but of more interest is the observation of chiral domains within the nematic phase, indicating a helical nature[77], despite being achiral at a molecular level.



Whilst for many years it seemed that deviating away from a linear, or near-linear molecular shape, would result in a detrimental effect upon mesophase generation, the advent of 'banana-shaped' liquid crystals changed the outlook of the liquid crystals field, and showed that it was possible to generate mesophases from a 'bent-core' structure, albeit of a different class to the 'conventional' calamitic phases. However, results such as shown for compounds **X**, **XI**, **XIII** and **XIV**, show that it is possible to bridge the gap between conventional and banana mesomorphism, indicating that there is a boundary between the two, relating to molecular structure. It is particularly interesting to note that the nematic phase of compound **XIV** exhibits chiral domains despite the molecules being achiral, indicating that the bent-molecular shape is conveying a degree of the properties from a reduced symmetry banana phase, into the calamitic nematic phase. The past decade has uncovered numerous interesting and exciting properties and observations regarding bent-core systems and banana phases, although as is the case for calamitic systems, there is yet more to explore and investigate.

1.6 Applications of Liquid Crystals

When considering the practical applications that have been developed as a result of the discovery of liquid crystals and their fascinating properties, it is easy to underestimate the actual length of time that liquid crystals in general have actually been in use. The use of lyotropic liquid crystals as soaps and detergents dates back nearly five thousand years[78], although, the concept of 'liquid crystals' was obvisouly not considered at the time. Whilst the action of soaps and detergents have become more and more advanced as the understanding of these liquid crystalline systems has been established, the most prominent application of liquid crystals has been in the field of displays and these displays can now be found in many devices, ranging from televisions, to mobile phones and even toasters!

1.6.1 Applications Based Upon the Nematic Phase

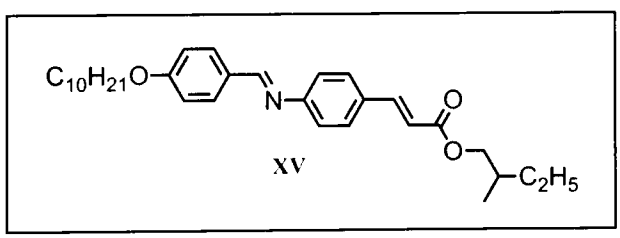
As was described in section 1.4.1.1, the introduction of chirality to the nematic phase results in a gradual rotation of the director of the nematic phase to form a helical structure (figure 1.6). If the pitch length of the helix is within the wavelength range of visible light, a selective reflection occurs, and therefore a colour is observed. The actual colour observed is dependent upon the pitch length, which in turn is dependent upon the temperature (an increase in temperature causes a shortening of the pitch length, whilst a decrease in temperature causes an increase in pitch length). This phenomenon forms the basis of the use of a chiral nematic in a thermochromic device, and has been used successfully in many applications such as thermometers and thermal imaging of conditions such as cancer, especially in remote locations[79], where access to full medical facilities is not possible. For mainly aesthetic reasons, thermochromic liquid crystals are also used in applications such as paints that change colour upon experiencing a change in temperature[9] and can be seen on some cars or even Formula 1 crash helmets![80]

However, it is the use of nematic liquid crystals in display devices (LCDs) that has been one of the catalysts of liquid crystalline research, since the possibility was discussed at the first ILCC meetings. Whilst the concept of using the nematic liquid crystal phase in a display device developed over the proceeding years, it was not until the breakthrough work of Gray at the University of Hull in the 1970s that the displays became a practical and commercially viable possibility. The cyanobiphenyls, synthesised by Gray, were the first liquid crystalline compounds that matched the required properties with which a display device could be made; firstly, the nematic phase of the compounds was exhibited at, or very close to, ambient

(room) temperature; secondly the compounds were stable and not prone to decomposition[81]. In reality, it is extremely unlikely that a single compound will match the exact requirements of a device and therefore mixtures of compounds are employed, so that an 'ideal' liquid crystalline mixture can be obtained. Indeed it is not always a requirement that a compound be liquid crystalline in order to be included in a liquid crystalline dispay mixture[82]. The twisted nematic liquid crystal display (TN-LCD) was developed in 1970 and soon became a prominent fixture within the display market for displays with relatively low information needs such as watches and calculators[83], due to the low power consumption of the devices[84]. As the electronics associated with the TN-LCDs developed, it was not long before displays were capable of exhibiting more complex information and flat-panel displays for use in laptop computers began to be developed and produced. Over time, variations of the TN-LCD have been developed that provide faster switching times, higher contrast ratios and better viewing angles. These include the super-twisted nematic[83, 85] (STN-LCD) and the vertically aligned nematic[83, 84] (VAN-LCD), which is found most commonly in displays such as computer monitors and televisions at present. Viewing angles have also been impoved through the use of discotic liquid crystals as compensation films[86].

1.6.2 Ferroelectric Displays

In 1974, Meyer showed that the chiral SmC phase should be ferroelectric, as a result of the reduced symmetry[36, 70, 87] (described in section 1.4.1.2) and a year later proved his theory by reporting the first ferroelectric compound, 2-methylbutyl 4-decyloxybenzylidene-4'-aminocinnamate (DOPAMBC, compound **XV**)[36, 87].



XV

As was shown in figure 1.8, the reduced symmetry of the SmC* phase gives rise to a spontaneous polarisation, which couples to an applied electric field. Reversal of the electric field therefore generates the potential for two distinct switched states, as respresented in figure 1.15, where as can be seen, the reversed electric field causes the tilt direction of the molecules to change, according to the coupling of the polarisation with the electric field (E).

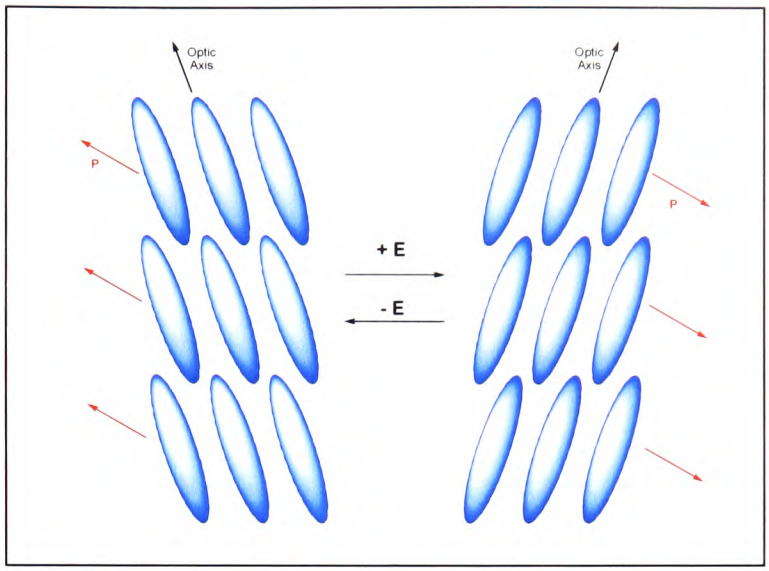


Figure 1.15. The two switched states of the ferroelectric SmC* phase.

As can be seen from figure 1.15, the direction of the optical axis also changes as the molecules are switched, therefore generating the potential for the use of the phase in a display device. In 1980 this potential was made reality by Clark and Lagerwall, who demonstrated the Surface Stabilised Ferroelectric Liquid Crystal Display (SSFLCD)[37, 87]. In the SSFLCD, the smectic layers are perpendicular to the electrodes of the device (as shown in figure 1.16). If the gap between the electrodes is smaller than that of the helical pitch length of the SmC* phase being employed, then the surfaces of the cell cause the helix to unwind, hence the unwound state is stabilised[87]. Figure 1.16a shows the SSFLCD in its 'dark state', where the optical axis of the phase is in line with the polariser and therefore light entering the device is extinguished. Reversal of the electric field causes the Ps to be reversed also, and therefore the tilted molecules undergo a rotation around a 'cone angle' depicted in the lower half of figure 1.16. The precise value of the cone angle is dependent upon the liquid crystalline material present in the cell, but the magnitude always twice that of the tilt angle, ie. 2θ. When the molecules have been 'switched' by reversal of the electric field, the optical axis is therefore no longer in line with the polariser (figure 1.16b), and therefore light entering the device is not extinguished, hence the cell is in its 'light state'. Removal of the electric field does not cause a relaxtion of the molecules, and therefore the two switched states are bistable. This property is one advantage over the TNLCD, as the bistable nature does not require constant power, instead only requiring the application of power to actually switch the display 'on' or 'off', therefore promoting battery life. A second advantage is the switching time, which is

quicker than found for a TNLCD, as a result of the molecules rotating around a cone, rather than a complete change of orientation in the TNLCD[88].

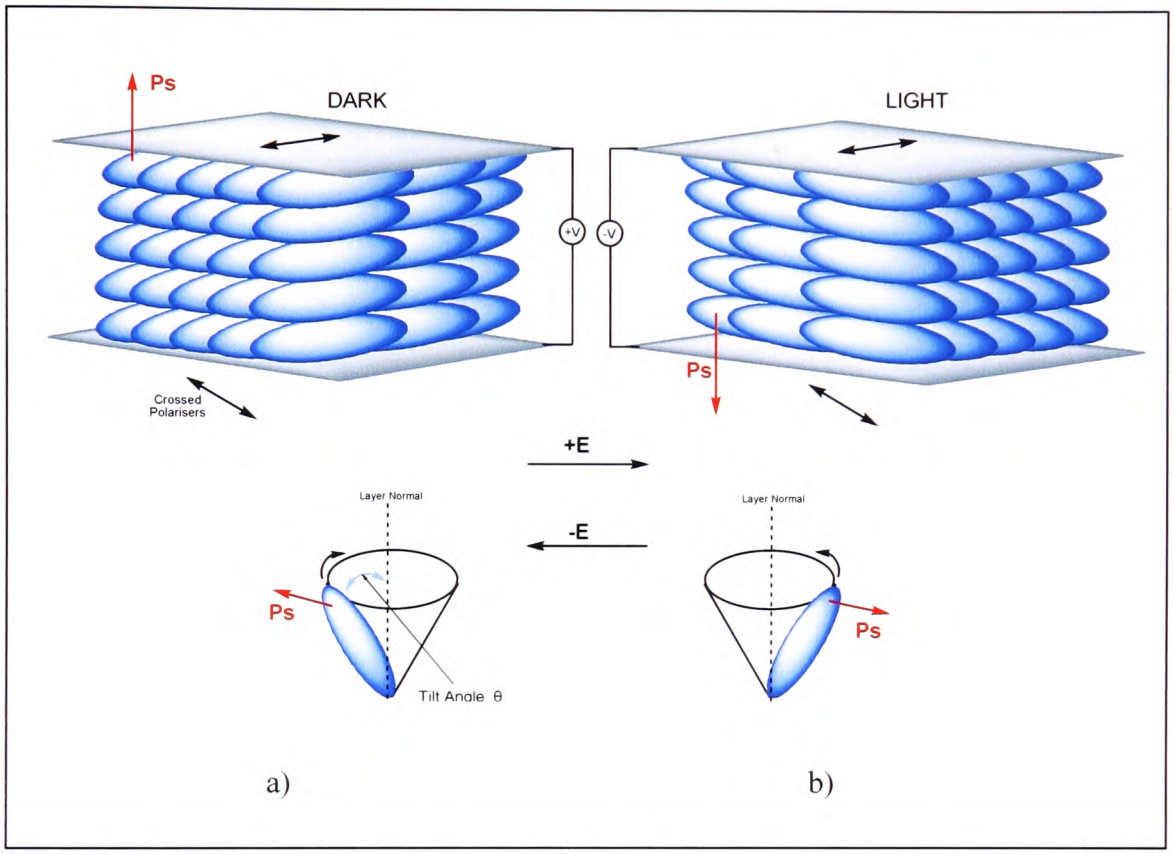
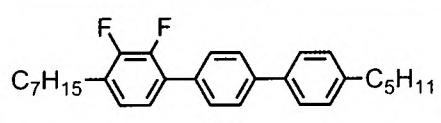


Figure 1.16. Surface Stabilised Ferroelectric Liquid Crystal Device (SSFLCD).

Whilst the market for large displays such as televisions is still dominated by nematic devices, the SSFLCD has found applications in smaller displays such as those found on digital cameras, and 'head mount' displays, such as those used by fighter pilots[79, 89]. In contrast to the TNLCD which requires a liquid crystalline material with positive dielectric anisotory, ferroelectric devices use materials with a negative dielectric anisotropy, of which difluoroterphenyls, such as compound **XVI**[9, 90], are a good example.



XVI

Cr 56.0 SmC 105.5 SmA 131.0 N 136.0 I

Similarly to the TNLCDs, a ferroelectric mixture is composed of a mitxture of compounds and usually consists of an achiral 'host' mixture with a chiral dopant added to generate the reduced symmetry required for the ferroelectric switching of the phase.

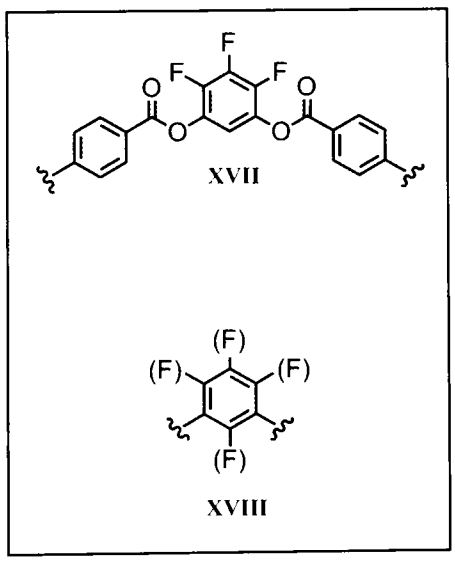
1.6.3 Potential use of Bent-core Liquid Crystals in Display Devices

Although at present the possibility of using bent-core liquid crystals within an application is still in its relative infancy, the potential is being explored, as the use of bent-core compounds may offer some advantages over existing technologies. One of the main difficulties that has to be overcome in any TNLCD or SSFLCD device is the issue of alignment of the constituent molecules within the cell. Alonso has recently reported a LCD using a non-oriented sample of bent-core molecules[91], using a sub-phase of the B_2 phase, which has an optically isotropic texture. Therefore the sample does not need to be aligned, which renders the device very easy to construct, and a large advantage over other display devices. Whilst the switching times and contrast ratios reported are also very comparable with other displays, the main problem at the moment is the lack of compounds exhibiting the required 'optically isotropic' phase and in addition, over the desired temperature ranges.

2. Aims and Objectives

2.1 Achiral Banana-shaped Compounds

The variety of banana phases and associated properties presents a very interesting area of research with regards to the structure-property relationships governing these observations. Of particular interest is the ability to generate calamitic nematic phases from seemingly banana-shaped molecules, as shown by compounds such as **XIII** and **XIV**, an observation not expected by the large deviation from linearity. It is intended within this work to further investigate this phenomenon, by introducing the trifluoro- bent-core reported previously by Hird[55] to a banana-shaped molecular structure, such as shown in structure **XVII**, in order to assess the effect of the fluoro-substituents upon the neighbouring linking groups. It is anticipated that by utilising the relatively flexible ester linking groups within the molecular structure will aid the generation of liquid crystalline phases from a molecular architecture that may not at first appear conducive to the generation of a mesophase. As has been shown in numerous examples found within the literature, the addition of various substituents at various positions upon the bent-core has interesting and sometimes very extreme effects upon the mesogenic properties of the compound.

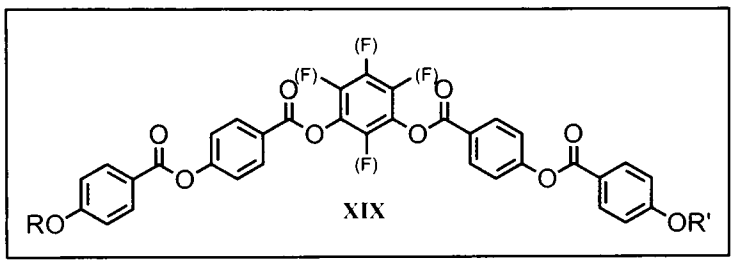


XVII

XVIII

It will therefore be of interest and relevance to investigate the effect of varying the degree of fluoro-substitution upon the bent-core structure, and synthesise mono-, di- and tri-fluoro

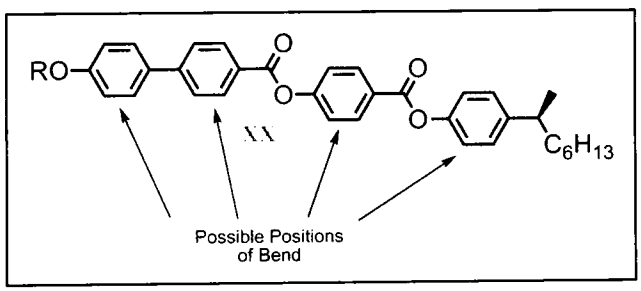
systems substituted in various patterns (structure **XVIII**). As a continuation upon the theme of asymmetry, this work will also investigate the effect of introducing asymmetry into the molecule in terms of the number of phenyl rings contained within the structure and also the length of the terminal alkoxy chains. It is therefore envisaged that overall the work will cover variations upon structure **XIX**, in order to assess the effects of firstly varying the degree and position of fluoro-substitution at the bent-core; and secondly also to look at how varying the symmetry of the molecule away from the bent-core affects the resultant mesophase generation and stability, whilst allowing for comparison with appropriate results reported in the literature.



XIX

2.2 Chiral Compounds Incorporating a Bent-core

As has been described in section 1.5, the 'B' phases exhibited by banana-shaped molecules generate a number of interesting properties, including the formation of chiral domains and ferroelectric / antiferroelectric responses to applied electric fields, despite the molecules being achiral in nature. Due to these properties, it is therefore possible to establish links and comparisons with the chiral Smectic C phase (SmC*), in particular in comparison to the tilted, layered nature of the B_2 ($SmCP_A$) phase. It has been shown in compounds such as VIII and IX that despite rendering the molecule non-linear, the introduction of a bend to a calamitic molecule does not result in a catastrophic failure upon the mesomorphic properties. It will therefore be of interest to investigate how the introduction of a significant bend to a chiral, calamitic molecule affects the generation, stability and properties of the resultant mesophase morphology. In the first instance, this work will focus upon how the position of a bend within a calamitic molecule affects its properties. This will be achieved by taking a calamitic molecule such as structure XX, and replacing the 1,4-disubstituted phenyl rings with 1,3-disubstituted 'bent-cores' as indicated by arrows, thus creating a similar bend to that employed in many achiral bent-core 'banana-shaped' systems.



Secondly, the trifluoro bent-core, as will be employed in the achiral section of this work, will also be investigated and it will be interesting to observe the effect that this has upon the neighbouring ester linking groups and therefore the conformational changes that will have a profound effect upon the mesomorphic properties.

3. Experimental

3.1 Experimental Introduction

3.1.1 Starting Materials, Reagents and Solvents

All starting materials were available commercially, and used without further purification, with the following exceptions:

Compounds 14 and 59 – provided by M. Hird
Compound 49 – provided by H.E. Metcalf

All solvents were used without further purification. In the case of low-temperature lithiaion reactions, anhydrous tetrahydrofuran (inhibitor free) from Aldrich was employed. *n*-Butyllithium was also acquired from Aldrich as a 2.5M solution in hexanes. Tetrakis(triphenylphosphine) palladium(0) was prepared according to the literature[92].

The following abbreviations for solvents and reagents are used throughout this thesis:

DCC	-	*N,N'*-Dicyclohexylcarbodiimide
DMAP	-	4-(N,N'-Dimethylaminopyridine)
n-BuLi	-	*n*-Butyllithium
sec-BuLi	-	*sec*-Butyllithium
LDA	-	Lithium diisopropylamide
PMHS	-	Polymethylhydrosiloxane
EtOH	-	Ethanol
DCM	-	Dichloromethane
THF	-	Tetrahydrofuran
DME	-	1,2-Dimethoxyethane
EtOAc	-	Ethyl acetate
Et_2O	-	Diethyl ether
DMF	-	N, N-Dimethylformamide

3.1.2 Thin Layer Chromatography (TLC)

Reactions progress, where appropriate, was monitored by TLC using either 100% dichloromethane, 1:1 hexane / dichloromethane or 10% ethyl acetate in hexane. Aluminium foil coated with silica gel 60 F_{254}, from Merck were used in conjunction with an ultra violet light (λ = 254 and 365 nm).

3.1.3 Column Chromatography

Column Chromatography – separations carried out using BDH silica gel, 33-70 μm, and eluted using the solvents stated in the appropriate preparation, under the influence of gravity. Final products were also filtered through Schleicher & Schuell filter papers to remove particulates.

3.1.3 Structural Determination and Purity

All compounds synthesised were subjected to a range of analytical techniques, as required, in order to assess both structure and purity. Intermediate compounds were subjected to ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy and Mass Spectrometry (MS) in most cases. Final compounds were subjected to additional ^{13}C NMR, High Performance Liquid Chromatography (HPLC), Elemental Analysis (EA) and Optical Rotation, as appropriate. The liquid crystalline properties of all final products were assessed using Polarising Optical Microscopy (POM) and confirmed by Differential Scanning Calorimetry (DSC).

3.1.3.1 ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR were recorded on a Jeol JNM ECP400 spectrometer with TMS δ_H = 0 as the internal standard or residual protic solvent ($CDCl_3$, δ_H = 7.26; $(CD_3)_2SO$, δ_H = 2.50). Chemical shifts are given in ppm (δ) and coupling constants (J) are given in Hertz (Hz). ^{1}H NMR were recorded at 400 MHz; ^{13}C NMR were recorded at 100.5 MHz ($CDCl_3$, δ_C = 77.0 ppm; $(CD_3)_2SO$, δ_C = 30.8) as the internal reference. Splitting patterns are described by the following abbreviations:

s	-	singlet	d	-	doublet
t	-	triplet	quart	-	quartet

quint	-	quintet	sext	-	sextet
dd	-	double doublet	ddd	-	double, double doublet
dddd	-	double, double, double doublet	dt	-	double triplet
m	-	multiplet			

3.1.3.2 Mass Spectrometry

Mass spectra were recorded using one of two instruments:

Solid Probe EI MS spectra were recorded using a Simadzu QP5050A quadropole GC/MS instrument at 70eV, with the probe heated to 350 °C to vapourise the sample. Data was processed on a PC running Shimadzu Class-5000 processing software.

MALDI MS spectra were recorded on a Bruker Reflex IV MALDI-TOF MS operating in reflection mode with accelerating voltage in the range 20-25 kV. The laser is a nitrogen lazer providing photons at 337 nm, with 100-150 laser shots accumulated and averaged. Data was processed on a PC running Bruker Compass software compriding FlexControl and FlexAnalysis packages. 2-(4-hydroxyphenylazo)benzoic acid (HABA) was used as the matrix.

3.1.3.3 High Performance Liquid Chromatography (HPLC)

Final products were subjected to analysis by HPLC on one of two systems:

a) Merck-Hitachi HPLC system comprising of L4000 UV detector, L6200 solvent pump, T6300 column oven, D6000 HPLC Manager software, Phenomenex Luna 5 μm C18 250 x 4.6 mm analytical column.
b) Gilson HPLC system comprising of 151 UV/VIS detector, 233XL autosampler/fraction collector, 321 binary solvent pump, Valvemate column changer, Unipoint ver. 3.3 software, Phenomenex Luna 5 μm C18 250 x 4.6 mm analytical column. In the case of compound 114, preparatory HPLC was carried out using this system, equipped with a Phenomenex Luna 5 μm C18 250 x 25 mm column.

3.1.3.4 Elemental Analysis (EA)

Elemental analysis was carried out using a Fissons EA1108 CHN Elemental Analyser.

3.1.3.5 Optical Rotation (OR)

The optical rotation of chiral final products was measured using one of two instruments, using chloroform as the solvent:

a) Optical Activity Ltd. AA-10 Automatic Polarimeter
b) Optical Activity Ltd. polar 3001

3.1.3.6 Polarising Optical Microscopy (POM)

Transitions were measured and observed using an Olympus BH2 polarising microscope, in conjunction with a Mettler FP5 controller and FP52 hotstage. Photomicrographs were taken using a JVC TK-C1481 colour video camera, and data captured on a PC running Mettler Studio Capture Software. Liquid crystal phase nomenclature is used according to the following abbreviations:

Cr	-	Crystalline State	I	-	Isotropic Liquid
N	-	Nematic Phase	SmA	-	Smectic A Phase
SmC	-	Smectic C Phase	B_n	-	'Banana' Phase, where 'n' corresponds to one of the eight banana phases

3.1.3.7 Differential Scanning Calorimetry (DSC)

Transitions observed via POM were confirmed by DSC on one of two instruments:

a) Perkin Elmer DSC7, calibrated with Indium (156.6 °C, 28.45 J/g) and lead (327.47 °C), gold reference. Data collected by a PC running Pyris software.
b) Mettler DSC822e, calibrated with Indium (156.6 °C, 28.45 J/g) and zinc (419.47 °C), aluminium reference. Data collected by a PC running STARe software.

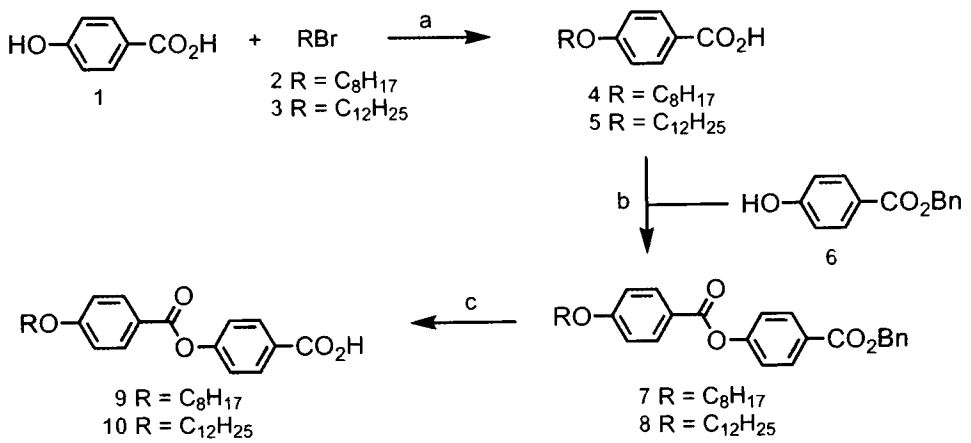
3.1.3.8 Electrooptical Measurements

Electrooptical measurements were carried out using 5 μm, antiparallel buffed polyimide cells, from Linkam Scientific, filled by flowing the material into the cell, at a temperature 10 °C above the clearing point. The filled cell was placed in a Linkam THM600 heating Stage, controlled by a Linkam TP61 temperature controller, on a Zeiss microscope. Ps measurements were made using an AC voltage, and a triangular waveform (the current reversal method)[40, 93]. Tilt angle measurements were made using the same voltage as applied to the current reversal method, but at a lower switching frequency, in order to allow the point of optical extinction to be observed, where upon the sample was rotated until the point of optical extinction was observed again. The angle measured represents 2θ (cone angle), where θ equals the tilt angle[40].

3.2 Synthetic Schemes

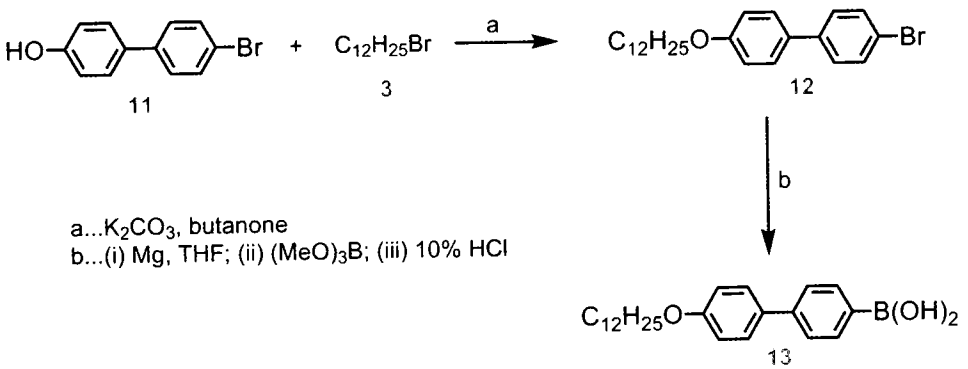
3.2.1 Intermediate Compounds

Scheme 1



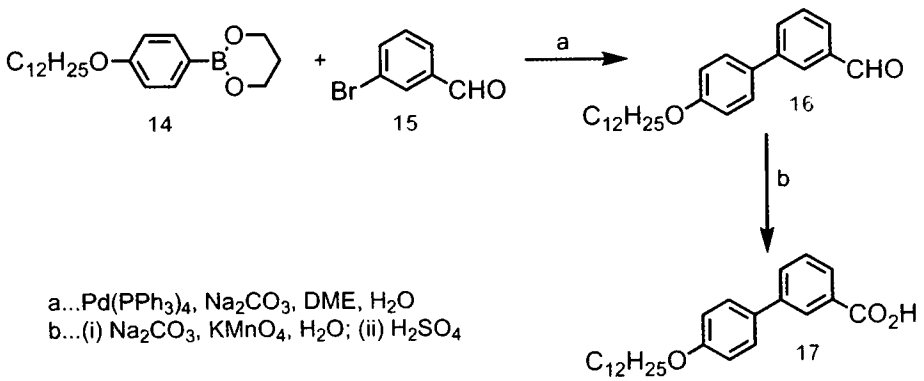
a...(i) NaOH, H_2O, EtOH; (ii) KOH, EtOH;
(iii) 10% HCl
b...DCC, DMAP, DCM
c...H_2, 10% Pd/C, THF

Scheme 2

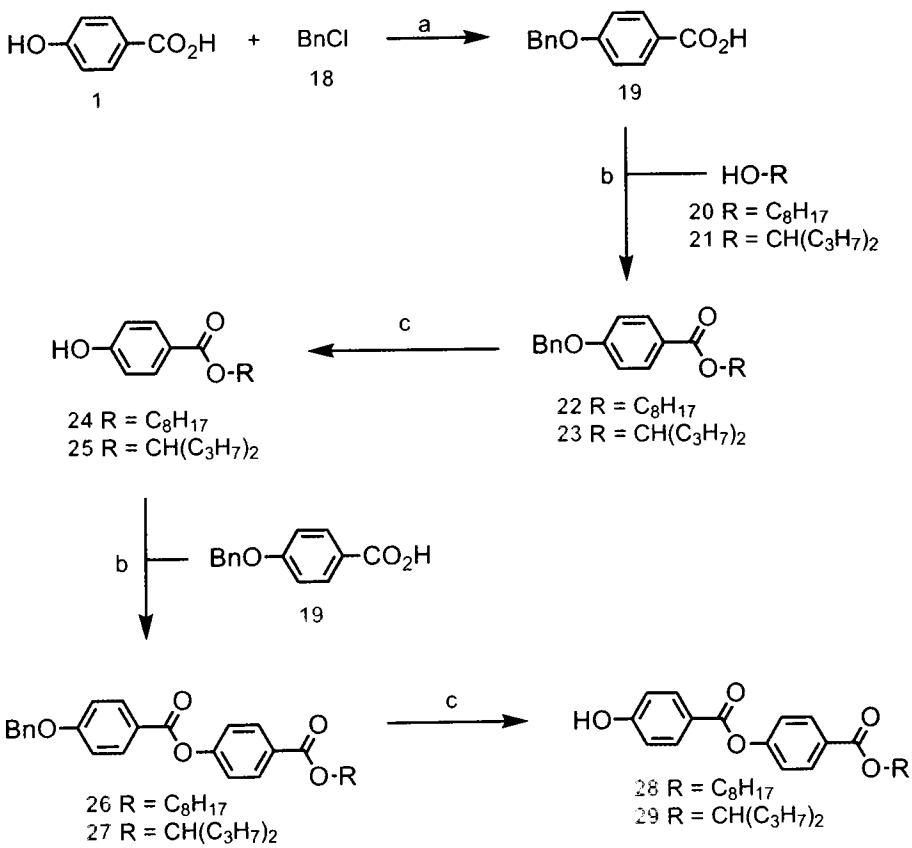


a...K_2CO_3, butanone
b...(i) Mg, THF; (ii) $(MeO)_3B$; (iii) 10% HCl

Scheme 3

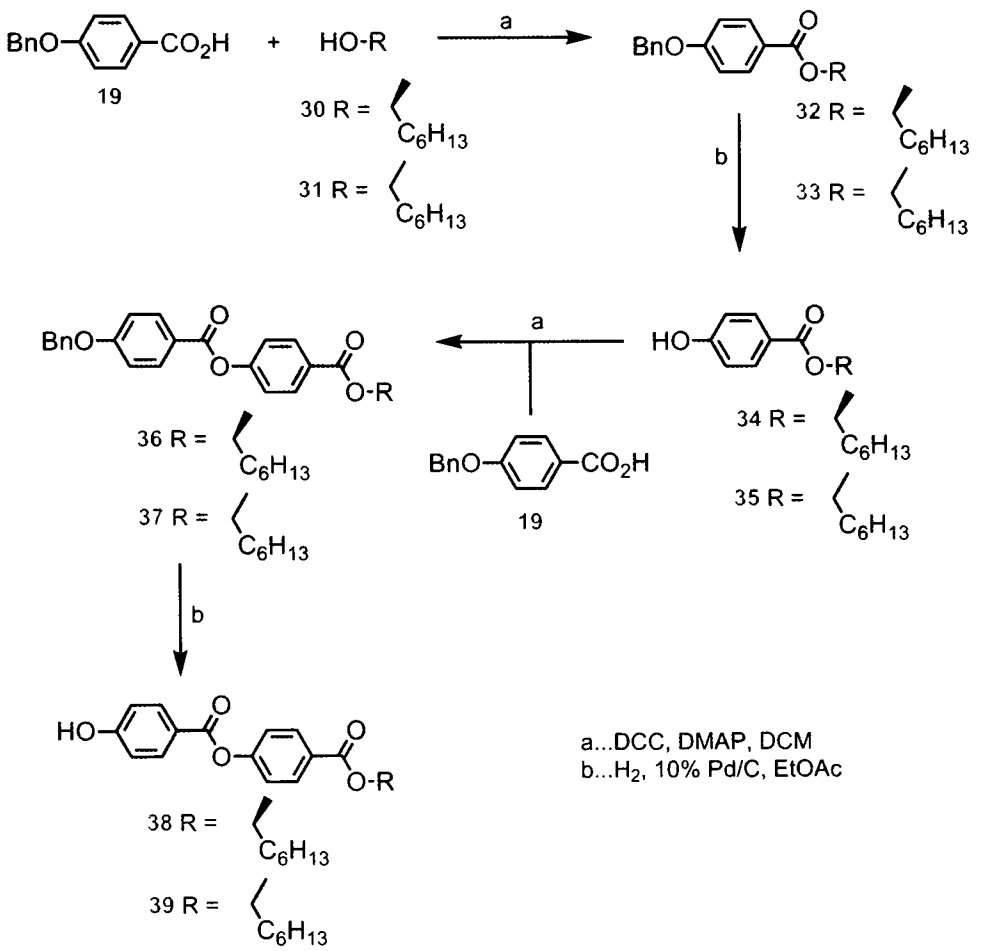


Scheme 4

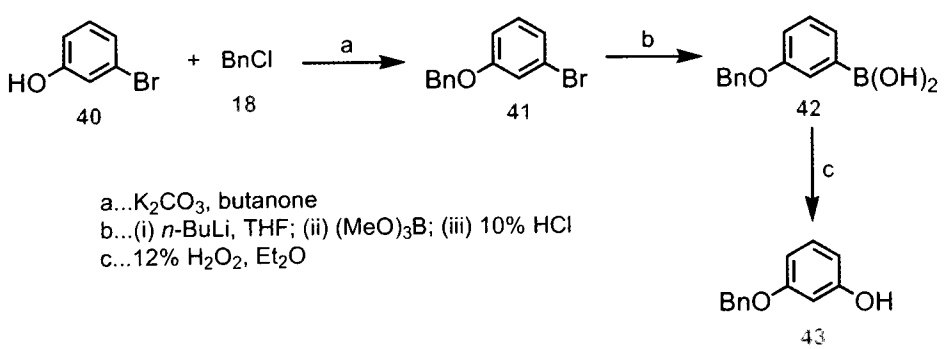


a...(i) NaOH, H_2O, EtOH; (ii) 10% HCl
b...DCC, DMAP, DCM
c...H_2, 10% Pd/C, EtOAc

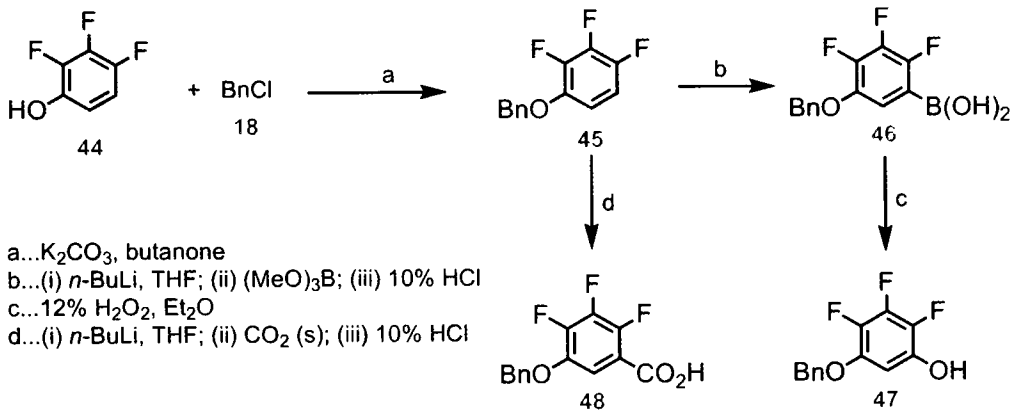
Scheme 5



Scheme 6

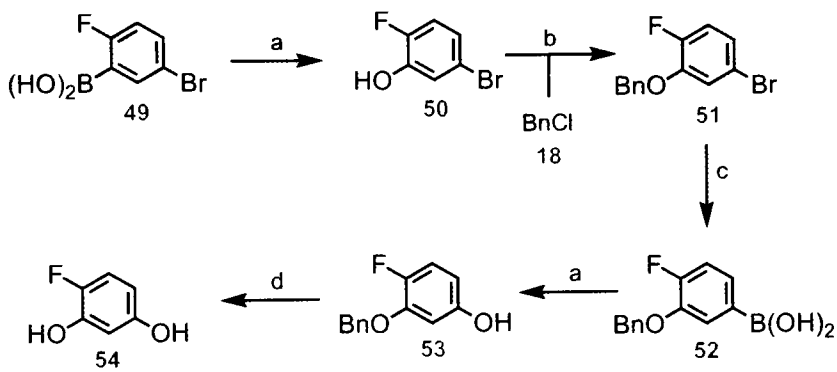


Scheme 7



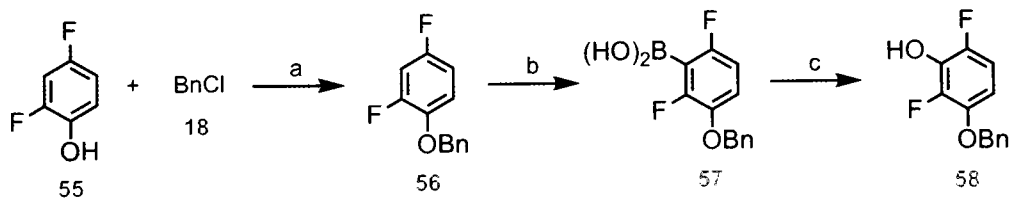
a...K_2CO_3, butanone
b...(i) *n*-BuLi, THF; (ii) $(MeO)_3B$; (iii) 10% HCl
c...12% H_2O_2, Et_2O
d...(i) *n*-BuLi, THF; (ii) CO_2 (s); (iii) 10% HCl

Scheme 8



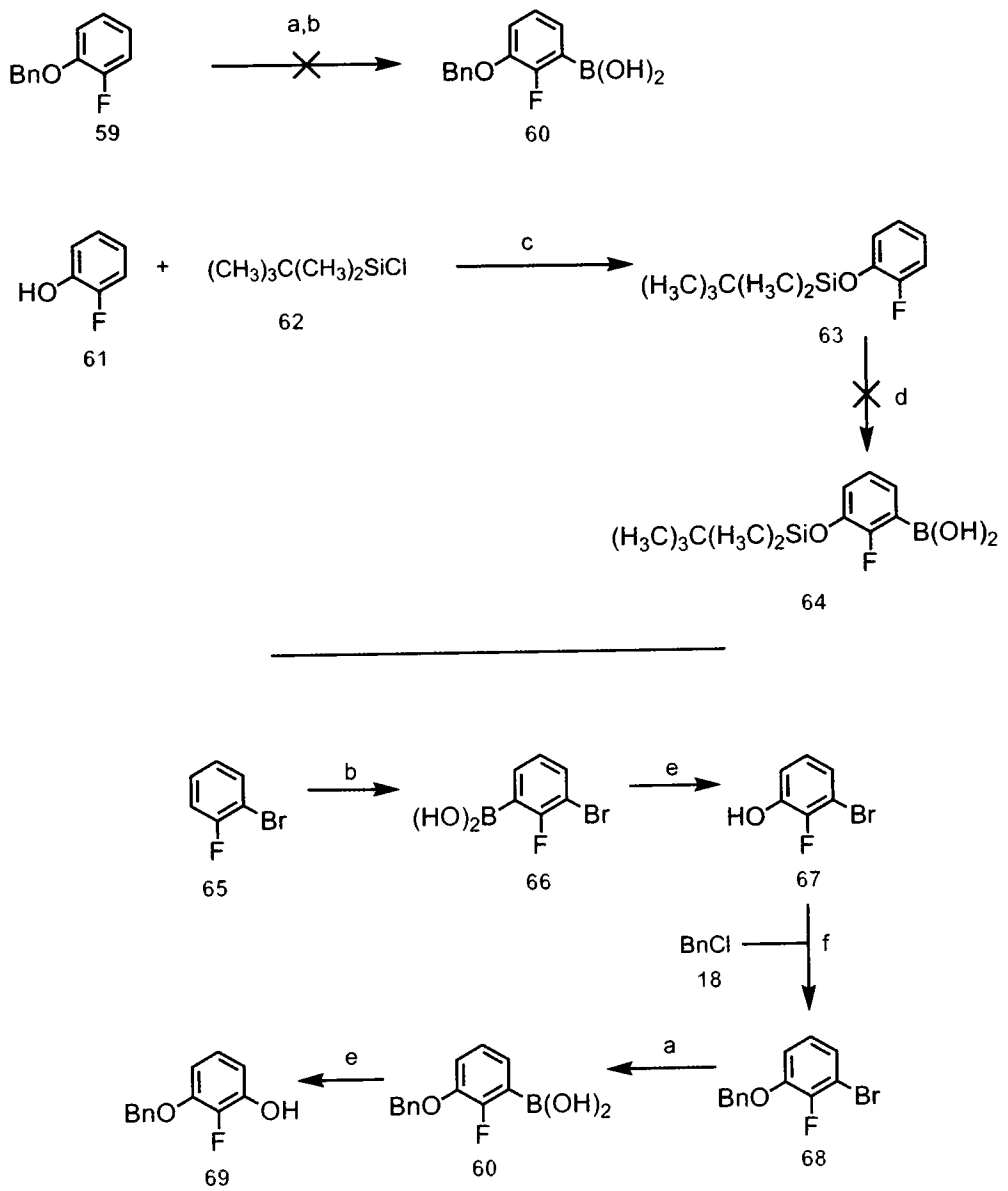
a...12% H_2O_2, Et_2O
b...K_2CO_3, butanone
c...(i) *n*-BuLi, THF; (ii) CO_2(s); (iii) 10% HCl
d...H_2, 10% Pd/C, EtOAc

Scheme 9



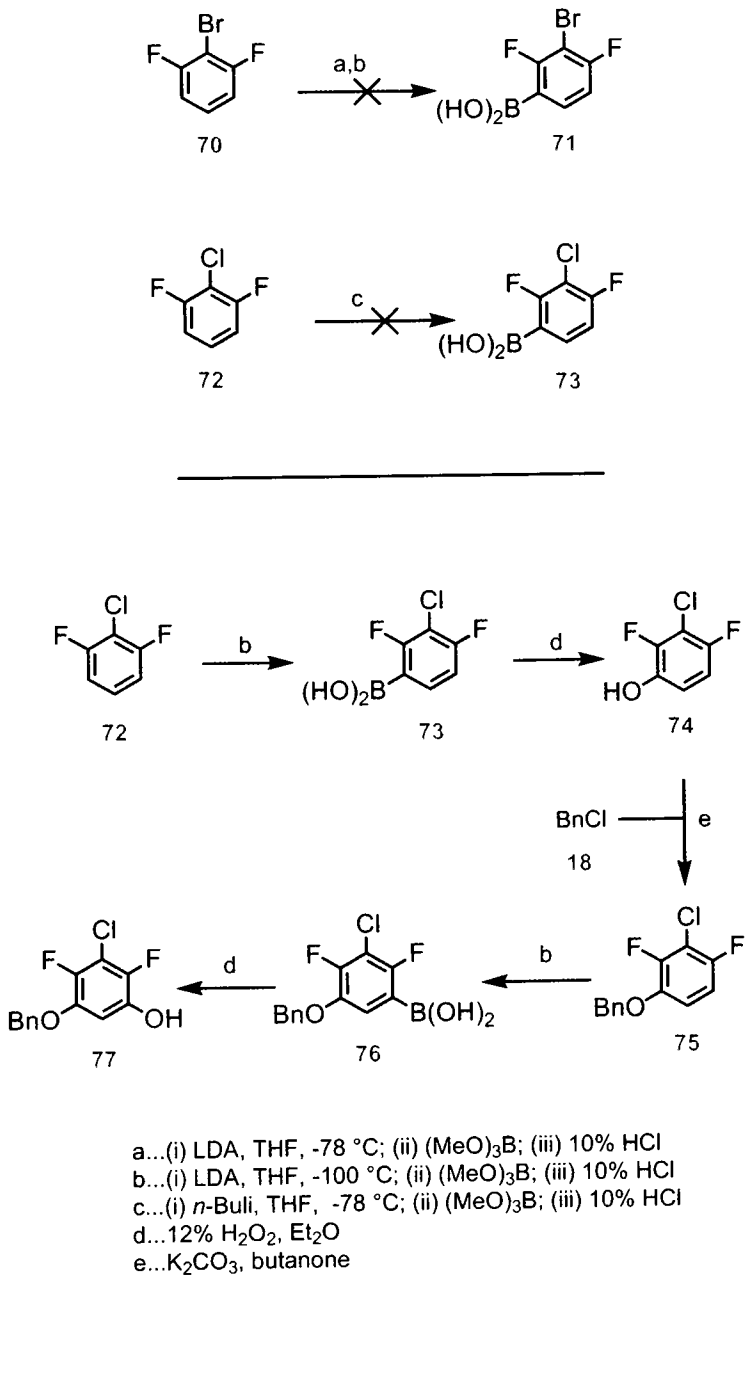
a...K_2CO_3, butanone
b...(i) *n*-BuLi, THF; (ii) $(MeO)_3B$; (iii) 10% HCl
c...12% H_2O_2, Et_2O

Scheme 10



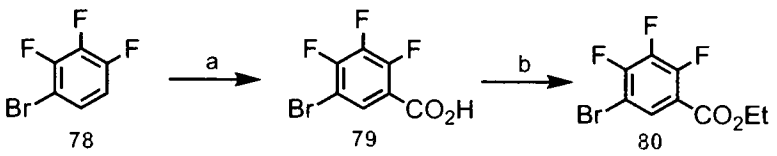
a...(i) *n*-BuLi, THF; (ii) $(MeO)_3B$; (iii) 10% HCl
b...(i) LDA, THF; (ii) $(MeO)_3B$; (iii) 10% HCl
c...Imidazole, DMF
d...(i) *sec*-BuLi, THF; (ii) $(MeO)_3B$; (iii) 10% HCl
e...12% H_2O_2, Et_2O
f...K_2CO_3, butanone

Scheme 11



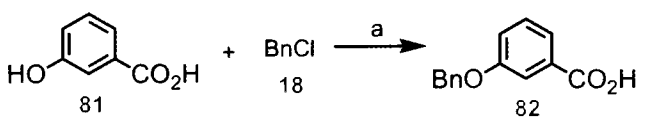
a...(i) LDA, THF, -78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl
b...(i) LDA, THF, -100 °C; (ii) $(MeO)_3B$; (iii) 10% HCl
c...(i) *n*-Buli, THF, -78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl
d...12% H_2O_2, Et_2O
e...K_2CO_3, butanone

Scheme 12



a...(i) LDA, THF; (ii) CO_2 (s); (iii) 10% HCl
b...EtOH, H_2SO_4

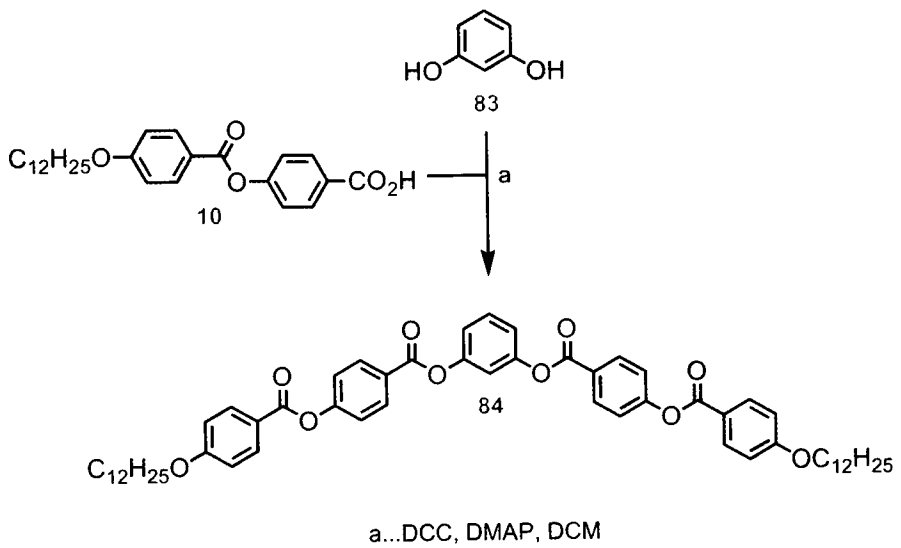
Scheme 13



a...(i) NaOH, H_2O, EtOH; (ii) 10% HCl

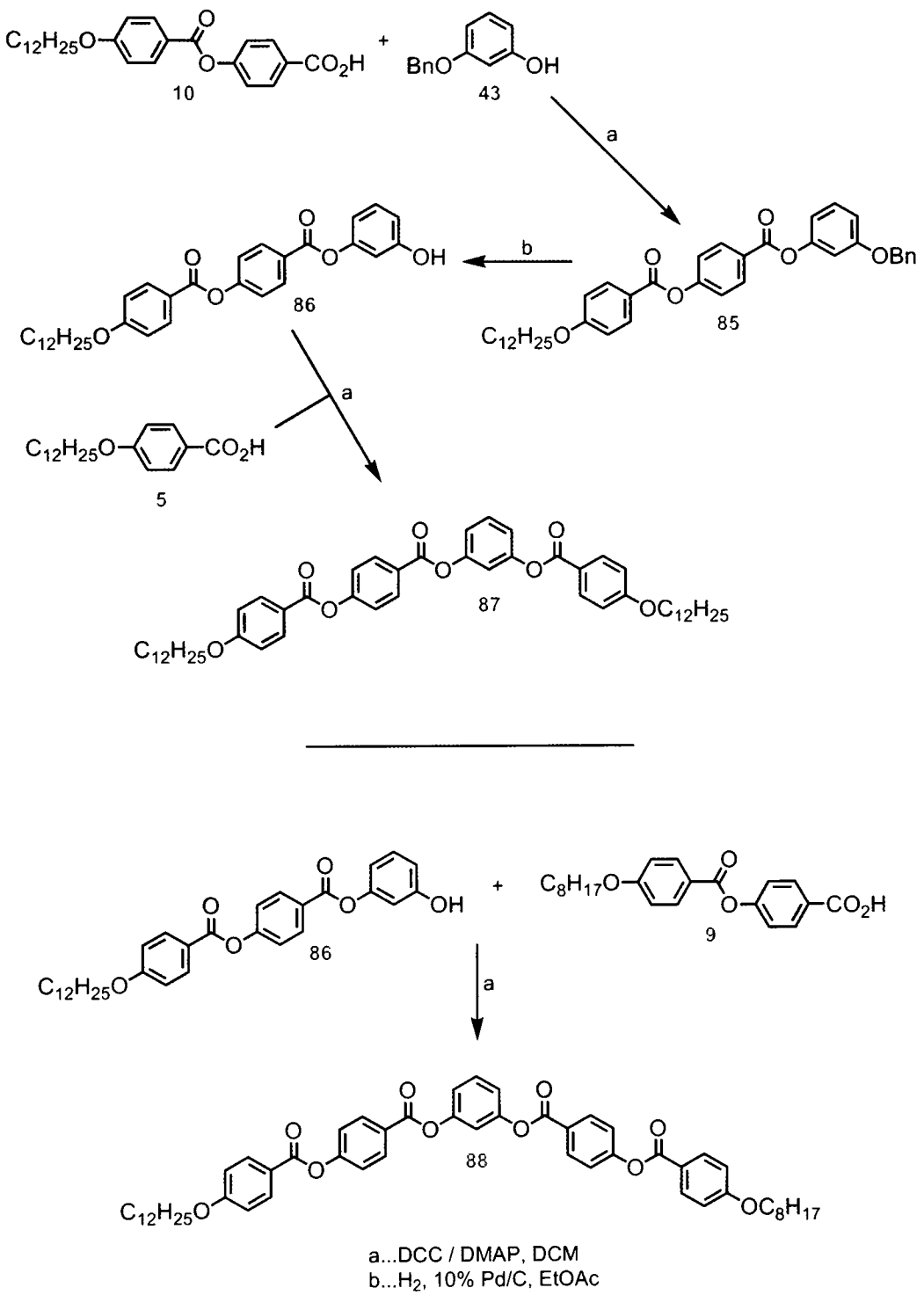
3.2.2 Achiral Products

Scheme 14

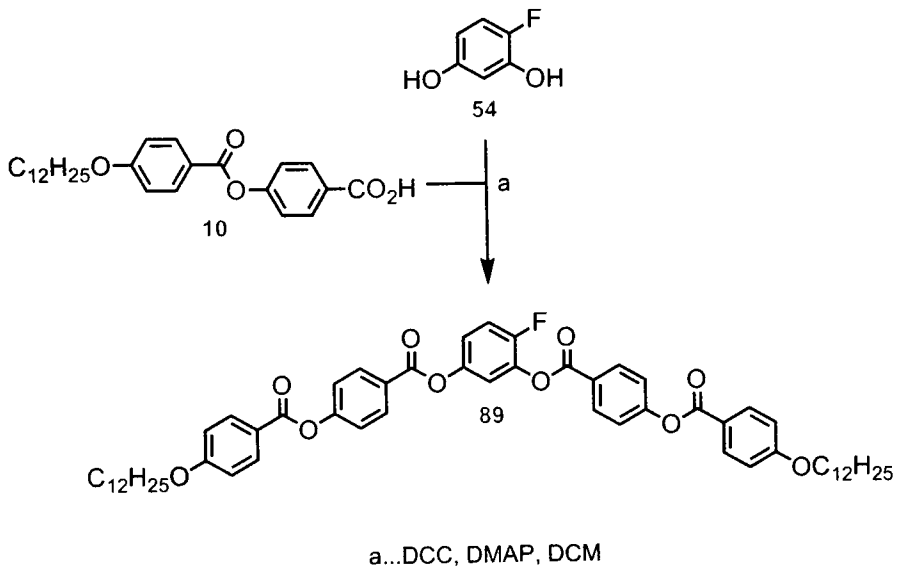


a...DCC, DMAP, DCM

Scheme 15

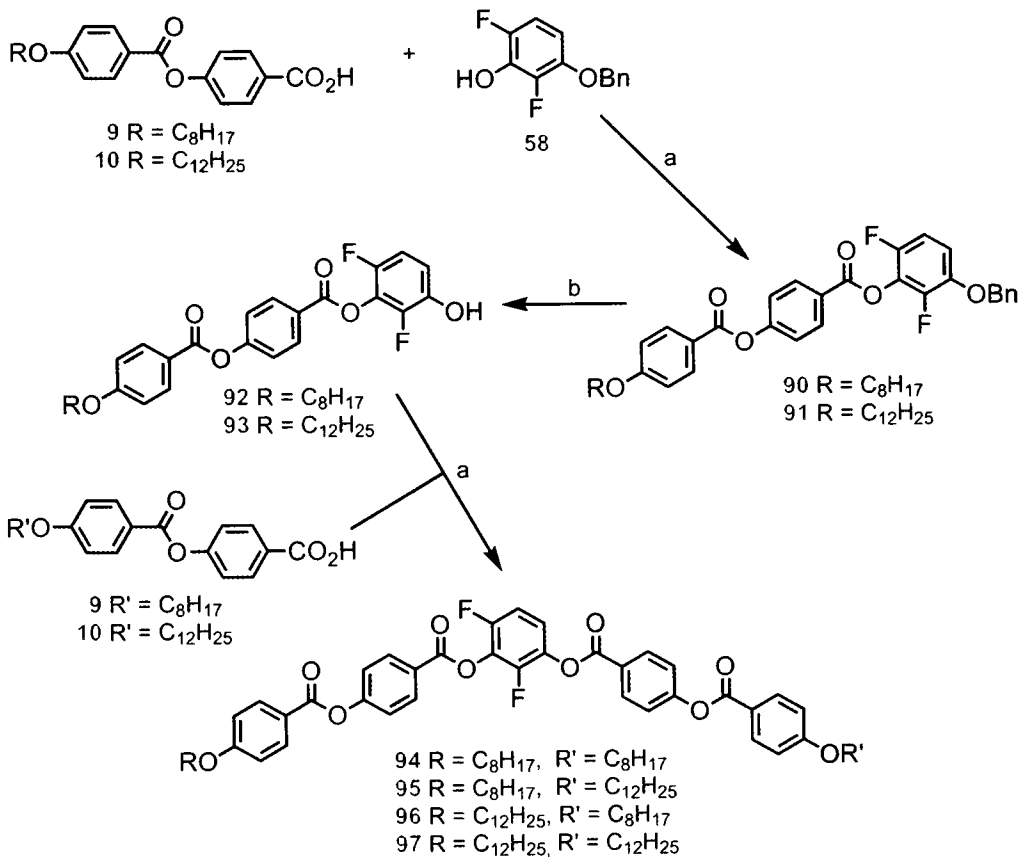


Scheme 16



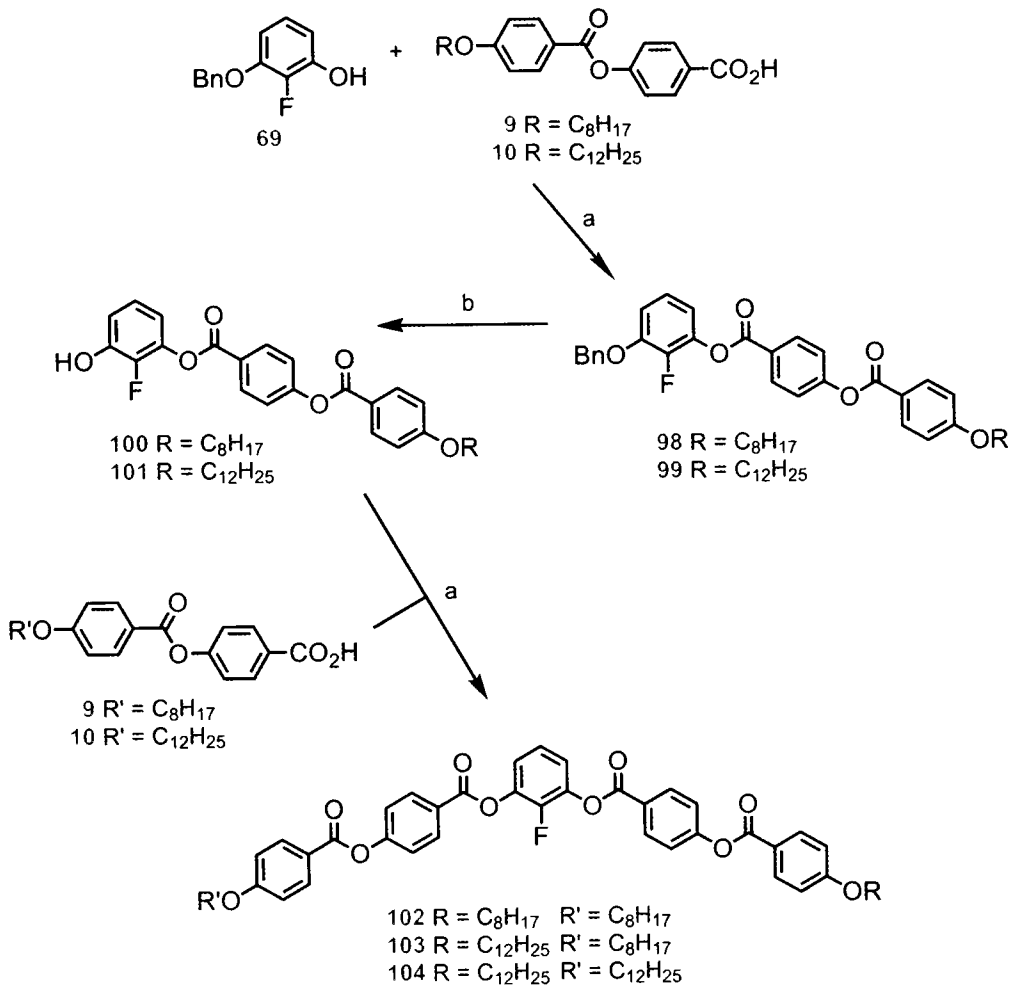
a...DCC, DMAP, DCM

Scheme 17



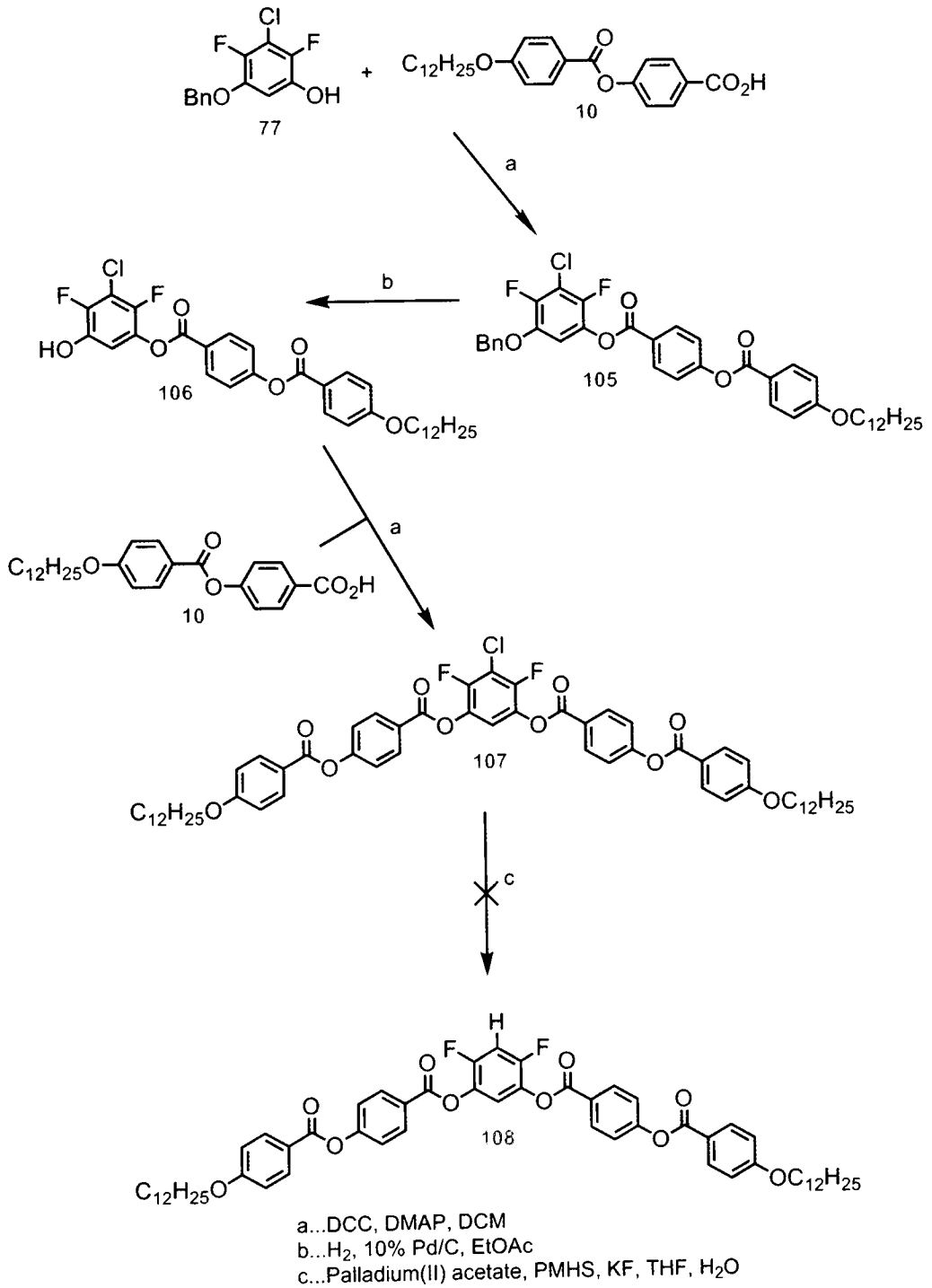
a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc

Scheme 18

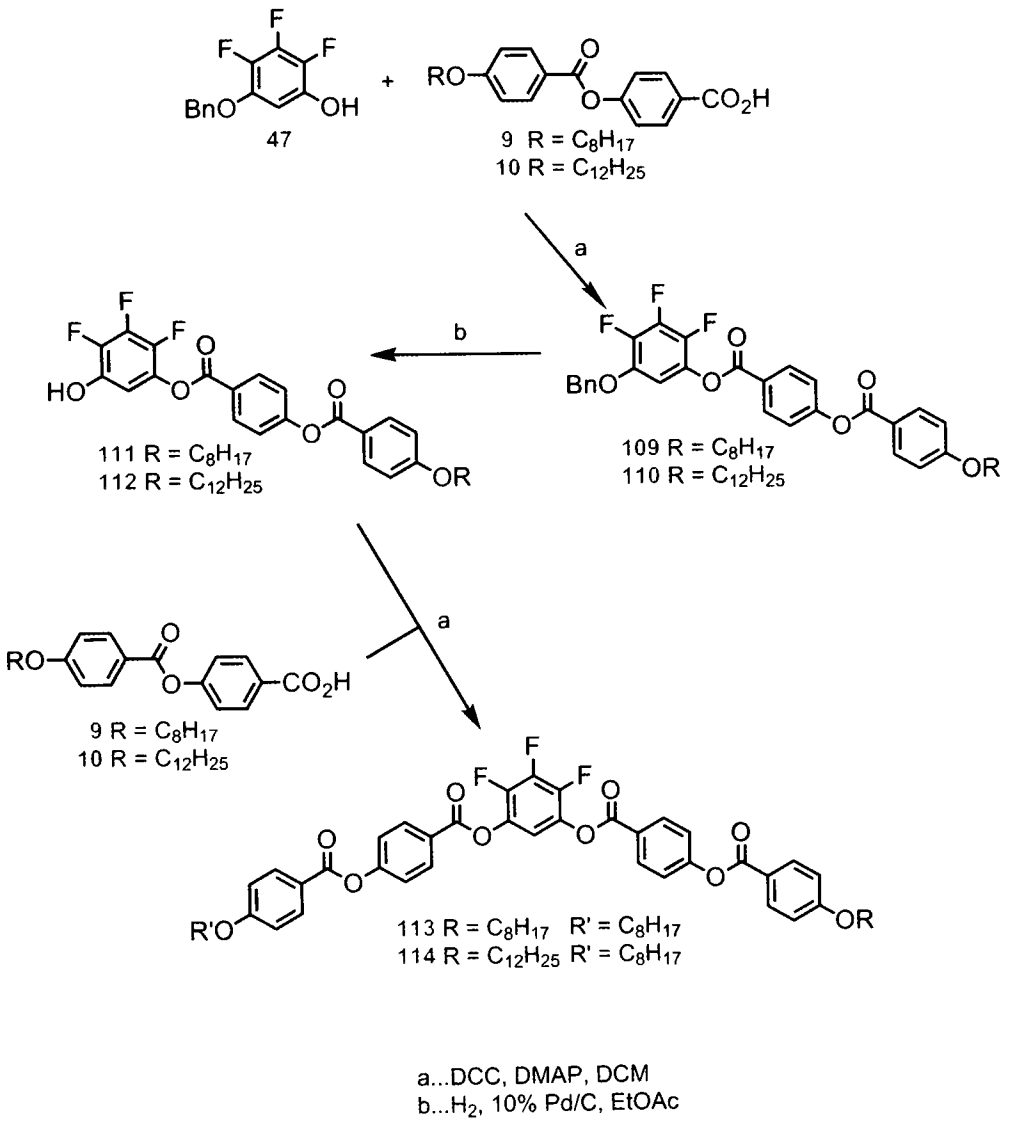


a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc

Scheme 19

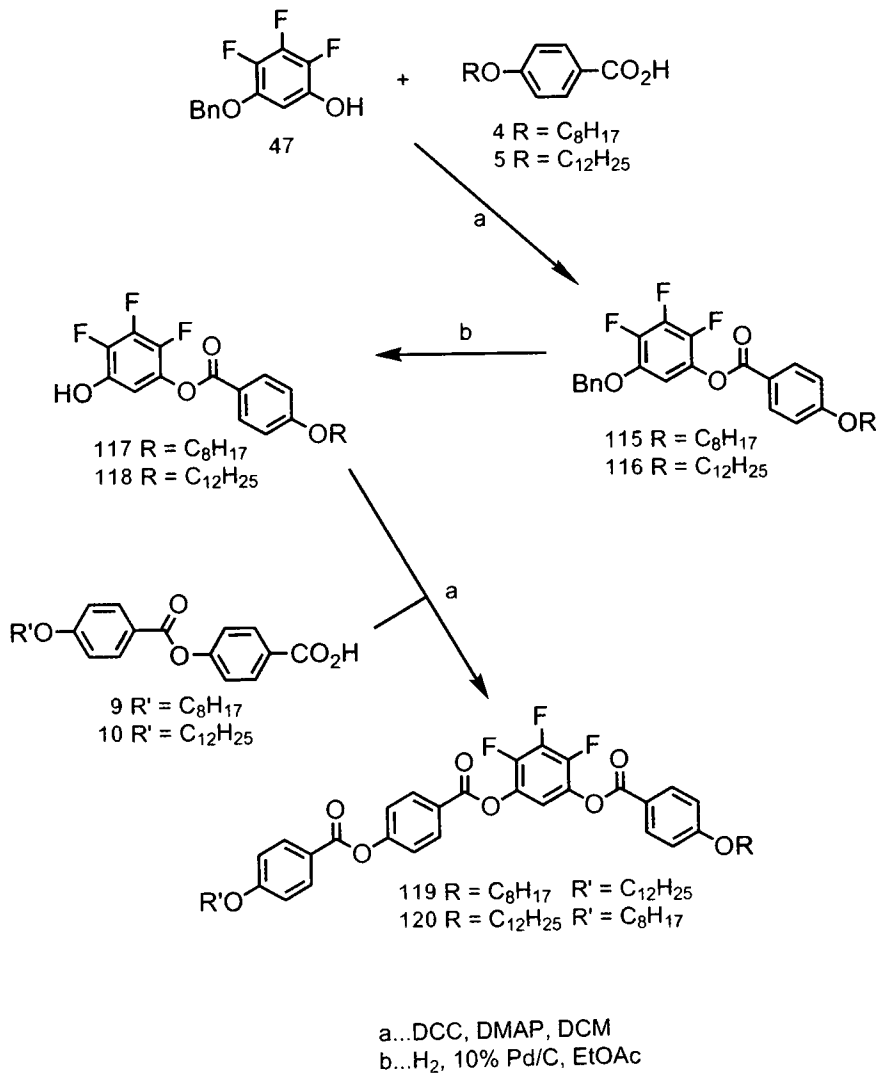

77
10
105
106
10
107
108
a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc
c...Palladium(II) acetate, PMHS, KF, THF, H_2O

Scheme 20



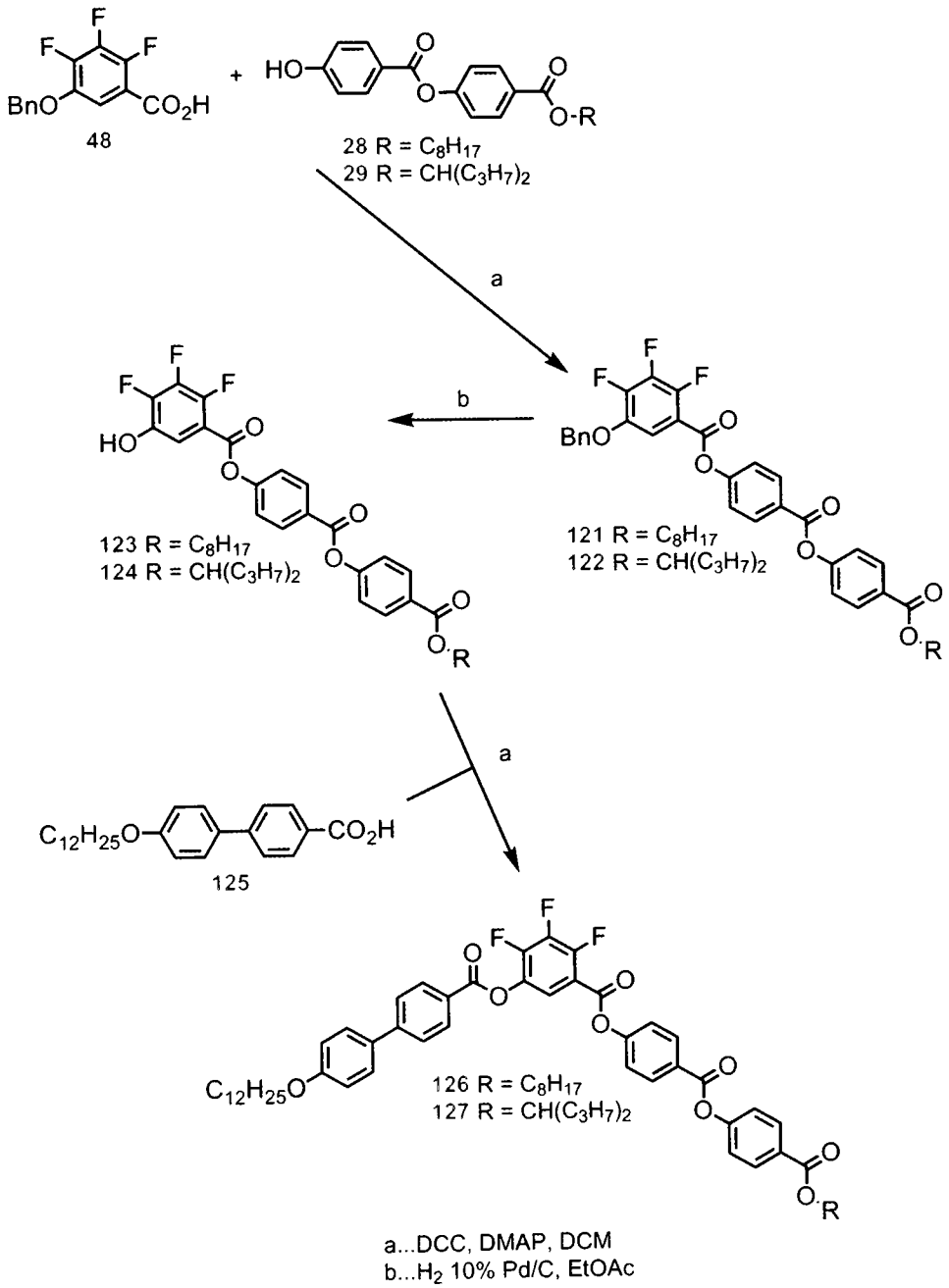
a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc

Scheme 21



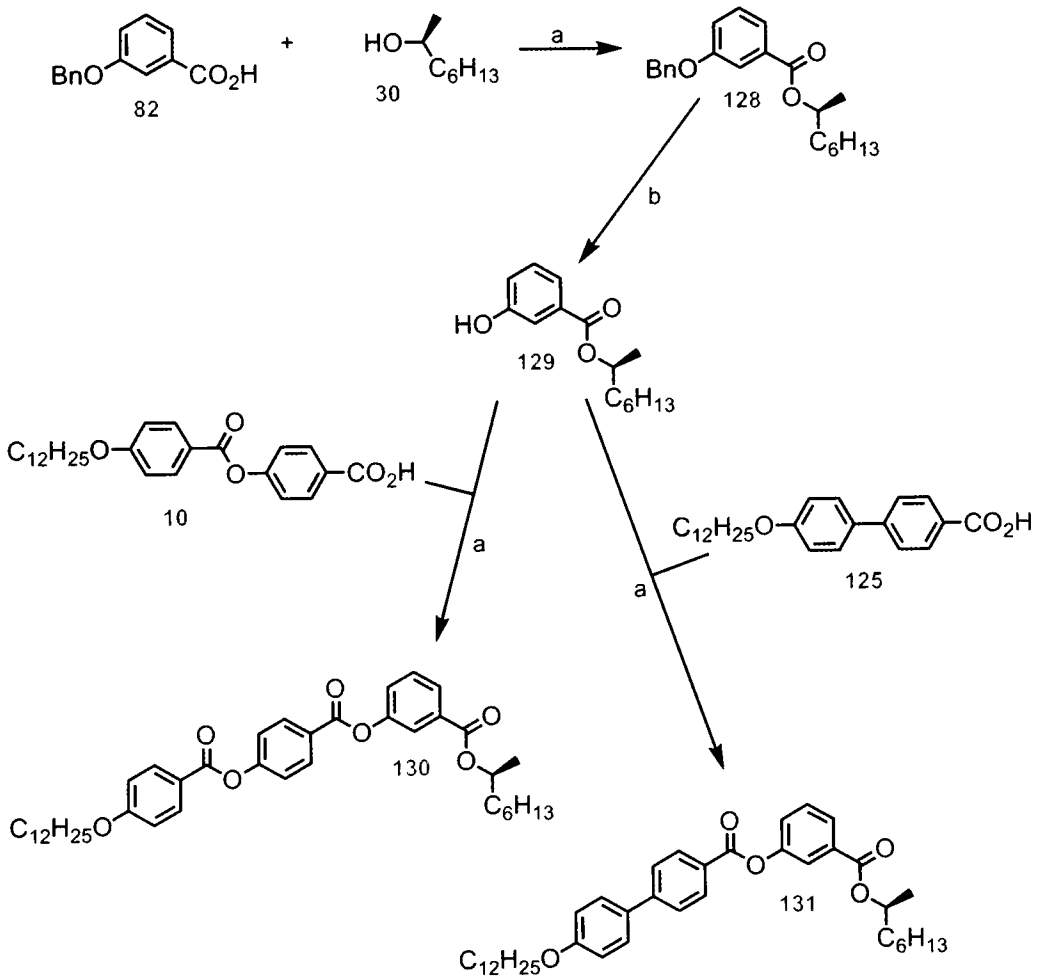
a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc

Scheme 22


48
28 R = C8H17
29 R = CH(C3H7)2
a
b
121 R = C8H17
122 R = CH(C3H7)2
123 R = C8H17
124 R = CH(C3H7)2
a
125
126 R = C8H17
127 R = CH(C3H7)2
a...DCC, DMAP, DCM
b...H2 10% Pd/C, EtOAc

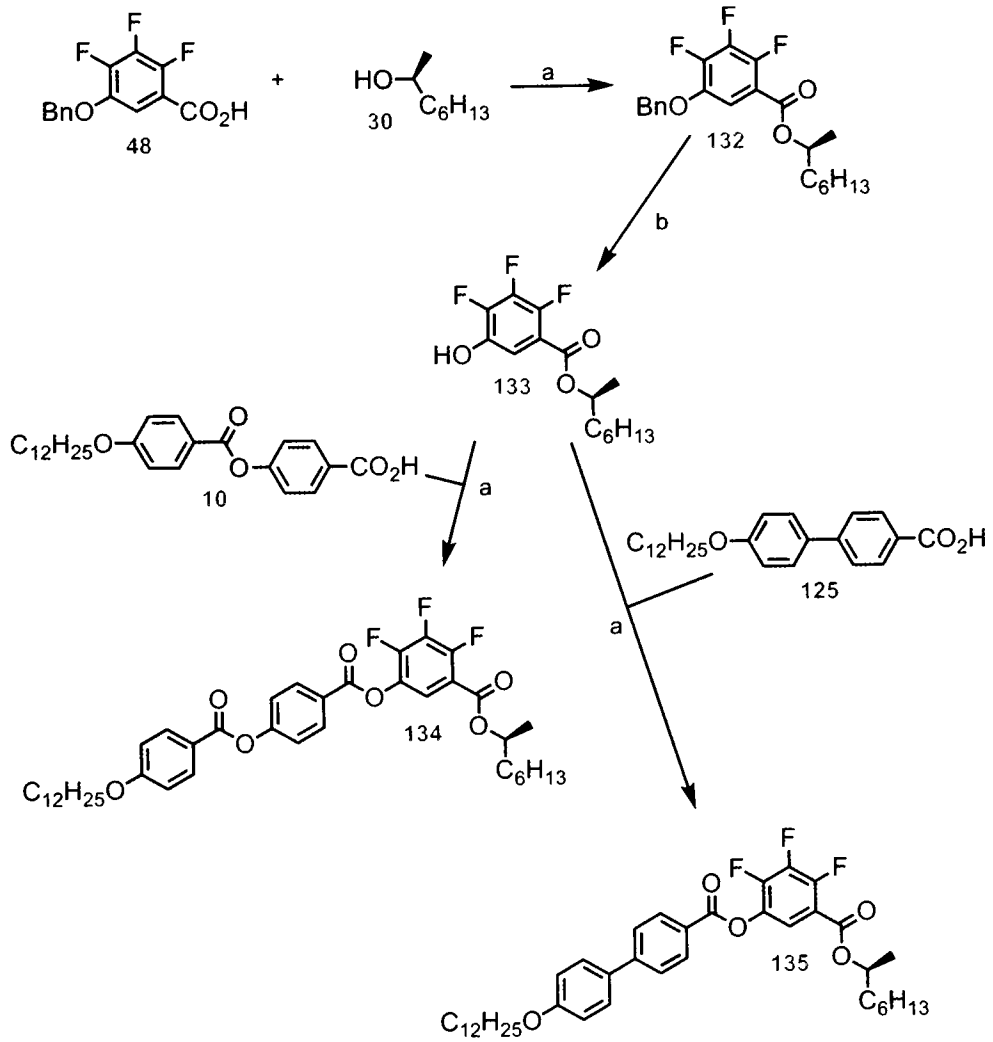
3.2.3 Chiral Products

Scheme 23



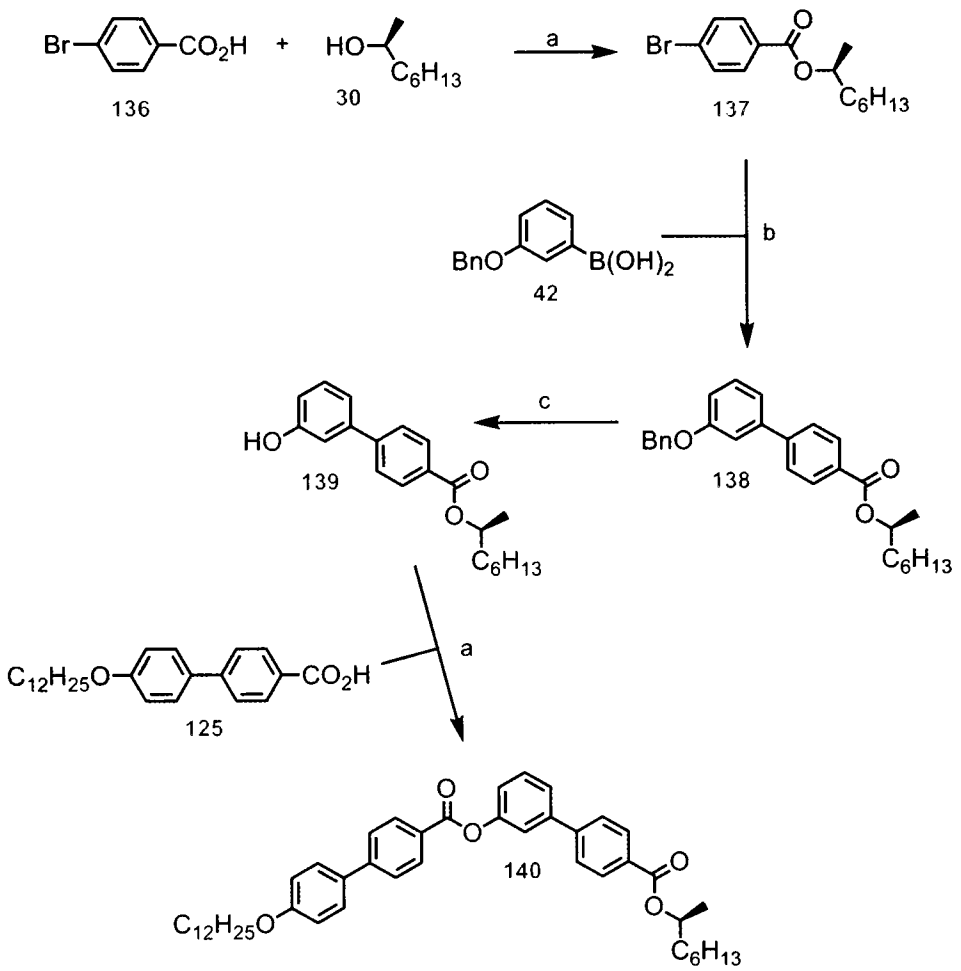
a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc

Scheme 24



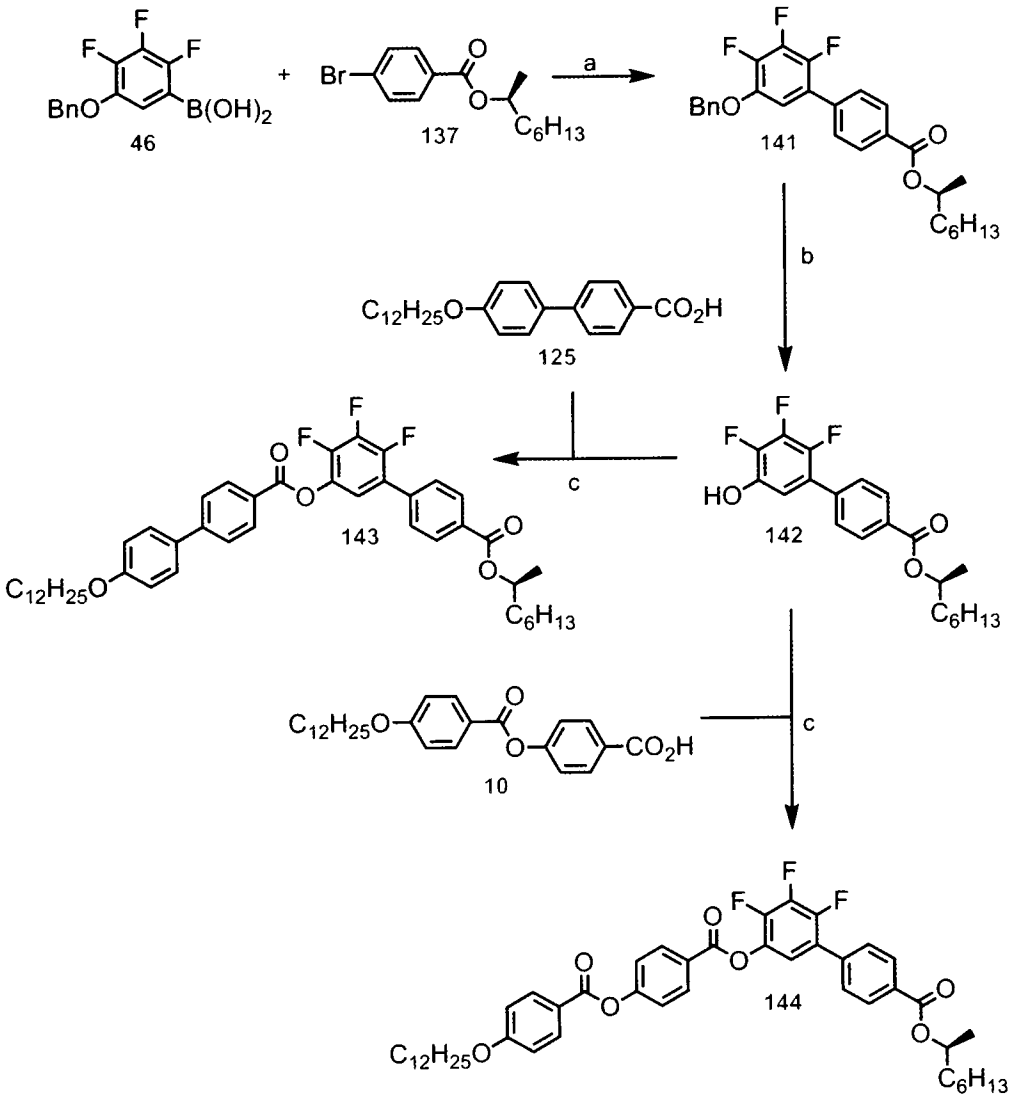
a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc

Scheme 25



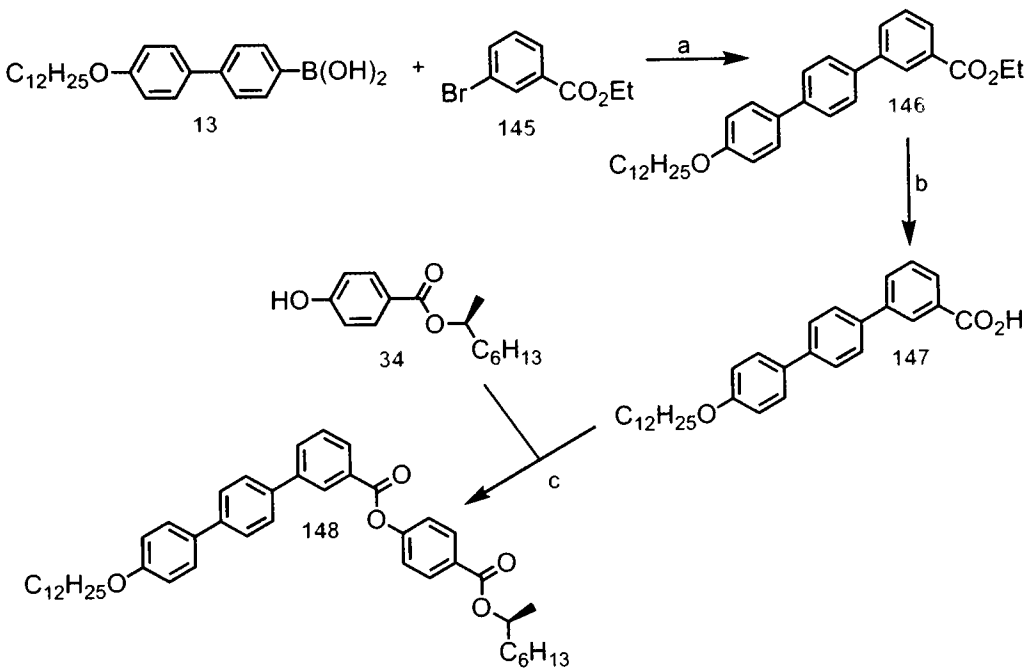
a...DCC, DMAP, DCM
b...$Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O
c...H_2, 10% Pd/C, EtOAc

Scheme 26



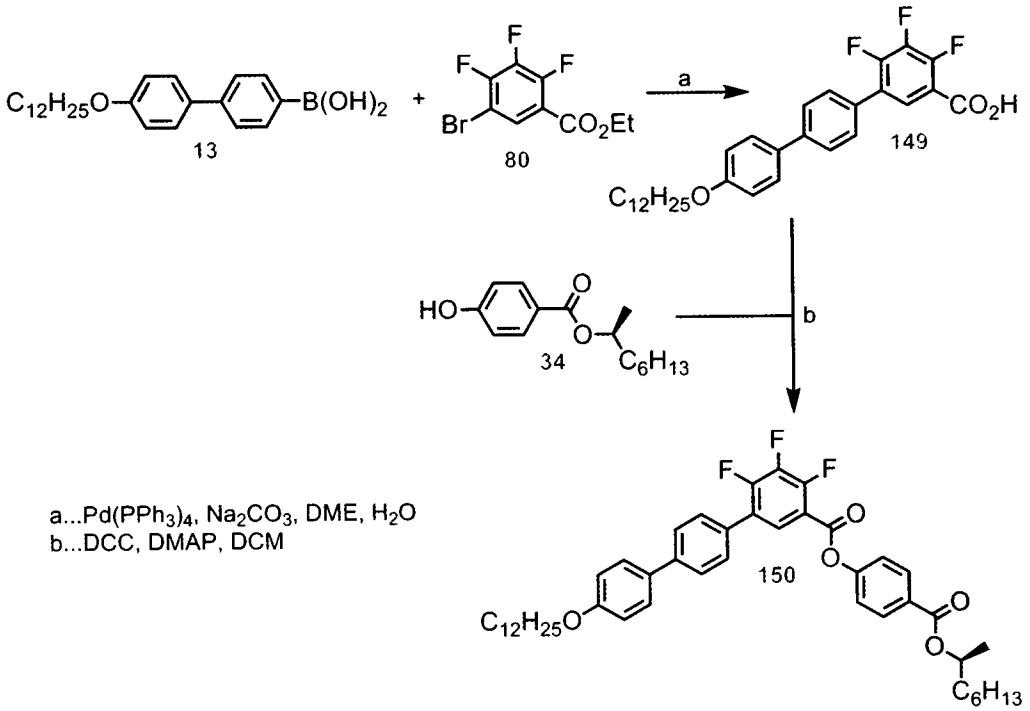
a...$Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O
b...H_2, 10% Pd/C, EtOAc
c...DCC, DMAP, DCM

Scheme 27

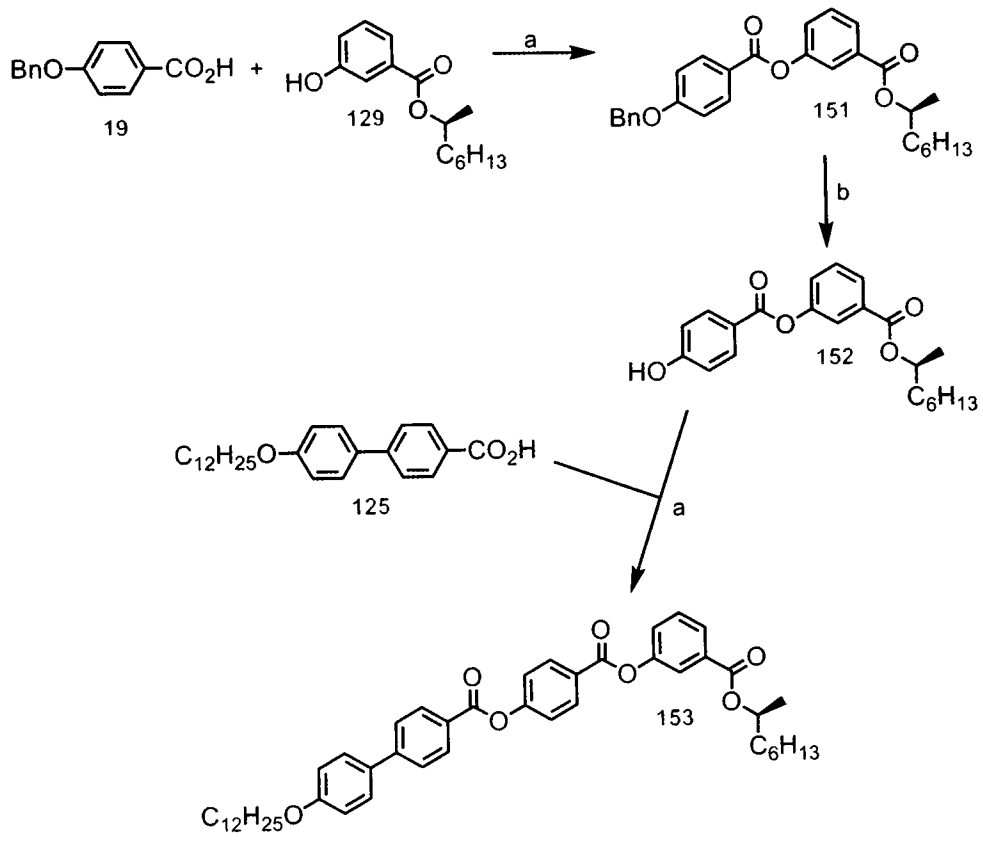


a...$Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O
b...(i) KOH, EtOH, H_2O; (ii) 10% HCl
c...DCC, DMAP, DCM

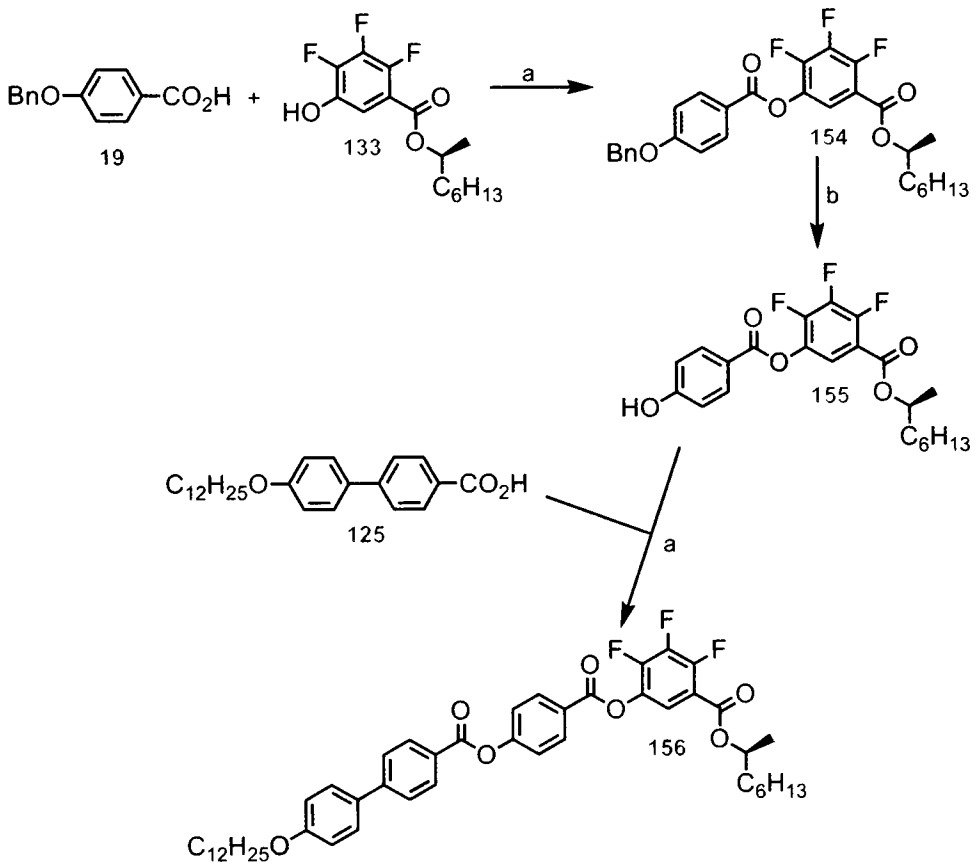
Scheme 28


C12H25O
B(OH)2
13
F
F
F
Br
CO2Et
80
a
149
CO2H
C12H25O
HO
O
O
C6H13
34
b
150
a...Pd(PPh3)4, Na2CO3, DME, H2O
b...DCC, DMAP, DCM

Scheme 29

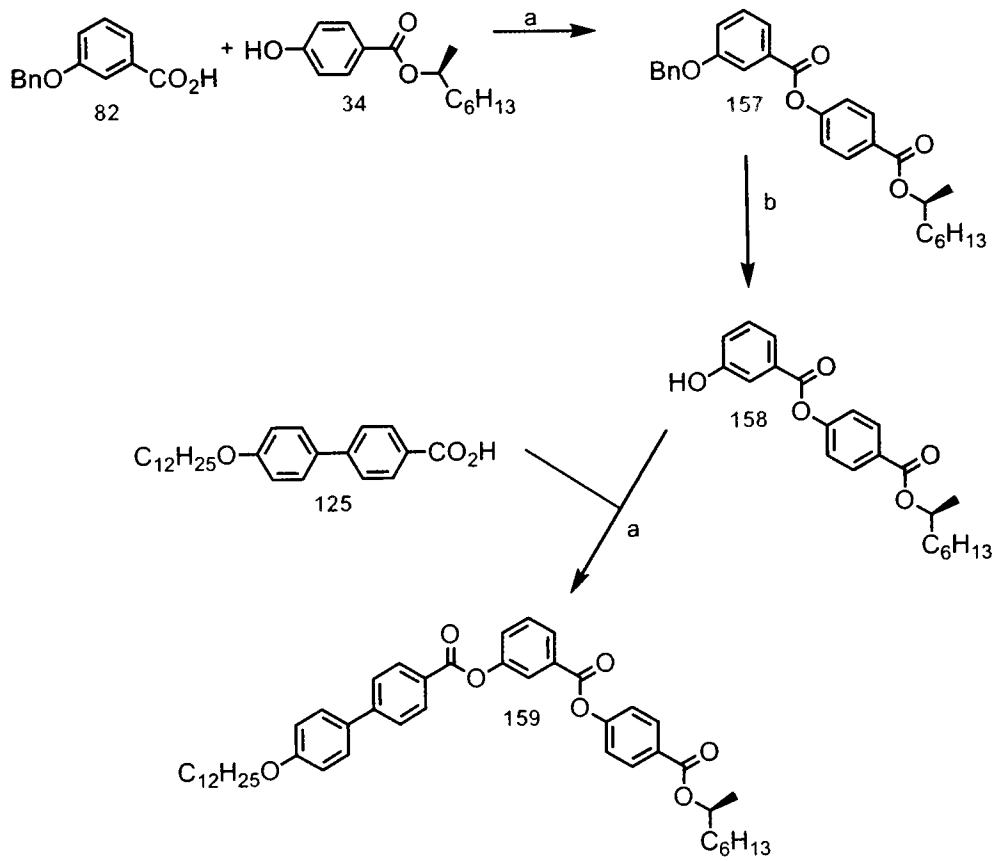

BnO
CO2H
19
HO
129
C6H13
a
151
b
152
C12H25O
125
153
a...DCC, DMAP, DCM
b...H2, 10% Pd/C, EtOAc

Scheme 30



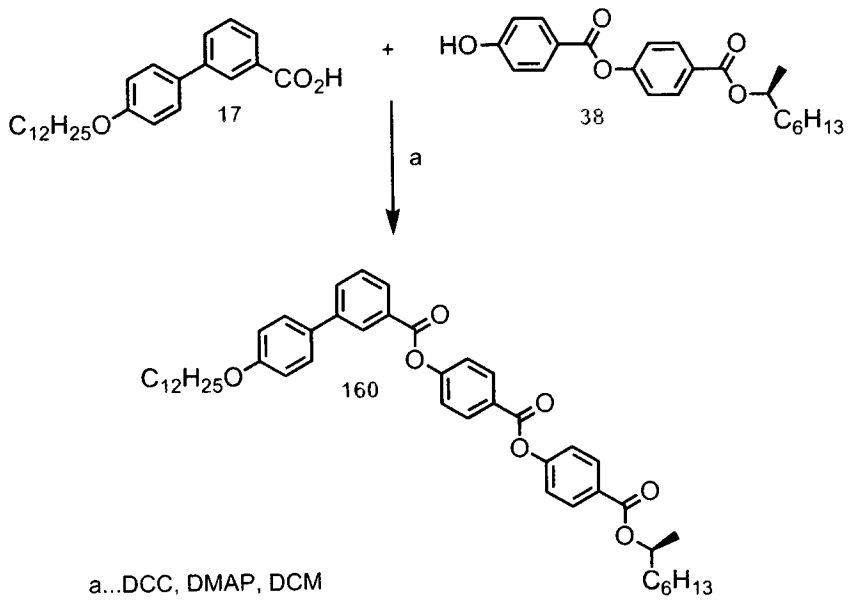
a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc

Scheme 31

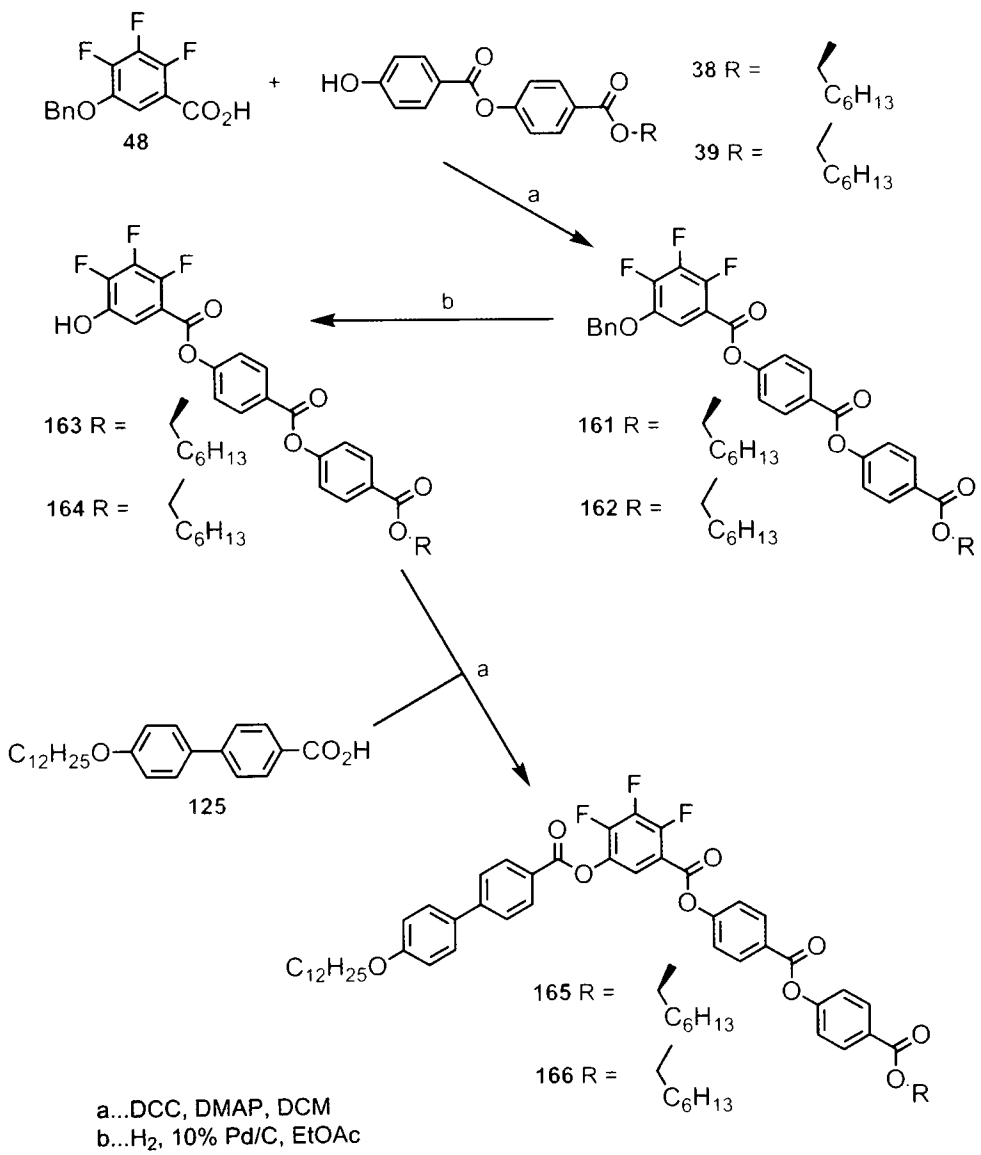


a...DCC, DMAP, DCM
b...H_2, 10% Pd/C, EtOAc

Scheme 32



Scheme 33


48
38 R =
39 R =
a
b
163 R =
164 R =
161 R =
162 R =
125
165 R =
166 R =
a...DCC, DMAP, DCM
b...H2, 10% Pd/C, EtOAc

3.3 Experimental Procedures

3.3.1 Intermediate Compounds

Scheme 1

4-Octyloxybenzoic acid (4)

Compound 2 (154.0 g, 0.80 mol) was added drop wise to a refluxing mixture of compound 1 (55.0 g, 0.40 mol), sodium hydroxide (32.0 g, 0.80 mol), ethanol (200 ml) and water (200 ml). The mixture was heated under reflux overnight. The ethanol was removed *in vacuo* and sodium hydroxide (40.0 g, 1.0 mol) in water (200 ml) added, then the mixture was returned to reflux for 5 hours. The resulting mixture was poured onto crushed ice and hydrochloric acid (36%) added to precipitate the product, which was recrystallised from ethanol and dried *in vacuo* to yield colourless crystals.

Yield: 86.7 g (87 %)

Transitions (°C): Cr 100.4 SmC 107.7 N 147.9 I

Cr 101 SmC 108 N 147 I[94]

^{1}H NMR (400 MHz, DMSO-D6) 0.81 (3H, t), 1.23 – 1.29 (8H, m), 1.35 (2H, quint), 1.66 (2H, quint), 3.96 (2H, t), 6.94 (2H, d), 7.85 (2H, d), OH proton not revealed

MS m/z 250 (M^+)

4-Dodecyloxybenzoic acid (5)

Quantities: Compound 3 (254.0 g, 1.02 mol), compound 1 (70.0 g, 0.51 mol), sodium hydroxide (2 x 40.0 g, 1.0 mol), ethanol (300 ml), water (300 ml). The experimental procedure was similar to the preparation of compound 4. Potassium hydroxide (40.0 g, 0.71 mol) in water (200 ml) was added to the crude product and the mixture returned to reflux overnight. The resulting mixture was poured onto crushed ice and hydrochloric acid (36%) added to precipitate the product, which was recrystallised from ethanol and dried *in vacuo* to yield colourless crystals.

Yield: 76.6 g (49 %)

Transitions (°C): Cr 93.4 SmC 130.1 N 138.9 I

Cr 88 SmC 130 N 137 I[95]

^{1}H NMR (400 MHz, DMSO-D6) 0.81 (3H, t), 1.12 – 1.30 (16H, m), 1.34 (2H, quint), 1.66 (2H, quint), 3.96 (2H, t), 6.94 (2H, d), 7.84 (2H, d), OH proton not revealed
MS m/z 306 (M^+)

Benzyl 4-(4-octyloxyphenylcarbonyloxy)benzoate (7)

DCC (15.0 g, 0.073 mol) was added to a stirred mixture of compound 4 (16.1 g, 0.064 mol), compound 6 and DMAP (2.42 g, 0.020 mol) in DCM (200 ml). The resulting solution was stirred at room temperature overnight (thin-layer chromatography revealed a complete reaction). The DCU precipitate was removed by filtration, and the crude product adsorbed onto silica gel *via* removal of the solvent *in vacuo*. The residue was purified by column chromatography (silica gel, hexane / DCM, 1:1, eluted with a gradual increase of the concentration of DCM), to yield a colourless solid.
Yield: 29.18 g (99 %)
Melting Point (°C): 58.5 – 64.1
^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.24 – 1.42 (8H, m), 1.47 (2H, quint), 1.83 (2H, quint), 4.04 (2H, t), 5.38 (2H, s), 6.98 (2H, d), 7.29 (2H, d), 7.33 – 7.48 (5H, m), 8.14 (2H, d), 8.15 (2H, d)
MS m/z 460 (M^+)

Benzyl 4-(4-dodecyloxyphenylcarbonyloxy)benzoate (8)

Quantities: Compound 5 (15.0 g, 0.049 mol), compound 6 (11.4 g, 0.050 mol), DCC (11.3 g, 0.055 mol), DMAP (1.8 g, 0.015 mol), DCM (250 ml). The experimental procedure was as described in the preparation of compound 7 to yield a colourless solid.
Yield: 23.5 g (93 %)
Melting Point (°C): 62.7 – 63.4
62 – 63[96]
^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22 - 1.52 (18H, m), 1.82 (2H, quint), 4.04 (2H, t), 5.38 (2H, s), 6.97 (2H, d), 7.30 (2H, d), 7.33 – 7.47 (5H, m), 8.13 (2H, d), 8.16 (2H, d)
MS m/z 516 (M^+)

4-(4-Octyloxyphenylcarbonyloxy)benzoic acid (9)

Compound 7 (29.2 g, 0.063 mol) was dissolved in THF (300 ml) and 10% palladium on carbon (2.0 g) added. Hydrogen gas was then applied at 40 psi and the mixture shaken overnight. The mixture was filtered through 'hyflo supercel' and the solvent removed *in vacuo*. The crude product was recrystallised from ethanol / ethyl acetate (1:1) and dried *in vacuo* over phosphorus pentoxide to yield colourless crystals.

Yield: 21.6 g (92 %)

Transitions (°C): Cr 128.9 SmC 157.6 N 233.2 I

^{1}H NMR (400 MHz, DMSO-D6) 0.81 (3H, t), 1.16 – 1.32 (8H, m), 1.36 (2H, quint), 1.69 (2H, quint), 4.04 (2H, t), 7.07 (2H, d), 7.34 (2H, d), 7.97 (2H, d), 8.02 (2H, d)

MS m/z 370 (M^+)

4-(4-Dodecyloxyphenylcarbonyloxy)benzoic acid (10)

Quantities: Compound 8 (13.4 g, 0.026 mol), THF (300 ml) and 10% palladium on carbon (1.5 g). The experimental procedure was as described in the preparation of compound 9, to yield colourless crystals.

Yield: 10.3 g (93 %)

Transitions (°C): Cr 121.2 SmC 203.6 N 218.9 I

Cr 120 SmC 209.0 N 220.5 I[96]

^{1}H NMR (400 MHz, DMSO-D6) 0.84 (3H, t), 1.16 – 1.37 (16H, m), 1.41 (2H, quint), 1.73 (2H, quint), 4.07 (2H, t), 7.10 (2H, d), 7.37 (2H, d), 8.00 (2H, d), 8.06 (2H, d), OH proton not revealed

MS m/z 426 (M^+)

Scheme 2

4-Bromo-4'-dodecyloxybiphenyl (12)

Compound 11 (18.00 g, 0.072 mol), compound 3 (21.60 g, 0.087 mol), potassium carbonate (29.80 g, 0.216 mol) and butanone (200 ml) were stirred under reflux overnight. The resulting mixture was allowed to cool, and the potassium carbonate removed *via* filtration. The solvent was removed in vacuo to yield the crude product, which was recrystallised from ethanol and dried *in vacuo* over phosphorus pentoxide to yield colourless crystals.

Yield: 19.23 g (64 %)

Melting Point (°C): 113.0 – 113.9

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.20 – 1.40 (16H, m), 1.46 (2H, quint), 1.80 (2H, quint), 3.98 (2H, t), 6.95 (2H, d), 7.40 (2H, d), 7.46 (2H, d), 7.52 (2H, d)

MS m/z 416, 418, 1:1 (M^+)

4'-Dodecyloxybiphenyl-4-boronic acid (13)

Magnesium turnings (0.60 g, 0.025 mol) were stirred under nitrogen for two hours. Compound 12 (8.00 g, 0.019 mol) was dissolved in THF (20 ml) and a small portion (3 ml) was added to the reaction vessel, along with a small crystal of iodine. The reaction was initiated *via* heating and then the remaining solution of compound 12 in THF was added drop wise. The resulting solution was stirred under reflux overnight and completion of the reaction was detected *via* GC analysis. The solution was then cooled (–78 °C) and trimethyl borate (6.00 g, 0.058 mol) added dropwise. The solution was allowed to warm to room temperature and acidified with 10% hydrochloric acid (200 ml). The crude product was stirred in hexane and the product filtered off to yield a colourless solid.

Yield: 4.77 g (66 %)

^{1}H NMR (400 MHz, DMSO-D6) 0.80 (3H, t), 1.10 – 1.30 (16H, m), 1.35 (2H, quint), 1.70 (2H, quint), 3.96 (2H, t), 6.97 (2H, d), 7.53 (2H, d), 7.57 (2H, d), 7.79 (2H, d), 8.03 (2H, s)

Scheme 3

4'-Dodecyloxybiphenyl-3-carboxaldehyde (16)

Compound 14 (11.91 g, 0.034 mol) was added to a stirred mixture of compound 15 (5.31 g, 0.029 mol), sodium carbonate (3.50 g, 0.033 mol), tetrakis(triphenylphosphine) palladium(0) (2.00 g, 0.0017 mol), DME (20 ml) and water (35 ml), under an atmosphere of nitrogen. The resulting mixture was heated under reflux overnight. The product was extracted into diethyl ether, and the ethereal layer washed successively with water and brine. The washings were backwashed with fresh diethyl ether, and the combined ethereal extracts dried ($MgSO_4$). The $MgSO_4$ was removed *via* filtration through hyflo supercel, and the solvent removed *in vacuo*. The crude product was adsorbed onto silica gel, and purified *via* column chromatography (silica gel, hexane / DCM, 1:1). The product was recrystallised from ethanol and dried *in vacuo* over phosphorus pentoxide, to yield colourless crystals.

Yield: 4.82 g (45 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.20 – 1.40 (16H, m), 1.50 (2H, quint), 1.81 (2H, quint), 4.00 (2H, t), 6.99 (2H, d), 7.56 (2H, d), 7.58 (1H, dd, J = 7.7, J = 7.7), 7.79 – 7.84 (2H, m), 8.06 (1H, dd, J = 1.8, J = 1.8), 8.06 (1H, s)

4'-Dodecyloxybiphenyl-3-carboxylic acid (17)

Compound 16 (4.82 g, 0.013 mol), sodium carbonate (10.00 g, 0.094 mol), potassium permanganate (20.00 g, 0.13 mol) and water (150 ml) were stirred under reflux overnight, until the purple colouration turned brown. The reaction mixture was then acidified with 30% sulphuric acid. Sodium metabisulphite was then added to yield a white precipitate in a colourless solution. Analysis indicated the presence of the sodium salt, so the product was extracted again in to diethyl ether, and acidified further to yield the carboxylic acid, which was recrystallised from ethanol to yield colourless crystals which were dried *in vacuo* over phosphorus pentoxide.

Yield: 2.00 g (41 %)

Melting Point (°C): 148.4 – 150.6

^{1}H NMR (400 MHz, DMSO-D6) 0.46 (3H, t), 0.78-1.00 (16H, m), 1.05 (2H, quint), 1.39 (2H, quint), 3.60 (2H, t), 6.58 (2H, d), 7.09 (1H, dd, J = 7.72, J = 7.72), 7.16 (2H, d), 7.35

(1H, ddd, J = 7.7, J = 1.7, J = 1.2), 7.53 (1H, ddd, J = 7.7, J = 1.2, J = 1.2), 7.81 (1H, dd, J = 1.7, J = 1.7)

MS m/z 382 (M^+)

Scheme 4

4-Benzyloxybenzoic acid (19)

Compound 18 (50.0 g, 0.35 mol) was added dropwise to a stirred mixture of compound 1 (24.0 g, 0.18 mol), NaOH (14.0 g, 0.35 mol), ethanol (150 ml) and water (100 ml). The resulting mixture was heated under reflux overnight. NaOH (14.0 g, 0.35 mol) in water (100 ml) was then added and the mixture allowed to reflux for a further two hours. The reaction mixture was then poured onto crushed ice and acidified with 37% HCl. The colourless precipitate was removed by filtration, recrystallised from ethanol, and dried *in vacuo* over phosphorus pentoxide to yield colourless crystals.

Yield: 32.2 g (80 %)

Melting Point (°C): 188.8 – 192.8

189 – 190[68]

^{1}H NMR (400 MHz, DMSO-D6) 5.14 (2H, s), 7.06 (2H, d), 7.28 – 7.42 (5H, m), 7.86 (2H, d), OH proton not revealed

MS m/z 228 (M^+)

Octyl 4-benzyloxybenzoate (22)

Quantities: Compound 19 (5.50 g, 0.024 mol), compound 20 (3.23 g, 0.025 mol), DCC (5.67 g, 0.028 mol), DMAP (0.92 g, 0.0075 mol), DCM (400 ml). The experimental procedure was as described in the preparation of compound 42 to yield a colourless oil.

Yield: 3.78 g (46 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.35 (8H, m), 1.42 (2H, quint), 1.74 (2H, quint), 4.27 (2H, t), 5.09 (2H, s), 6.98 (2H, d), 7.30 – 7.44 (5H, m), 7.99 (2H, d)

MS m/z 340 (M^+)

1-Propylbutyl 4-hydroxybenzoate (23)

Quantities: Compound 19 (12.00 g, 0.053 mol), compound 21 (6.29 g, 0.054 mol), DCC (12.24 g, 0.060 mol), DMAP (1.98 g, 0.016 mol), DCM (400 ml). The experimental procedure was as described in the preparation of compound 42 to yield a colourless oil.

Yield: 3.32 g (19 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.92 (6H, t), 1.39 (4H, m), 1.62 (4H, m), 5.11 (2H,s), 5.14 (1H, m), 6.98 (2H, d), 7.30 – 7.44 (5H, m), 8.01 (2H, d)

MS m/z 326 (M^+)

Octyl 4-hydroxybenzoate (24)

Quantities: Compound 22 (3.78 g, 0.011 mol) was dissolved in EtOAc (200 ml), and 10% Pd/C (1.00 g), added. Hydrogen was then applied at atmospheric pressure, and the mixture stirred overnight. The mixture was filtered through hyflo supercel and the solvent removed *in vacuo* to yield a colourless solid, which was dried *in vacuo*.

Yield: 2.64 g (96 %)

Melting Point (°C): 43.9 – 47.6

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.23 – 1.38 (8H, m), 1.42 (2H, quint), 1.75 (2H, quint), 4.29 (2H, t), 5.92 (1H, s, broad), 6.88 (2H, d), 7.97 (2H, d)

MS m/z 250 (M^+)

1-Propylbutyl 4-hydroxybenzoate (25)

Quantities: Compound 23 (3.32 g, 0.010 mol), 10% Pd/C (0.50 g), EtOAc (200 ml). The experimental procedure was as described in the preparation of compound 24 to yield a colourless oil.

Yield: 2.25 g (96 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.92 (3H, t), 1.38 (4H, m), 1.62 (4H, m), 5.14 (1H, m), 6.88 (2H, d), 7.94 (2H, d), OH proton not revealed

MS m/z 237 ($M^+ + 1$)

Octyl 4-(4-benzyloxyphenylcarbonyloxy)benzoate (26)

Quantities: Compound 19 (2.48 g, 0.011 mol), compound 24 (2.64 g, 0.011 mol), DCC (2.49 g, 0.012 mol), DMAP 0.40 g, 0.0033 mol), DCM (300 ml). The experimental procedure was as described in the preparation of compound 42 to yield a colourless solid.

Yield: 1.70 g (34 %)

Melting Point (°C): 94.2 – 98.2

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.24 – 1.49 (10H, m), 1.77 (2H, quint), 4.32 (2H, t), 5.17 (2H, s), 7.07 (2H, d), 7.28 (2H, d), 7.33-7.47 (5H, m), 8.12 (2H, d), 8.16 (2H, d)

MS m/z 460 (M^+)

1-Propylbutyl 4-(4-benzyloxyphenylcarbonyloxy)benzoate (27)

Quantities: Compound 19 (2.25 g, 0.010 mol), compound 25 (2.40 g, 0.010 mol), DCC (2.27 g, 0.011 mol), DMAP (0.37 g, 0.0030 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 42 to yield a colourless solid.

Yield: 4.00 g (90 %)

Melting Point (°C): 105.1 – 108.4

^{1}H NMR (400 MHz, $CDCl_3$) 0.93 (6H, t), 1.40 (4H, m), 1.64 (4H, m), 5.16 (2H, s), 5.17 (1H, s), 7.06 (2H, d), 7.27 (2H, d), 7.32 – 7.46 (5H, m), 8.12 (2H, d), 8.16 (2H, d)

MS m/z 446 (M^+)

Octyl 4-(4-hydroxyphenylcarbonyloxy)benzoate (28)

Quantities: Compound 26 (1.70 g, 0.0037 mol), 10% Pd/C (0.50 g), EtOAc (250 ml). The experimental procedure was as described in the preparation of compound 24 to yield a pale yellow oil.

Yield: 1.30 g (95 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.40 (11H, m), 1.44 (2H, quint), 1.77 (2H, quint), 4.33 (2H, t), 5.06 (1H, s, broad), 6.93 (2H, d), 7.30 (2H, d), 8.13 (4H, 2 x d)

MS m/z 370 (M^+)

1-Propylbutyl 4-(4-hydroxyphenylcarbonyloxy)benzoate (29)

Quantities: Compound 27 (4.00 g, 0.0090 mol), 10% Pd/C (1.00 g), EtOAc (200 ml). The experimental procedure was as described in the preparation of compound 24. The crude product was purified *via* column chromatography (silica gel, hexane / DCM, 1:1, with a gradual increase in the quantity of DCM) to yield a yellow / brown oil.

Yield: 2.88 g (90 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.93 (6H, t), 1.40 (4H, m), 1.65 (4H, m), 5.17 (1H, m), 6.93 (2H, d), 7.28 (2H, d), 8.11 (2H, d), 8.12 (2H, d)

MS m/z 356 (M^+)

Scheme 5

(*S*)-1-Methylheptyl 4-benzyloxybenzoate (32)

Quantities: Compound 19 (3.50 g, 0.015 mol), compound 30 (2.04 g, 0.016 mol), DCC (3.50 g, 0.017 mol), DMAP (0.59 g, 0.0048 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 42 to yield a colourless oil.

Yield: 1.83 g (37 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.79 (3H, t), 1.12 – 1.35 (11H, m, includes 3H, d), 1.50 (1H, m), 1.65 (1H, m), 5.03 (2H, s), 5.03 (1H, sext), 6.91 (2H, d), 7.23 – 7.37 (5H, m), 7.91 (2H, d)

MS m/z 340 (M^+)

(±)-1-Methylheptyl 4-benzyloxybenzoate (33)

Quantities: Compound 19 (10.00 g, 0.044 mol), compound 31 (5.89 g, 0.045 mol), DCC (10.20 g, 0.50 mol), DMAP (1.65 g, 0.014 mol), DCM (300 ml). The experimental procedure was as described in the preparation of compound 42, to yield a colourless oil.

Yield: 8.10 g (54 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 1.24 – 1.44 (11H, m, includes 3H, d), 1.59 (1H, m), 1.72 (1H, m), 5.12 (2H, s), 5.12 (1H, sext), 6.99 (2H, d), 7.32 – 7.45 (5H, m), 8.00 (2H, d)

MS m/z 340 (M^+)

(*S*)-1-Methylheptyl 4-hydroxybenzoate (34)

Quantities: Compound 32 (3.14 g, 0.0092 mol), 10% Pd/C (1.00 g), EtOAc (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless oil.

Yield: 1.86 g (81 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.79 (3H, t), 1.14 – 1.36 (11H, m, includes 3H, d), 1.52 (1H, m), 1.64 (1H, m), 5.05 (1H, sext), 6.67 (1H, s, broad), 6.82 (2H, d), 7.87 (2H, d)

MS m/z 250 (M^+)

(±)-1-Methylheptyl 4-hydroxybenzoate (35)

Quantities: Compound 33 (3.57 g, 0.011 mol), 10% Pd/C (1.00 g), EtOAc (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless oil.

Yield: 2.38 g (91 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.86 (3H, t), 1.21 – 1.43 (11H, m, includes 3H, d), 1.59 (1H, m), 1.72 (1H, m), 5.12 (1H, sext), 6.91 (2H, d), 7.26 (1H, s, broad), 7.95 (2H, d)

MS m/z 250 (M^+)

(*S*)-1-Methylheptyl 4-(4-benzyloxyphenylcarbonyloxy)benzoate (36)

Quantities: Compound 19 (0.72 g, 0.0031 mol), compound 34 (0.80 g, 0.0032 mol), DCC (0.73 g, 0.0035 mol), DMAP (0.12 g, 0.00096 mol) DCM (100 ml). The experimental procedure was as described in the preparation of compound 7, to yield an off-white powder.

Yield: 1.24 g (87 %)

Melting Point (°C): 108.4 – 10.8

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.25 – 1.46 (11H, m, includes 3H, d), 1.62 (1H, m), 1.74 (1H, m), 5.17 (2H, s), 5.17 (1H, sext), 7.08 (2H, d), 7.28 (2H, d), 7.34 – 7.48 (5H, m), 8.12 (2H, d), 8.17 (2H, d)

MS m/z 460 (M^+)

(±)-1-Methylheptyl 4-(4-benzyloxyphenylcarbonyloxy)benzoate (37)

Quantities: Compound 19 (3.75 g, 0.016 mol), compound 35 (4.24 g, 0.017 mol), DCC (3.85 g, 0.019 mol), DMAP (0.62 g, 0.0051 mol), DCM (300 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 6.24 g (85 %)

Melting Point (°C): 88.3 – 91.0

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.24 – 1.44 (11H, m, includes 3H, d), 1.62 (1H, m), 1.74 (1H, m), 5.17 (1 H, sext), 5.17 (2H, s), 7.18 (2H, d), 7.28 (2H, d), 7.34 – 7.48 (5H, m), 8.12 (2H, d), 8.17 (2H, d)

MS m/z 460 (M^+)

(*S*)-1-Methylheptyl 4-(4-hydroxyphenylcarbonyloxy)benzoate (38)

Quantities: Compound 36 (2.60 g, 0.0057 mol), 10% Pd/C (0.75 g), EtOAc (300 ml). The experimental procedure was as described in the preparation of compound 9. The crude product was purified *via* column chromatography (silica gel, hexane / DCM, 1:1, with a gradual increase in the quantity of DCM) to yield a colourless solid.

Yield: 1.35 g (64 %)

Melting Point (°C): 59.2 – 62.9

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22 – 1.42 (11H, m, includes 3H, d), 1.62 (1H, m), 1.74 (1H, m), 5.16 (1H, sext), 5.73 (1H, s, broad), 6.94 (2H, s), 7.28 (2H, d), 8.12 (4H, 2 x d)

MS m/z 370 (M^+)

(±)-1-Methylheptyl 4-(4-hydroxyphenylcarbonyloxy)benzoate (39)

Quantities: Compound 37 (3.18 g, 0.0069 mol), 10% Pd/C (1.00 g), EtOAc (200 ml). The experimental procedure was as described in the preparation of compound 9, to yield a colourless oil which crystallised to a colourless solid.

Yield: 2.51 g (98 %)

Melting Point (°C): 70.7 – 75.0

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 1.22 – 1.44 (11H, m, includes 3H, d), 1.62 (1H, m), 1.74 (1H, m), 5.16 (1H, sext), 6.92 (2H, d and 1H, s, broad), 7.28 (2H, d), 8.10 (2H, d), 8.12 (2H, d)

MS m/z 370 (M^+)

Scheme 6

1-Benzyloxy-3-bromobenzene (41)

A mixture of compound 40 (50.0 g, 0.29 mol), compound 18 (32.8 g, 0.26 mol), potassium carbonate (119.6 g, 0.87 mol) and butanone (400 ml) was heated under reflux overnight. The mixture was then allowed to cool and the potassium carbonate removed by filtration. The solvent was removed *in vacuo*, the crude product adsorbed onto silica gel and purified *via* column chromatography (silica gel, packed in hexane, with the gradual introduction of DCM) to yield a colourless solid.

Yield: 63.6 g (93 %)

Melting Point (°C): 58.3 – 60.9

^{1}H NMR (400 MHz, $CDCl_3$) 5.05 (2H, s), 6.92 (1H, ddd, J = 7.9, J = 2.6, J = 1.3), 7.11 (1H, ddd, J = 7.9, J = 1.3, J = 1.3), 7.15 (1H, dd, J = 7.9, J = 7.9), 7.16 (dd, J = 2.6, J = 2.6), 7.32 – 7.45 (5H, m)

MS m/z 262, 264, 1:1 (M^+)

3-Benzyloxyphenylboronic acid (42)

n-Butyllithium (6.48 g, 0.10 mol, 40.7 ml, 2.5M) was added drop wise to a stirred, cooled (–78 °C) of compound 41 (23.00 g, 0.088 mol) in THF (600 ml), under nitrogen. The resulting solution was allowed to stir for one hour, and trimethyl borate (31.11 g, 0.30 mol) added drop wise. The solution was allowed to warm to room temperature overnight, acidified with 10% HCl (120 ml), and stirred for three hours. The crude product was extracted into diethyl ether, washed with water, two portions, which were back-washed with fresh diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was stirred in hexane to yield a colourless powder.

Yield: 13.23g (66 %)

^{1}H NMR (400 MHz, DMSO-D6) 5.01 (2H, s), 6.96 (1H, ddd, J = 8.4, J = 2.5, J = 1.2), 7.17 (1H, dd, J = 8.4, J = 8.4), 7.22 – 7.42 (7H, m), 7.98 (2H, s)

3-Benzyloxyphenol (43)

Hydrogen peroxide (9.52 g, 0.28 mol, 83 ml, 12%), was added in small portions to a stirred, refluxing mixture of compound 42 (7.88 g, 0.035 mol) in diethyl ether (200 ml). The

resulting solution was heated under reflux overnight, and then cooled to room temperature. The product was extracted into diethyl ether and washed with water, iron sulphate, and a second portion of water. The washings were back-washed with fresh diethyl ether and the combined ethereal extracts dried ($MgSO_4$). The solvent was removed *in vacuo*, the crude product adsorbed onto silica gel, and purified *via* column chromatography (silica gel, hexane with the gradual introduction of DCM) to yield a pale yellow oil which crystallised to an off-white solid.

Yield: 5.47 g (78 %)

Melting Point (°C): 43.4 – 46.9

^{1}H NMR (400 MHz, $CDCl_3$) 5.03 (2H, s), 5.65 (1H, s, broad), 6.47 (1H, ddd, J = 8.1, J = 2.4, J = 0.8), 6.52 (1H, dd, J = 2.4, J = 2.4), 6.62 (1H, ddd, J = 8.1, J = 2.4, J = 0.8), 7.16 (1H, dd, J = 8.1, J = 8.1), 7.33 – 7.47 (5H, m)

MS m/z 200 (M^+)

Scheme 7

1-Benzyloxy-2,3,4-trifluorobenzene (45)

Quantities: Compound 44 (10.00 g, 0.068 mol), compound 18 (7.72 g, 0.061 mol), potassium carbonate (28.20 g, 0.20 mol), butanone (200 ml). The experimental procedure was as described in the preparation of compound 41 with the exception that the crude product was recrystallised from ethanol, rather than purification *via* column chromatography, to yield colourless crystals.

Yield: 11.26 g (70 %)

Melting Point (°C): 48.3 – 51.7

^{1}H NMR (400 MHz, $CDCl_3$) 5.11 (2H, s), 6.69 (1H, dddd), 6.83 (1H, dddd), 7.31 – 7.44 (5H, m)

MS m/z 238 (M^+)

5-Benzyloxy-2,3,4-trifluorophenylboronic acid (46)

Quantities: Compound 45 (31.5 g, 0.13 mol), *n*-butlyllithium (9.6 g, 0.15 mol, 60 ml, 2.5M), THF (700 ml), trimethyl borate (32.0 g, 0.31 mol), 10% HCl (100 ml). The experimental procedure was as described in the preparation of compound 42, to yield a colourless powder.

Yield: 34.3 g (94 %)

^{1}H NMR (400 MHz, DMSO-D6) 5.19 (2H, s), 7.23 (1H, ddd, J = 8.9, J = 4.4, J = 2.2), 7.23 – 7.41 (5H, m), 8.48 (2H, s)

5-Benzyloxy-2,3,4-trifluorophenol (47)

Quantities: Compound 46 (22.44 g, 0.080 mol), hydrogen peroxide (24.00 g, 0.67 mol, 200 ml, 12%), diethyl ether (300 ml). The experimental procedure was as described in the preparation of compound 43, except that purification *via* column chromatography was not required, to yield a colourless powder.

Yield: 17.59 g (87 %)

Melting Point (°C): 80.6 – 83.2

^{1}H NMR (400 MHz, $CDCl_3$) 5.00 (1H, d, J = 3.8), 5.07 (2H, s), 6.46 (1H, ddd, J = 8.0, J = 8.0, J = 2.3), 7.31 – 7.43 (5H, m)

MS m/z 254 (M^+)

5-Benzyloxy-2,3,4-trifluorobenzoic acid (48)

n-Butyllithium (4.03 g, 0.063 mol, 25.2 ml, 2.5M) was added dropwise to a cooled (−78 °C, stirred solution of compound 45 (15.00 g, 0.063 mol) in THF (300 ml). The resulting solution was stirred for one hour, poured onto solid carbon dioxide, and allowed to warm to room temperature overnight. The reaction mixture was acidified with 10% HCl (100 ml), and the product extracted into diethyl ether. The ethereal extract was washed with water (two portions), and the water washings back-washed with fresh diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent removed in vacuo to yield an off-white solid which was recrystallised from EtOH, and dried *in vacuo* over phosphorus pentoxide, to yield colourless crystals.

Yield: 7.88 g (44 %)

Melting Point (°C): 170.8 – 174.6

^{1}H NMR (400 MHz, DMSO-D6) 5.17 (2H, s), 7.24 – 7.44 (6H, m), OH proton not revealed

MS m/z 282 (M^+)

Scheme 8

5-Bromo-2-fluorophenol (50)

Quantities: Compound 49 (19.50 g, 0.089 mol), hydrogen peroxide (20.26 g, 0.89 mol, 250 ml, 12%), diethyl ether (200 ml). The experimental procedure was as described in the preparation of compound 47 to yield a yellow oil.

Yield: 13.45 g (79 %)

^{1}H NMR (400 MHz, $CDCl_3$) 5.42 (1H, s, broad), 6.86 (1H, dd, J = 8.6, J = 8.6), 6.90 (1H, ddd), 7.08 (1H, dd, J = 7.6, J = 2.0)

MS m/z 190, 192, 1:1 (M^+)

1-Benzyloxy-5-bromo-2-fluorobenzene (51)

Quantities: Compound 50 (6.00 g, 0.031 mol), compound 18 (3.53 g, 0.028 mol), potassium carbonate (12.83 g, 0.093 mol), butanone (200 ml). The experimental procedure was as described in the preparation of compound 41, to yield a colourless solid.

Yield: 7.51 g (95 %)

Melting Point (°C): 42.1 – 46.6

^{1}H NMR (400 MHz, $CDCl_3$) 5.11 (2H, s), 6.98 (1H, dd, J = 10.2, J = 8), 7.04 (1H, ddd, J = 8.0, J = 5.8, J = 2.2), 7.16 (1H, dd, J = 7.3, J = 2.2), 7.33 – 7.48 (5H, m)

MS m/z 280, 282, 1:1 (M^+)

3-Benzyloxy-4-fluorophenylboronic acid (52)

Quantities: Compound 51 (4.00 g, 0.014 mol), magnesium (0.44 g, 0.018 mol), trimethyl borate (4.37 g, 0.042 mol), THF (300 ml), 10% HCl (100 ml). The experimental procedure was as described in the preparation of compound 13, to yield an off-white solid.

Yield: 2.05 g (60 %)

^{1}H NMR (400 MHz, DMSO-D6) 5.14 (2H, s), 7.16 (1H, dd, J = 11.1, J = 7.8), 7.30 – 7.47 (6H, m), 7.64 (1H, dd, J = 11.1, J = 1.1), 8.10 (2H, s)

3-Benzyloxy-4-fluorophenol (53)

Quantities: Compound 52 (2.00 g, 0.0081 mol), hydrogen peroxide (2.20 g, 0.065 mol, 19 ml, 12%), diethyl ether (200 ml). The experimental procedure was as described in the preparation of compound 47, to yield a yellow-brown oil.

Yield: 1.57 g (89 %)

^{1}H NMR (400 MHz, $CDCl_3$) 5.06 (2H, s), 5.51 (1H, s, broad), 6.31 (1H, ddd, J = 8.37, J = 3.3), 6.52 (1H, dd, J = 6.5, J = 3.3), 6.94 (1H, dd, J = 9.7, J = 9.0), 7.31 – 7.44 (5H, m)

MS m/z 218 (M^+)

4-Fluororesorcinol (54)

Quantities: Compound 53 (1.57 g, 0.0072 mol), 10% Pd/C (1.00 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield an off-white solid.

Yield: 0.78 g (85 %)

Melting Point (°C): 91.4 – 96.2

^{1}H NMR (400 MHz, $CDCl_3$) 4.68 (1H, s), 5.15 (1H, d, J = 4.0), 6.30 (1H, ddd, J = 8.8, J = 8.8, J = 3.2), 6.51 (1H, dd, J = 6.7, J = 3.2), 6.93 (1H, dd, J = 9.6, J = 8.8)

MS m/z 128 (M^+)

Scheme 9

1-Benzyloxy-2,4-difluorobenzene (56)

Quantities: Compound 55 (25.0 g, 0.19 mol), compound 18 (21.9 g, 0.17 mol), potassium carbonate (78.7 g, 0.57 mol), butanone (400 ml). The experimental procedure was as described in the preparation of compound 41. The product was recrystallised from ethanol / ethyl acetate to yield colourless crystals.

Yield: 25.34 g (68 %)

Melting Point (°C): 52.1 – 52.9

^{1}H NMR (400 MHz, $CDCl_3$) 5.10 (2H, s), 6.75 (1H, dddd, J = 9.1, J = 7.5, J = 3.1, J = 1.6), 6.87 (1H, ddd, J = 10.6, J = 8.0, J = 3.1), 6.93 (1H, ddd, J = 9.1, J = 9.1, J = 5.3), 7.30 – 7.44 (5H, m)

MS m/z 220 (M^+)

3-Benzyloxy-2,6-difluorophenylboronic acid (57)

Quantities: Compound 56 (15.0 g, 0.068 mol), *n*-Butyllithium (4.15 g, 0.065 mol, 26.0 ml, 2.5M), trimethyl borate (21.2 g, 0.20 mol), 10% HCl (100 ml), THF (200 ml). The experimental procedure was as described in the preparation of compound 42 to yield an off-white powder.

Yield: 9.68 g (56 %)

^{1}H NMR (400 MHz, DMSO-D6) 5.04 (2H, s), 6.80 (1H, ddd, J = 9.3, J = 7.7, J = 1.5), 7.09 (1H, ddd, J = 9.3, J = 9.3, J = 5.5), 7.32 – 7.40 (5H, m), 8.64 (2H, s)

3-Benzyloxy-2,6-difluorophenol (58)

Quantities: Compound 57 (9.61 g, 0.036 mol), hydrogen peroxide (12.24 g, 0.36 mol, 100 ml, 12%), diethyl ether (200 ml). The experimental procedure was as described in the preparation of compound 43, to yield a yellow oil.

Yield: 5.10 g (60 %)

^{1}H NMR (400 MHz, $CDCl_3$) 5.16 (2H, s), 5.46 (1H, s, broad), 6.50 (1H, ddd, J = 9.3, J = 8.6, J = 4.8), 6.78 (1H, ddd, J = 9.3, J = 9.3, J = 2.4), 7.33 – 7.47 (5H, m)

MS m/z 236 (M^+)

Scheme 10

3-Benzyloxy-2-fluorophenylboronic acid (60)

(Attempted synthesis)

Method a

Quantities: Compound 59 (11.71 g, 0.058 mol), *n*-butyllithium (4.26 g, 0.067 mol, 26.8 ml, 2.5M), trimethyl borate (17.68 g, 0.17 mol), 10% HCl (100 ml), THF (400 ml). The experimental procedure was as described in the preparation of compound 42. However, after the ethereal extraction, no product was acquired.

(Attempted synthesis)

Method b

n-Butyllithium (1.56 g, 0.024 mol, 9.6 ml, 2.5M) was added dropwise to a cooled (– 78°C), stirred solution of diisopropylamine (2.75 g, 0.027 mol) in THF (300 ml). Compound 59 (5.00 g, 0.025 mol) was dissolved in THF and added dropwise to the resultant mixture, maintaining the temperature at –78 °C. The solution was stirred for twenty minutes before the dropwise addition of trimethyl borate (7.80 g, 0.075 mol), and then allowed to warm to room temperature overnight. 10 % hydrochloric acid (40 ml) was added to acidify the product, which was then extracted into diethyl ether, and washed with water. The washings were back-washed with fresh diethyl ether, and the combined ethereal extracts dried ($MgSO_4$). The $MgSO_4$ was removed by filtration and the solvent removed *in vacuo*. However, at this point, no product was acquired.

1-*t*-Butyldimethylsiloxy-2-fluorobenzene (63)

Compound 62 (8.13 g, 0.054) was added drop wise to a stirred solution of compound 61 (5.00 g, 0.045 mol) in DMF (50 ml), under nitrogen. The resulting solution was allowed to stir overnight, and then the product was extracted into diethyl ether. The ethereal layer was washed with water (two portions), and the washings back-washed with fresh diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a yellow oil, which was purified *via* column chromatography (silica gel, hexane, with the gradual introduction of DCM), and dried *in vacuo*.

Yield: 5.46 g (54 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.15 (6H, d), 0.97 (9H, s), 6.81 (1H, dddd), 6.87 (1H, ddd, J = 7.8, J = 7.8, J = 2.0), 6.94 (1H, dddd, J = 7.9, J = 7.3, J = 2.0, J = 1.0)

MS m/z 226 (M^+)

3-*t*-Butyldimethylsiloxy-2-fluorophenylboronic acid (64)

(Attempted synthesis)

sec-Butyllithium (1.43 g, 0.022 mol, 15.71 ml, 1.4M) was added drop wise to a cooled (–78 °C) stirred solution of compound 63 (5.30 g, 0.023 mol) in THF (200 ml), under nitrogen. The resultant solution was allowed to stir for one hour, and then trimethyl borate (4.58 g, 0.044 mol) in THF (50 ml) added drop wise. The solution was allowed to warm to room temperature overnight, and then acidified with 10% HCl (100 ml). The product was extracted into diethyl ether, and the ethereal layer was washed with water (two portions), and the washings back-washed with fresh diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a mixture of a yellow oil and an off-white solid. The crude product was stirred in hexane, with a few drops of water, for four hours. The solid product was removed by filtration and dried under suction. Upon ^{1}H NMR analysis, it was found that during the reaction, the *t*-butyldimethylsiloxy- protecting group had also been removed, and therefore 2-fluoro-3-hydroxy-phenyl-1-boronic acid was afforded as the product.

Yield: 1.16 g (34 %)

^{1}H NMR (400 MHz, DMSO-D6) 6.82 – 6.90 (3H, m), 8.10 (2H, s), 9.50 (1H, s)

3-Bromo-2-fluorophenylboronic acid (66)

n-Butyllithium (9.14 g, 0.14 mol, 56 ml, 2.5M) was added dropwise to a cooled (-78 °C) solution of diisopropylamine (17.00 g, 0.17 mol) in THF (500 ml), under an atmosphere of nitrogen. The resulting solution was stirred for thirty minutes, and then a solution of compound 65 in THF (200 ml) was added slowly, and the temperature maintained below -70 °C. The reaction mixture was then stirred, maintaining the temperature below -70 °C for one hour, before the dropwise addition of trimethyl borate (44.00 g, 0.42 mol). Upon complete addition of trimethyl borate, the reaction mixture was stirred overnight, and allowed to warm to room temperature overnight. 10 % HCl (100 ml) was added, and the resulting mixture

stirred for one hour. The product was extracted into diethyl ether, and washed with water twice. The washings were back-washed with a second portion of diethyl ether, and the combined ethereal extracts dried ($MgSO_4$) and the solvent removed *in vacuo* to yield an off-white solid, which was stirred in hexane, and filtered off.

Yield: 27.08 g (88 %)

^1H NMR (400 MHz, DMSO-D6) NMR inconclusive, to be discussed in section 4.1.

3-Bromo-2-fluorophenol (67)

Quantities: Compound 66 (10.00 g, 0.046 mol), hydrogen peroxide (15.64 g, 0.46 mol, 130 ml, 12%), diethyl ether (200 ml). The experimental procedure was as described in the preparation of compound 43, to yield a pale yellow solid.

Yield: 5.84 g (66 %)

Melting Point (°C): 48.3 – 50.9

^1H NMR (400 MHz, $CDCl_3$) 5.27 (1H, d, J = 8.3), 6.89 (1H, ddd, J = 8.5, J = 8.5, J = 1.3), 6.94 (1H, ddd, J = 8.5, J = 8.5, J = 2.1), 7.05 (1H, ddd, J = 8.5, J = 6.0, J = 2.1)

^{13}C NMR (100 MHz, CDCl3) 108.9 (d, J = 19.5), 116.5 (d, J = 2.0), 124.5 (s), 125.2 (d, J = 7.0), 144.5 (d, J = 15.0), 148.3 (d, J = 236.0)

MS m/z 190, 192, 1:1 (M^+)

1-Benzyloxy-3-bromo-2-fluorobenzene (68)

Quantities: Compound 67 (5.50 g, 0.029 mol), compound 18 (3.49 g, 0.028 mol), potassium carbonate (12.00 g, 0.087 mol), butanone (200 ml). The experimental procedure was as described in the preparation of compound 41, to yield a pale yellow oil.

Yield: 7.42 g (94 %)

^1H NMR (400 MHz, $CDCl_3$) 5.16 (2H, s), 6.90 – 6.99 (2H, m), 7.15 (1H, ddd, J = 7.3, J = 5.7, J = 2.4)

MS m/z 280, 282, 1:1 (M^+)

3-Benzyloxy-2-fluorophenylboronic acid (60)

Quantities: Compound 68 (7.22 g, 0.026 mol), *n*-butyllithium (1.56 g, 0.024 mol, 9.6 ml, 2.5M), trimethyl borate (8.11 g, 0.078 mol), THF (300 ml), 10% HCl (100 ml). The

experimental procedure was as described in the preparation of compound 42, to yield an off-white solid.

Yield: 3.62 g (61 %)

^{1}H NMR (400 MHz, DMSO-D6) 5.16 (2H, s), 7.04 (2H, m), 7.20 (1H, ddd, J = 9.6, J = 6.4, J = 3.5), 7.29 – 7.46 (5H, m)

3-Benzyloxy-2-fluorophenol (69)

Quantities: Compound 60 (3.55 g, 0.014 mol), hydrogen peroxide (4.92 g, 0.14 mol, 38.9 ml, 12%), diethyl ether (200 ml). The experimental procedure was as described in the preparation of compound 43, to yield an off-white solid.

Yield: 2.37 g (78 %)

Melting Point (°C): 50.8 – 52.6

^{1}H NMR (400 MHz, $CDCl_3$) 5.14 (2H, s), 5.29 (1H, s, broad), 6.57 (1H, ddd, J = 8.3, J = 7.4, J = 1.4), 6.4 (1H, ddd, J = 8.3, J = 7.4, J = 1.4), 6.90 (1H, ddd, J = 8.3, J = 8.3, J = 1.8)

MS m/z 218 (M^+)

Scheme 11

3-Bromo-2,4-difluorophenylboronic acid (71)

(Attempted synthesis)
Method a

Quantities: Diisopropylamine (5.78 g, 0.057 mol), *n*-butyllithium (3.33 g, 0.052 mol, 20.8 ml, 2.5M), THF (200 ml), compound 70 (10.00 g, 0.052 mol), trimethyl borate (16.22 g, 0.16 mol), 10% HCl (100 ml). The experimental procedure was as described in the preparation of compound 67.
Analysis by NMR revealed a mixture of two products and will be discussed in section 4.1.

(Attempted synthesis)
Method b

Quantities: Diisopropylamine (5.78 g, 0.057 mol), *n*-butyllithium (3.33 g, 0.052 mol, 20.8 ml, 2.5M), THF (200 ml), compound 70 (10.00 g, 0.052 mol), trimethyl borate (16.22 g, 0.16 mol), 10% HCl (100 ml). The experimental procedure was as described in the preparation of compound 67, except that a lower temperature of −100 °C was employed.
Analysis by NMR revealed a mixture of two products and will be discussed in section 4.1.

3-Chloro-2,4-difluorophenylboronic acid (73)

(Attempted synthesis)
Quantities: *n*-butyllithium (3.45 g, 0.054 mol, 21.6 ml, 2.5M), THF (200 ml), compound **72** (8.00 g, 0.054 mol), trimethyl borate (16.85 g, 0.16 mol), 10% HCl (100 ml). The experimental procedure was as described in the preparation of compound 42.
Analysis by NMR revealed a mixture of two products and will be discussed in section 4.1.

3-Chloro-2,4-difluorophenylboronic acid (73)

Quantities: Diisopropylamine (5.78 g, 0.057 mol), *n*-BuLi (3.33 g, 0.052 mol, 20.8 ml, 2.5M), THF (200 ml), compound 72 (8.00 g, 0.054 mol), trimethyl borate (16.22 g, 0.16 mol), 10% HCl (100 ml). The experimental procedure was as described in the preparation of compound 74.

Yield: 6.75 g (65 %)

^{1}H NMR (400 MHz, DMSO-D6) 7.22 (1H, ddd, J = 8.4, J = 8.4, J = 1.6), 7.52 (1H, ddd, J = 8.4, J = 6.8, J = 6.8), 8.40 (2H, s, broad)

3-Chloro-2,4-difluorophenol (74)

Quantities: Compound 73 (6.75 g, 0.035 mol), hydrogen peroxide (11.90 g, 0.35 mol, 103.6 ml, 12%), diethyl ether (300 ml). The experimental procedure was as described in the preparation of compound 43, to yield a colourless solid.

Yield: 3.10 g (54 %)

Melting Point (°C): 38.2 – 43.6

^{1}H NMR (400 MHz, $CDCl_3$) 5.17 (1H, s, broad), 6.84 – 6.93 (2H, m)

^{13}C NMR (100 MHz, CDCl3), 110.0 (dd, J = 22.3, J = 18.5), 111.2 (dd, J = 22.3, J = 3.8), 114.8 (dd, J = 8.5, J = 2.3), 140.4 (dd, J = 14.2, J = 3.8), 147.5 (dd, J = 241.0, J = 3.8), 152.6 (dd, J = 243.3, J = 2.3)

MS m/z 164, 166, 3:1 (M^+)

1-Benzyloxy-3-chloro-2,4-difluorobenzene (75)

Quantities: Compound 74 (3.00 g, 0.018 mol), compound 18 (2.26 g, 0.018 mol), potassium carbonate (7.45 g, 0.054 mol), butanone (200 ml). The experimental procedure was as described in the preparation of compound 41, to yield a colourless oil.

Yield: 3.91 g (85 %)

^{1}H NMR (400 MHz, $CDCl_3$) 5.09 (2H, s), 6.78 – 6.86 (2H, m), 7.30 – 7.42 (5H, m)

MS m/z 254, 256, 3:1 (M^+)

5-Benzyloxy-3-chloro-2,4-difluorophenylboronic acid (76)

Quantities: Diisopropylamine (1.72 g, 0.017 mol), *n*-butyllithium (0.96 g, 0.015 mol, 6 ml, 2.5M), THF (200 ml), compound 75 (3.91 g, 0.015 mol), trimethyl borate (4.68 g, 0.045

mol), 10% HCl (50 ml). The experimental procedure was as described in the preparation of compound 74, to yield an off-white solid.

Yield: 1.61 g (36 %)

^{1}H NMR (400 MHz, DMSO-D6) 5.14 (2H, s), 7.28 – 7.42 (6H, m), 8.43 (2H, s)

5-Benzyloxy-3-chloro-2,4-difluorophenol (77)

Quantities: Compound 76 (1.61 g, 0.0054 mol), hydrogen peroxide (1.84 g, 0.054 mol, 16 ml, 12%), diethyl ether (150 ml). The experimental procedure was as described in the preparation of compound 43, to yield a colourless oil.

Yield: 0.86 g (78 %)

^{1}H NMR (400 MHz, $CDCl_3$) 5.08 (2H, s), 6.62 (1H, dd, J = 7.9, J = 7.9), 7.31 – 7.43 (5H, m)

MS m/z 270, 272, 3:1 (M^+)

Scheme 12

5-Bromo-2,3,4-trifluorobenzoic acid (79)

n-Butyllithium (4.48 g, 0.070 mol, 28 ml, 2.5M) was added dropwise to a stirred, cooled (–78 °C) solution of diisopropylamine (7.90 g, 0.078 mol) in THF (200 ml) under an atmosphere of nitrogen. The resulting solution was allowed to stir for 30 mintues and compound 78 (15.00 g, 0.071 mol) in THF (20 ml) added dropwise. After 45 minutes the reaction mixture was poured onto solid carbon dioxide and allowed to warm to room temperature overnight. The product was extracted as the lithium salt into 10% sodium hydroxide and washed with diethyl ether (two portions). The diethyl ether washings were back-washed with fresh sodium hydroxide solution and the combined basic extracts acidified with 36% HCl. The product was then extracted into diethyl ether, washed with water (two portions) and the washings back-washed with fresh diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to yield colourless crystals, which were recrystallised from ethanol / hexane, 1:3.

Yield: 8.42 g (47 %)

^{1}H NMR (400 MHz, DMSO-D6) 7.96 (1H, ddd, J = 7.4, J = 7.4, J = 2.6), OH proton not revealed

Ethyl 5-bromo-2,3,4-trifluorobenzoate (80)

Compound 79 (8.42 g, 0.033 mol), ethanol (200 ml) and sulphuric acid (0.5 ml) were heated at reflux overnight. After cooling to room temperature, the reaction mixture was poured into water (300 ml) and the product extracted into diethyl ether. The ethereal layer was washed successively with sodium hydrogen carbonate solution and brine. Each washing was back-washed with fresh diethyl ether, and the combined ethereal extracts dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a colourless oil.

Yield: 2.82 g (30 %)

^{1}H NMR (400 MHz, $CDCl_3$) 1.32 (3H, t), 4.32 (2H, quart), 7.87 (1H, ddd, J = 6.1, J = 6.1, J = 2.0)

Scheme 13

3-Benzyloxybenzoic acid (82)

Quantities: Compound **81** (70.0 g, 0.51 mol), compound **18** (144.0 g, 1.12 mol), sodium hydroxide (2 x 40.0 g, 1.00 mol), ethanol (200 ml), water (100 ml). The experimental procedure was as described in the preparation of compound **4**, to yield colourless crystals.

Yield: 72.3 g (62 %)

Melting Point (°C): 131.0 – 133.4

^{1}H NMR (400 MHz, DMSO-D6) 4.33 (2H, s), 6.37 (1H, ddd, J = 8.3, J = 2.4, J = 1.3) 6.47 – 6.66 (6H, m), 6.73 – 6.77 (2H, m)

MS m/z 228 (M^+)

3.3.2 Achiral Products

Scheme 14

1,3-Phenylene bis[4-(4-dodecyloxyphenylcarbonyloxy)benzoate] (84)

Quantities: Compound 10 (1.66 g, 0.0039 mol), compound 83 (0.26 g, 0.0023 mol), DCC (0.52 g, 0.0026 mol), DMAP (0.08 g, 0.00069 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 7. The product was then recrystallised from ethanol / ethyl acetate, to yield colourless crystals which were dried *in vacuo* over phosphorus pentoxide.

Yield: 0.40 g (22 %)

Transitions (°C): Cr 104.2 B_2 115.9 I

Cr 106.0 B_2 116.5 I[97]

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (6H, t), 1.23 – 1.42 (32H, m), 1.48 (4H, quint), 1.83 (4H, quint), 4.06 (4H, quint), 6.99 (4H, d), 7.19 (2H, dd, J = 8.0, J = 1.8), 7.21 (1H, dt, J = 1.8, J = 0.9), 7.38 (4H, d), 7.50 (1H, dt, J = 8.0, J = 0.9), 8.16 (4H, d), 8.28 (4H, d)

^{13}C NMR (100 MHz, CDCl3), 14.1, 22.7, 26.0, 29.1, 29.3, 29.5, 29.6 (x3), 31.9, 68.4 (alkyl chains, 12 required, 11 found); 114.4, 115.8, 119.3, 120.9, 122.1, 126.6, 129.9, 131.9, 132.4, 151.4, 155.5, 163.8 (aromatic carbons, 12 required, 12 found); 164.1, 164.3 (carbonyl carbons, 2 required, 2 found)

MS m/z 950 (M^+ + 1 + Na), 966 (M^+ + 1 + K)

HPLC 98.9 %

Elemental analysis: $C_{58}H_{70}O_{10}$ requires C 75.12 %, H 7.62 %; found C 74.86 %, H 7.46 %

Scheme 15

3-Benzyloxyphenyl 4-(4-dodecyloxyphenylcarbonyloxy)benzoate (85)

Quantities: Compound 10 (5.22 g, 0.012 mol), compound 43 (2.50 g, 0.013 mol), DCC (2.83 g, 0.014 mol), DMAP (0.46 g, 0.0034 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 6.76 g (90 %)

Melting Point (°C): 93.2 – 97.7

97 – 98[96]

^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (3H, t), 1.25 – 1.34 (16H, m), 1.41 (2H, quint), 1.76 (2H, quint), 3.98 (2H, t), 5.01 (2H, s), 6.77 (1H, ddd, J = 8.1, J = 2.3, J = 0.8), 6.80 (1H, dd, J = 2.3, J = 2.3), 6.83 (1H, ddd, J = 8.1, J = 2.3, J = 0.8), 6.92 (2H, d), 7.23 – 7.39 (8H, m), 8.08 (2H, d), 8.20 (2H, d)

3-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]phenol (86)

Quantities: Compound 85 (6.76 g, 0.011 mol), ethyl acetate (200 ml), ethanol (100 ml), and 10% Pd/C (1.00 g). The experimental procedure was as described in the preparation of compound 9, to yield an off-white solid, which was dried *in vacuo* over phosphorus pentoxide.

Yield: 5.47 g (96 %)

Melting Point (°C): 122.8 – 126.4

124.5 – 125.5[96]

^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (3H, t), 1.24 – 1.34 (16H, m), 1.40 (2H, quint), 1.75 (2H, quint), 3.98 (2H, t), 5.52 (1H, s, broad), 6.60 – 6.65 (2H, d), 6.70 (1H, ddd, J = 8.0, J = 1.4, J = 1.4), 6.91 (2H, d), 7.18 (1H, dd, J = 8.2, J = 8.2), 7.28 (2H, d), 8.08 (2H, d), 8.19 (2H, d)

MS m/z 518 (M^+)

1-(4-Dodecyloxyphenylcarbonyloxy)-3-[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (87)

Quantities: Compound 5 (0.70 g, 0.0023 mol), compound 86 (1.21 g, 0.0023 mol), DCC (0.52 g, 0.0025 mol), DMAP (0.08 g, 0.00069 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 1.31 g (73 %)

Transitions (°C): Cr 80.0 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (6H, 2 x t), 1.14 – 1.33 (32H, m), 1.41 (4H, quint), 1.75 (4H, quint), 3.97 (2H, t), 3.98 (2H, t), 6.90 (2H, d), 6.91 (2H, d), 7.07 – 7.12 (2H, m), 7.30 (2H, d), 7.40 (1H, ddd, J = 8.3, J = 8.3, J = 0.9), 8.06 (2H, d), 8.08 (2H, d), 8.20 (2H, d)

^{13}C NMR (100 MHz, CDCl3), 14.2, 22.7, 26.0, 29.1, 29.4, 29.6, 29.7, 32.0, 68.4 (x2) (Alkyl chains, 24 required, 10 found); 114.4, 114.5, 115.9, 119.0, 119.4, 121.0, 121.3, 122.2, 126.7, 129.8, 131.9, 132.4, 132.5, 151.4, 151.7, 155.5, 163.7, 163.9 (Aromatic carbons, 22 Required, 18 found); 164.2, 164.3, 164.6 (Carbonyl carbons, 3 Required, 3 found)

MS m/z 830 (M^+ + 1 + Na)

HPLC 98.1 %

Elemental analysis: $C_{57}H_{66}O_8$ requires C 75.88 %, H 8.26 %; found C 75.91 %, H 8.54 %

1-[4-(4-Octyloxyphenylcarbonyloxy)phenylcarbonyloxy]-3-[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (88)

Quantities: Compound 9 (0.77 g, 0.0021 mol), compound 86 (1.09 g, 0.0021 mol, DCC (0.48 g, 0.0023 mol), DMAP (0.08 g, 0.00063 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 1.30 g (72 %)

Transitions (°C): Cr 107.4 (B_1 105.9) I

Cr 103 (B_1 102) I[44, 98]

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 0.89 (3H, t), 1.22 – 1.42 (24H, m), 1.47 (4H, quint), 1.82 (4H, quint), 4.05 (4H, 2 x t), 6.98 (4H, 2 x d), 7.18 (2H, 2 x dd, J = 9.8, J = 2.1), 7.20 (1H, ddd, J = 2.1, J = 2.1, J = 0.7), 7.37 (4H, 2 x d), 7.50 (1H, ddd, J = 9.8, J = 9.8, J = 0.7), 8.15 (4H, 2 x d), 8.28 (4H, 2 x d)

^{13}C NMR (100 MHz, CDCl3), 14.1 (x2), 22.6, 22.7, 25.9, 29.0, 29.2, 29.3 (x2), 29.5, 29.6 (x3), 31.8, 31.9, 68.4 (Alkyl chains, 20 required, 16 found); 114.4, 115.8, 119.3, 120.9, 122.1, 126.6, 129.9, 131.8, 132.4, 151.4, 155.4, 163.8 (Aromatic carbons, 22 required, 12 found); 164.1, 164.3 (Carbonyl carbons, 4 required, 2 found)

MS m/z 894 (M^+ 1 + Na)

HPLC 99.6 %

Elemental analysis: $C_{54}H_{62}O_{10}$ requires C 74.45 %, H 7.19 %; found C 74.67 %, H 7.46 %

Scheme 16

1,3-Di[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-4-fluorobenzene (89)

Quantities: Compound **10** (2.10 g, 0.0049 mol), compound **54** (0.35 g, 0.0027 mol), DCC (1.11 g, 0.0054 mol), DMAP (0.10 g, 0.00081 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound **84**, to yield colourless crystals.

Yield: 1.21 g (52 %)

Transitions (°C): Cr 101.1 (B_2 91.3 N 94.3) I

^{1}H NMR (400 MHz, CD_2Cl_2) 0.90 (6H, 2 x t), 1.22 – 1.44 (30H, m), 1.49 (4H, quint), 1.82 (4H, quint), 4.06 (4H, t), 7.01 (4H, 2 x d), 7.19 (1H, ddd, J = 9.2, J = 3.8, J = 2.9), 7.29 (1H, dd, J = 6.2, J = 2.9), 7.31 (1H, dd, J = 9.2, J = 9.2) 7.39 (2H, d), 7.41 (2H, d), 8.14 (4H, 2 x d), 8.27 (2H, d), 8.29 (2H, d)

^{13}C NMR (100 MHz, CDCl3), CD_2Cl_2) 14.3, 23.1, 26.3, 29.5, 29.7, 30.0 (x4), 32.3, 68.8 (Alkyl chains, 24 required, 11 found); 114.8, 117.2 (d, J = 20.7), 118.3, 120.8 (d, J = 6.9), 121.3, 122.6 (d, J = 6.9), 126.1, 126.8, 132.1, 132.3, 132.7, 138.8 (d, J = 15.1), 147.0 (d, J = 2.3), 152.4 (d, J = 244.5), 156.0, 156.2, 163.5, 164.3 (Aromatic carbons, 22 Required, 18 found), 164.5 (x2), 164.6 (Carbonyl carbons, 4 required, 3 found)

MS m/z 968 (M^+ + 1 + Na)

HPLC 100 %

Elemental analysis: $C_{58}H_{69}O_{10}F$ requires C 73.73 %, H 7.31 %; found C 73.49 %, H 7.57 %

Scheme 17

3-Benzyloxy-2,6-difluorophenyl 4-(4-octyloxyphenylcarbonyloxy)benzoate (90)

Quantities: Compound 9 (3.50 g, 0.0095 mol), compound 58 (2.35 g, 0.010 mol), DCC (2.27 g, 0.011 mol), DMAP (0.37 g, 0.0030 mol), DCM (300 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 3.64 g (65 %)

Melting Point (°C): 82.4 – 87.2

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.24 – 1.42 (8H, m), 1.48 (2H, quint), 1.83 (2H, quint), 4.04 (2H, t), 5.14 (2H, s), 6.84 – 6.92 (2H, m), 6.99 (2H, d), 7.32 – 7.46 (7H, m, includes 2H, d), 8.15 (2H, d), 8.30 (2H, d)

MS m/z 588 (M^+)

3-Benzyloxy-2,6-difluorophenyl 4-(4-dodecyloxyphenylcarbonyloxy)benzoate (91)

Quantities: Compound 10 (4.13 g, 0.010 mol), compound 58 (2.30 g, 0.010 mol), DCC (2.27 g, 0.011 mol), DMAP (0.37 g, 0.0030 mol), DCM (300 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless oil, which crystallised to a colourless solid after drying *in vacuo*.

Yield: 5.08 g (79 %)

Melting Point (°C): 64.5 – 70.2

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22 – 1.42 (16H, m), 1.47 (2H, quint), 1.81 (2H, quint), 4.03 (2H, t), 5.11 (2H, s), 6.82 – 6.91 (2H, m), 6.98 (2H, d), 7.31 – 7.45 (7H, m, includes 2H, d), 8.15 (2H, d), 8.29 (2H, d)

MS m/z 678 (M^+ +1 + Na)

3-[4-(4-Octyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,4-difluorophenol (92)

Quantities: Compound 90 (3.60 g, 0.0061 mol), 10% Pd/C (0.50 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless solid.

Yield: 2.92 g (96 %)

Melting Point (°C): 123 – 125.2

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.40 (8H, m), 1.48 (2H, quint), 1.83 (2H, quint), 4.05 (2H, t), 5.25 (1H, s, broad), 6.84 – 6.94 (2H, m), 6.99 (2H, d), 7.39 (2H, d), 8.15 (2H, d), 8.29 (2H, d)

MS m/z 498 (M^+)

3-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,4-difluorophenol (93)

Quantities: Compound 91 (5.00 g, 0.0078 mol), 10% Pd/C (0.75 g), ethyl acetate (300 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless solid.

Yield: 3.99 g (92 %)

Melting Point (°C): 109.4 – 114.0

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.20 – 1.48 (18H, m), 1.81 (2H, quint), 4.06 (2H, t), 5.12 (1H, s, broad), 6.84 – 6.95 (2H, m), 6.99 (2H, d), 7.39 (2H, d), 8.15 (2H, d), 8.30 (2H, d)

MS m/z 554 (M^+)

1,3-Difluoro-2,4-di[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (94)

Quantities: Compound 9 (0.65 g, 0.0018 mol), compound 92 (0.92 g, 0.0019 mol), DCC 0.43 g, 0.0021 mol), DMAP (0.07 g, 0.00057 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.99 g (65 %)

Transitions (°C): Cr 109.0 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (6H, 2 x t), 1.25 – 1.42 (16H, m), 1.48 (4H, 2 x quint), 1.83 (4H, 2 x quint), 4.05 (4H, 2 x t), 6.99 (4H, 2 x d), 7.09 (1H, ddd, J = 8.9, J = 8.9, J = 2.2), 7.21 (1H, ddd, J = 8.9, J = 7.8, J = 5.0), 7.38 (2H, d), 7.40 (2H, d), 8.16 (4H, 2 x d), 8.29 (2H, d), 8.31 (2H, d)

^{13}C NMR (100 MHz, CDCl3) 14.1, 22.6, 25.9, 29.0, 29.2, 29.3, 31.7, 68.3 (alkyl chains, 16 required, 8 found); 111.0 (dd, J = 20.4, J = 3.8), 114.6, 120.4 (d, J = 8.5), 120.8, 122.2, 125.0, 125.5, 128.3 (dd, J = 16.9, J = 13.8), 132.0, 132.3, 132.4, 135.3 (dd, J = 11.5, J = 3.8), 147.8 (dd J = 252.1, J = 4.6), 153.0 (dd, J = 249.1, J = 3.1), 155.7, 155.8, 162.2, 163.1, 163.8, 164.2 (x2) (aromatic carbons + carbonyl carbons, 26 required, 21 found)

MS m/z 874 (M^+ + 1 + Na)

HPLC 100 %

Elemental analysis: $C_{50}H_{52}O_{10}F_2$ requires C 70.59 %, H 6.12 %; found C 70.42 %, H 6.35 %

1-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,4-difluoro-3-[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (95)

Quantities: Compound 10 (0.71 g, 0.0017 mol), compound 92 (0.93 g, 0.0019 mol), DCC (0.43 g, 0.0021 mol), DMAP (0.07 g, 0.00057 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 1.04 g (68 %)

Transitions (°C): Cr 112.0 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 0.89 (3H, t), 1.22 – 1.42 (24H, m), 1.48 (4H, 2 x quint), 1.83 (4H, 2 x quint), 4.05 (4H, 2 x t), 6.99 (4H, 2 x d), 7.09 (1H, ddd, J = 9.3, J = 9.3, J = 1.7), 7.21 (1H, ddd, J = 9.3, J = 7.5, J = 4.9), 7.38 (2H, d), 7.40 (2H, d), 8.15 (4H, 2 x d), 8.29 (2H, d), 8.31 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (x2), 22.6, 22.7, 25.9, 29.0, 29.2, 29.3 (x2), 29.5, 29.6 (x3), 31.8, 31.9, 68.3 (alkyl chains, 20 required, 16 found); 110.9 (dd, J = 20.8, J = 3.8), 114.4, 120.4 (d, J = 8.5), 120.8, 122.2, 125.0, 125.5, 128.3 (dd, J = 16.9, J = 13.8), 132.1, 132.2, 132.4, 135.2 (dd, J = 11.5, J = 3.8), 147.8 (dd, J = 254.4, J = 3.8), 153.0 (dd, J = 249.1, J = 3.1), 154.3, 155.8, 162.2, 163.1, 163.8, 164.2 (x2) (aromtaic + carbonyl carbons, 26 required, 20 found)

MS m/z 930 (M^+ + 1 + Na)

HPLC 93%

Elemental analysis: $C_{54}H_{60}O_{10}F_2$ requires C 71.52 %, H 6.62 %; found C 71.82 %, H 6.70 %

1-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,6-difluoro-3-[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (96)

Quantities: Compound 9 (0.61 g, 0.0017 mol), compound 93 (1.04 g, 0.0019 mol), DCC (0.43 g, 0.0021 mol), DMAP (0.07 g, 0.00057 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.47 g (31 %)

Transitions (°C): Cr 90 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 0.90 (3H, t), 1.22 – 1.42 (24H, m), 1.48 (4H, 2 x quint), 1.83 (4H, 2 x quint), 4.05 (4H, 2 x t), 6.99 (4H, 2 x d), 7.09 (1H, ddd, J = 9.2, J = 9.2, J = 2.1), 7.21 (1H, ddd, J = 9.2, J = 7.6, J = 4.8), 7.38 (2H, d), 7.40 (2H, d), 8.15 (2H, 2 x d), 8.29 (2H, d), 8.31 (2H, d)

^{13}C NMR (100 MHz, CDCl3) 14.1, 22.6, 22.7, 26.0, 29.1, 29.3 (x3), 29.5, 29.6 (x3), 31.8, 31.9, 68.4 (alkyl chains, 20 required, 20 found); 114.4, 120.8, 122.3 (x2), 132.I, 132.2, 132.4, 155.8, 155.9, 162.3, 163.2, 163.8, 164.3 (x2) (aromatic + carbonyl carbons, 26 required, 14 found)

MS m/z 930 (M^+ + 2 + Na)

HPLC 90.5 %

Elemental analysis: $C_{54}H_{60}O_{10}F_2$ requires C 71.52 %, H 6.62 %; found C 71.80 %, H 6.74 %

1,3-Di[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,4-difluorobenzene (97)

Quantities: Compound **10** (0.66 g, 0.0016 mol), compound **93** (0.91 g, 0.0016 mol), DCC (0.36 g, 0.0018 mol), DMAP (0.06 g, 0.00048 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound **84**, to yield colourless crystals.

Yield: 0.42 g (27 %)

Transitions (°C): Cr 87.5 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (6H, 2 x t), 1.20 – 1.40 (32H, m), 1.46 (4H, 2 x quint), 1.82 (4H, 2 x quint), 4.05 (4H, 2 x t), 6.99 (4H, 2 x d), 7.09 (1H, ddd, J = 9.2, J = 9.2, J = 2.2), 7.21 (1H, ddd, J = 9.2, J = 7.7, J = 5.1), 7.39 (2H, d), 7.40 (2H, d), 8.15 (4H, 2 x d), 8.29 (2H, d), 8.31 (2H, d)

^{13}C NMR (100 MHz, CDCl3) 14.1, 22.7, 26.0, 29.1, 29.3, 29.5, 29.6 (x3), 31.9, 68.4 (alkyl chains, 24 required, 11 found); 114.4, 120.8, 122.3 (x2), 125.1, 125.6, 132.1, 132.3, 132.4, 155.7, 155.9, 163.2, 163.8, 164.2, 164.3 (aromatic + carbonyl carbons, 26 required, 15 found)

MS m/z 986 (M^+ + 1 + Na)

HPLC 100 %

Elemental analysis: $C_{58}H_{68}O_{10}F_2$ requires C 72.35 %, H 7.07 %; found C 72.60 %, H 7.30 %

Scheme 18

3-Benzyloxy-2-fluorophenyl 4-(4-octyloxyphenylcarbonyloxy)benzoate (98)

Quantities: Compound 9 (1.67 g, 0.0045 mol), compound 71 (1.00 g, 0.0046 mol), DCC (1.04 g, 0.0051 mol), DMAP (0.17 g, 0.0014 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 2.12 g (83 %)

Melting Point (°C): 103.2 – 105.6

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.25 – 1.42 (8H, m), 1.48 (2H, quint), 1.84 (2H, quint), 4.06 (2H, t), 5.19 (2H, s), 6.88 (1H, ddd, J = 8.4, J = 6.4, J = 1.5), 6.94 (1H, ddd, J = 8.4, J = 7.3, J = 1.5), 6.99 (2H, d), 7.07 (1H, ddd, J = 8.4, J = 8.4, J = 2.0), 7.32 – 7.48 (7H, m), 8.16 (2H, d, 8.30 (2H, d)

MS m/z 570 (M^+)

3-Benzyloxy-2-fluorophenyl 4-(4-dodecyloxyphenylcarbonyloxy)benzoate (99)

Quantities: Compound 10 (1.90 g, 0.0045 mol), compound 71 (1.00 g, 0.0046 mol), DCC (1.04 g, 0.0051 mol), DMAP (0.17 g, 0.0014 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 84, to yield a colourless solid.

Yield: 1.24 g (44 %)

Melting Point (°C): 95.0 – 98.1

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22 – 1.42 (16H, m), 1.48 (2H, quint), 1.83 (2H, quint), 4.05 (2H, t), 5.18 (2H, s), 6.87 (1H, ddd, J = 8.4, J = 6.4, J = 1.5), 6.94 (1H, ddd, J = 8.4, J = 7.3, J = 1.5), 6.99 (2H, d), 7.06 (1H, ddd, J = 8.4, J = 8.4, J = 2.0), 7.30 – 7.47 (7H, m), 8.15 (2H, d), 8.29 (2H, d)

MS m/z 626 (M^+)

2-Fluoro-3-[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]phenol (100)

Quantities: Compound 98 (2.12 g, 0.0037 mol), 10% Pd/C (0.50 g), ethyl acetate (300 ml). The experimental procedure was as described in the preparation of compound 24. The product was purified *via* column chromatography (silica gel, hexane, with the gradual introduction of ethyl acetate) to yield a colourless solid.

Yield: 1.57 g (88 %)

Melting Point (°C): 122.2 – 125.3

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.20 – 1.40 (8H, m), 1.46 (2H, quint), 1.83 (2H, quint), 4.06 (2H, t), 5.23 (1H, s, broad), 6.82 (1H, ddd, J = 8.3, J = 6.6, J = 1.7), 6.95 (1H, ddd, J = 8.3, J = 7.7, J = 1.7), 6.99 (2H, d), 7.07 (1H, ddd, J = 8.3, J = 8.3, J = 1.9), 7.39 (2H, d), 8.16 (2H, d), 8.30 (2H, d)

MS m/z 480 (M^+)

3-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2-fluorophenol (101)

Quantities: Compound 99 (1.50 g, 0.0024 mol), 10% Pd/C (0.50 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 24. The product was recrystallised from ethanol to yield colourless crystals.

Yield: 0.67 g (52 %)

Melting Point (°C): 117.0 – 118.4

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.42 (16H, m), 1.48 (2H, quint), 1.83 (2H, quint), 4.05 (2H, t), 5.40 (1H, s, broad), 6.81 (1H, ddd, J = 8.3, J = 6.8, J = 1.7), 6.93 (1H, ddd, J = 8.3, J = 8.3, J = 1.7), 6.99 (2H, d), 7.06 (1H, ddd, J = 8.3, J = 8.3, J = 1.8), 7.38 (2H, d), 8.16 (2H, d), 8.29 (2H, d)

MS m/z 535 (M^+)

2-Fluoro-1,3-di[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (102)

Quantities: Compound 9 (0.53 g, 0.0014 mol), compound 100 (0.69 g , 0.0014 mol), DCC (0.32 g, 0.0015 mol), DMAP (0.05 g, 0.00042 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.61 g (52 %)

Transitions (°C): Cr 133.0 (X_1 119.0) I

^{1}H NMR (400 MHz, CD_2Cl_2) 0.88 (6H, t), 1.23 – 1.54 (16H, m), 1.48 (4H, quint), 1.83 (4H, quint), 4.05 (4H, t), 6.99 (4H, d), 7.21 – 7.25 (3H, m), 7.38 (4H, d), 8.15 (4H, d), 8.30 (4H, d)

^{13}C NMR (100 MHz, CD_2Cl_2) 14.1, 22.6, 25.9, 29.0, 29.2, 29.3, 31.8, 68.3 (alkyl chains, 8 required, 8 found); 114.4, 120.8, 121.3, 122.2, 123.6 (d, J = 4.6), 125.8, 132.1, 132.4, 139.4 (d, J = 10.8), 146.8 (d, J = 252.9), 155.6, 163.1 (aromatic carbons, 12 required, 12 found); 163.8, 164.2 (carbonyl carbons, 2 required, 2 found)

MS m/z 856 (M^+ + 1 + Na)

HPLC 99.8 %

Elemental analysis: $C_{50}H_{53}O_{10}F_1$ requires C 72.11 %, H 6.37 %; found C 72.38 %, H 6.63 %

1-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2-fluoro-3-[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (103)

Quantities: Compound **10** (0.58 g, 0.0014 mol), compound **100** (0.69 g, 0.0014 mol), DCC (0.32 g, 0.0015 mol), DMAP (0.05 g, 0.00042 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound **84**, to yield colourless crystals.

Yield: 0.69 g (56 %)

Transitions (°C): Cr 112.4 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 0.89 (3H, t), 1.22 – 1.42 (24H, m), 1.47 (4H, 2 x quint), 1.83 (4H, 2 x quint), 4.04 (4H, 2 x t), 6.99 (4H, 2 x d), 7.21 – 7.28 (3H, m), 7.38 (4H, 2 x d), 8.15 (4H, 2 x d), 8.29 (4H, 2 x d)

^{13}C NMR (100 MHz, CDCl3), 14.1 (x2), 22.6, 22.7, 25.9, 29.0, 29.2, 29.3 (x2), 29.5, 29.6 (x3), 31.8, 31.9, 68.4 (Alkyl chains, 20 required, 16 found); 114.4, 120.8, 121.3, 122.2, 123.6 (d, J = 4.6), 125.8, 132.1, 132.4, 139.4 (d, J = 10.8), 146.8 (d, J = 252.9), 155.6, 163.2 (Aromatic carbons, 22 required, 12 found); 163.8, 164.2 (carbonyl carbons, 4 required, 2 found)

MS m/z 912 (M^+ + 1 + Na)

HPLC 98.7 %

Elemental analysis: $C_{54}H_{61}O_{10}F_1$ requires C 72.97 %, H 6.87 %; found C 73.17 %, H 7.03 %

1,3-Di[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2-fluorobenzene (104)

Quantities: Compound **10** (0.39 g, 0.00090 mol), compound **101** (0.50 g, 0.00093 mol), DCC (0.21 g, 0.0010 mol), DMAP (0.03 g, 0.00028 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound **84**, to yield colourless crystals.

Yield: 0.56 g (66 %)

Transitions (°C): Cr 117.3 (X_2 105.6) I

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (6H, t), 1.20 – 1.40 (32H, m), 1.48 (4H, quint), 1.83 (4H, quint), 4.05 (4H, t), 6.99 (4H, d), 7.20 – 7.28 (3H, m), 7.39 (4H, d), 8.15 (4H, d), 8.30 (4H, d)

^{13}C NMR (100 MHz, CDCl3), 14.1, 22.7, 26.0, 29.1, 29.3, 29.5, 29.6 (x3), 31.9, 68.4 (Alkyl chains, 12 required, 11 found); 114.4, 120.9, 121.3, 122.2, 123.6 (d, J = 5.4), 125.8, 132.1,

132.4, 139.4 (d, J = 10.8), 146.9 (d, J = 252.9), 155.6, 163.8 (Aromatic carbons, 12 required, 12 found); 163.2, 164.2 (Carbonyl carbons, 2 required, 2 found)

MS m/z 968 (M^+ 1 + Na)

HPLC 99.9 %

Elemental analysis: $C_{58}H_{69}O_{10}F_1$ requires C 73.73 %, H 7.31 %; found C 74.00 %, H 7.41 %

Scheme 19

5-Benzyloxy-3-chloro-2,4-difluorophenyl 4-(4-dodecyloxyphenylcarbonyloxy)benzoate (105)

Quantities: Compound 10 (1.70 g, 0.0040 mol), compound 77 (0.86 g, 0.0041 mol), DCC (0.93 g, 0.0045 mol), DMAP (0.15 g, 0.0012 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 1.38 g (52 %)

Melting Point (°C): 113.1 – 115.0

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.42 (16H, m), 1.48 (2H, quint), 1.83 (2H, quint), 4.06 (2H, t), 5.12 (2H, s), 6.90 (1H, dd, J = 7.5, J = 7.5), 6.99 (2H, d), 7.33 – 7.45 (7H, m), 8.15 (2H, d), 8.26 (2H, d)

MS m/z 678, 680, 3:1 (M^+)

3-Chloro-5-[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,4-difluorophenol (106)

Quantities: Compound 105 (1.38 g, 0.0020 mol), 10% Pd/C (0.50 g), ethyl acetate (250 ml). The experimental procedure was as described in the preparation of compound 86, with the exception that drying *in vacuo* over phosphorus pentoxide was not required, to yield a colourless solid.

Yield: 1.12 g (95 %)

Melting Point (°C): 98.8 – 99.4

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.42 (16H, m), 1.48 (2H, quint), 1.83 (2H, quint), 4.06 (2H, t), 5.37 (1H, d, J = 3.2), 6.90 (1H, dd, J = 8.3, J = 7.2), 6.99 (2H, d), 7.38 (2H, d), 8.16 (2H, d), 8.26 (2H, d)

3-Chloro-1,5-di[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,4-difluorobenzene (107)

Quantities: Compound 10 (0.77 g, 0.0018 mol), compound 106 (1.10 g, 0.0019 mol), DCC (0.43 g, 0.0021 mol), DMAP (0.07 g, 0.00057 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid. Approximately 0.30 g of the crude product was recrystallised from ethanol / ethyl acetate, to

yield colourless crystals, whilst the remaining crude product was used in the attempted synthesis of compound 108.

Yield: 0.94 g (52 %), (0.30 g returned from recrystallisation)

Transitions (°C): Cr 88.0 (N 59.4) I

^{1}H NMR (400 MHz, $CDCl_3$) 0.80 (6H, t), 1.14 – 1.32 (32H, m), 1.39 (4H, quint), 1.74 (4H, quint), 3.98 (4H, t), 6.92 (4H, d), 7.23 (1H, t, J = 7.2), 7.33 (4H, d), 8.05 (4H, d), 8.19 (4H, d)

^{13}C NMR (100 MHz, CDCl3), 14.1, 22.7, 25.9, 29.0, 29.3, 29.5, 29.6 (x3), 31.9, 68.4 (alkyl chains, 12 required, 11 found); 112.3 (t, J = 20.0), 114.4, 116.9, 120.7, 122.3, 125.1, 132.1, 132.4, 134.4 (dd, J = 13.8, J = 4.6), 149.1 (d, J = 252.1), 155.9, 163.8 (aromatic carbons, 12 required, 12 found); 162.8, 164.2 (carbonyl carbons, 2 required, 2 found)

MS m/z 1020, 1022, 1:1 (M^+ + Na)

HPLC 100 %

Elemental analysis: $C_{58}H_{67}O_{10}F_2Cl$ requires C 69.84 %, H 6.72 %; found C 69.59 %, H 6.92 %

1,5-Di[-4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,4-difluorobenzene (108)

(Attempted Synthesis)

Palladium (II) acetate (1.60 mg, 0.0071 mmol) was added to a solution of compound 107 (0.71 g, 0.00071 mol) in THF (50 ml), under an atmosphere of nitrogen. Potassium fluoride (0.08 g, 0.0014 mol) in water (10 ml) was then added, followed by the drop wise addition of polymethylhydrosiloxane (0.13 g, 0.0028 mol). The resultant solution was allowed to stir overnight, and then the product was extracted into diethyl ether. The ethereal layer was washed with water (2 portions), and the washings backwashed with fresh diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a colourless solid. However, NMR analysis revealed only the starting material (107).

Scheme 20

5-Benzyloxy-2,3,4-trifluorophenyl 4-(4-octyloxyphenylcarbonyloxy)benzoate (109)

Quantities: Compound 9 (4.00 g, 0.011 mol), compound 47 (2.88 g, 0.011 mol), DCC (2.49 g, 0.012 mol), DMAP (0.40 g, 0.0033 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 4.57 g (69 %)

Melting Point (°C): 102.3 – 103.4

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.24 – 1.42 (8H, m), 1.48 (2H, quint), 1.83 (2H, quint), 4.05 (2H, t), 5.11 (2H, s), 6.75 (1H, ddd, J = 6.8, J = 6.8, J = 2.4), 7.00 (2H, d), 7.33 – 7.45 (7H, m), 8.15 (2H, d), 8.25 (2H, d)

MS m/z 606 (M^+)

5-Benzyloxy-2,3,4-trifluorophenyl 4-(4-dodecyloxyphenylcarbonyloxy)benzoate (110)

Quantities: Compound 10 (3.50 g, 0.0082 mol), compound 47 (2.13 g, 0.0084 mol), DCC (1.90 g, 0.0092 mol). DMAP (0.31 g, 0.0025 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 5.03 g (93 %)

Melting Point (°C): 97 – 100.5

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22 – 1.42 (14H, m), 1.47 (2H, quint), 1.82 (2H, quint), 4.05 (2H, t), 5.11 (2H, s), 6.75 (1H, ddd, J = 6.8, J = 6.8, J = 2.6), 6.98 (2H, d), 7.33 – 7.45 (7H, m), 8.14 (2H, d), 8.25 (2H, d)

2,3,4-Trifluoro-5-[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]phenol (111)

Quantities: Compound 109 (4.57 g, 0.0075 mol), 10% Pd/C (1.00 g), ethyl acetate (300 ml). The experimental procedure was as described in the preparation of compound 106, to yield a light-brown solid.

Yield: 3.64 g (94 %)

Transitions (°C): Cr 117.9 N 132.7 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.24 – 1.42 (8H, m), 1.48 (2H, quint), 1.82 (2H, quint), 4.06 (2H, t), 5.53 (1H, s, broad), 6.73 (1H, ddd, J = 9.2, J = 6.8, J = 2.6), 6.99 (2H, d), 7.38 (2H, d), 8.15 (2H, d), 8.25 (2H, d)

MS m/z 517 (M^+)

5-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,3,4-trifluorophenol (112)

Quantities: Compound 110 (5.03 g, 0.0076 mol), 10% Pd/C (1.00 g), ethyl acetate (100 ml), ethanol (100 ml). The experimental procedure was as described in the preparation of compound 86, to yield a colourless solid.

Yield: 3.90 g (90 %)

Transitions (°C): Cr 111.9 N 125.3 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.23 – 1.42 (16H, m), 1.49 (2H, quint), 1.82 (2H, quint), 4.04 (2H, t), 5.23 (1H, s, broad), 6.74 (1H, ddd, J = 8.0, J = 6.7, 2.6), 6.99 (2H, d), 7.37 (2H, d), 8.15 (2H, d), 8.26 (2H, d)

2,3,4-Trifluoro-1,5-di[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (113)

Quantities: Compound 9 (0.85 g, 0.0023 mol), compound 111 (1.22 g, 0.0024 mol), DCC (0.54 g, 0.0026 mol), DMAP (0.09 g, 0.00072 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 1.48 g (74 %)

Transitions (°C): Cr 109.0 (B_1 87.9 N 103.9) I

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (6H, t), 1.23 – 1.41 (14H, m), 1.48 (4H, quint), 1.82 (4H, quint), 4.06 (4H, t), 6.99 (4H, d), 7.12 (1H, dt, J = 6.8, J = 2.4), 7.40 (4H, d), 8.15 (4H, d), 8.27 (4H, d)

^{13}C NMR (100 MHz, CDCl3), 14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 68.4 (Alkyl chains, 8 required, 8 found);

MS m/z 892 (M^+ + 1 + Na)

HPLC 99.9 %

Elemental analysis: $C_{50}H_{51}O_{10}F_3$ requires C 69.12 %, H 5.88 %; found C 68.99 %, H 6.06 %

1-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,3,4-trifluoro-5-[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (114)

Quantities: Compound 9 (0.81 g, 0.0022 mol), compound 112 (1.32 g, 0.0023 mol), DCC (0.52 g, 0.0025mol), DMAP (0.08 g, 0.00069 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals. HPLC analysis revealed that the compound was a mixture of 3 components, and will be discussed in section 4.2. The compound was purified *via* preparatory HPLC, and recrystallised from ethanol / ethyl acetate to yield colourless crystals.

Initial Yield: 1.31 g (64 %) approximately 300 mg then purified to yield approximately 200 mg

Transitions (°C): Cr 85.1 (B_1 59.7) N 96.2 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 0.89 (3H, t), 1.22 – 1.42 (24H, m), 1.48 (4H, 2 x quint), 1.82 (4H, 2 x quint), 4.05 (4H, 2 x t), 6.99 (4H, 2 x d), 7.12 (1H, ddd, J = 6.8, J = 6.8, J = 2.6), 7.40 (4H, 2 x d), 8.15 (4H, 2 x d), 8.27 (4H, 2 x d)

^{13}C NMR (100 MHz, CDCl3) 14.1 (x2), 14.2, 22.6, 22.7, 26.0, 29.1, 29.2, 29.3 (x3), 29.5, 29.6 (x3), 31.8, 31.9, 68.4 (alkyl chains, 20 required, 16 found); 112.9, 114.4, 120.8, 122.4, 125.1, 132.2, 132.4 (ddd), 141.3 (ddd), 142.2 (ddd), 156.0, 163.9 (aromatic carbons, 22 required, 12 found); 162.8, 164.2 (carbonyl carbons, 4 required, 2 found)

MS m/z 948 (M^+ + 1 + Na)

HPLC 100 %

Elemental analysis: $C_{54}H_{59}O_{10}F_3$ requires C 70.10 %, H 6.44 %; found C 70.23 %, H 6.52 %

Scheme 21

5-Benzyloxy-2,3,4-trifluorophenyl 4-octyloxybenzoate (115)

Quantities: Compound 4 (2.10 g, 0.0084 mol), compound 47 (2.20 g, 0.0087 mol), DCC (1.97 g, 0.0096 mol), DMAP (0.32 g, 0.0026 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 3.68 g (90 %)

Melting Point (°C): 78.8 – 79.1

^{1}H NMR (400 MHz, $CDCl_3$) 0.91 (3H, t), 1.25 – 1.43 (8H, m), 1.48 (2H, quint), 1.84 (2H, quint), 4.05 (2H, t), 5.10 (2H, s), 6.75 (1H, ddd, J = 6.5, J = 6.5, J = 1.6), 6.98 (2H, d), 7.33 – 7.46 (5H, m), 8.12 (2H, d)

MS m/z 486 (M^+)

5-Benzyloxy-2,3,4-trifluorophenyl 4-dodecyloxybenzoate (116)

Quantities: Compound 5 (2.58 g, 0.0084 mol), compound 47 (2.20 g, 0.0087 mol), DCC (1.97 g, 0.0096 mol), DMAP (0.32 g, 0.0026 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 4.18 g (92 %)

Melting Point (°C): 79.8 – 81.4

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.23 – 1.42 (16H, m), 1.48 (2H, quint), 1.83 (2H, quint), 4.06 (2H, t), 5.11 (2H, s), 6.75 (1H, ddd, J = 7.2, J = 7.2, J = 2.2), 6.99 (2H, d), 7.34 – 7.46 (5H, m), 8.13 (2H, d)

MS m/z 542 (M^+)

2,3,4-Trifluoro-5-(4-octyloxyphenylcarbonyloxy)phenol (117)

Quantities: Compound 115 (3.68 g, 0.0076 mol), 10% Pd/C (1.00 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless solid.

Yield: 2.72 g (90 %)

Melting Point (°C): 93.9 – 96.2

^{1}H NMR (400 MHz, $CDCl_3$) 0.82 (3H, t), 1.15 – 1.32 (8H, m), 1.40 (2H, quint), 1.75 (2H, quint), 3.97 (2H, t), 5.63 (1H, s, broad), 6.60 (1H, ddd, J = 8.1, J = 6.8, J = 2.6), 6.90 (2H, d), 8.04 (2H, d)

MS m/z 396 (M^+)

5-(4-Dodecyloxyphenylcarbonyloxy)-2,3,4-trifluorophenol (118)

Quantities: Compound 116 (4.18 g, 0.0077 mol), 10% Pd / C (1.00 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless oil which crystallised to an off-white solid.

Yield: 3.16 g (91 %)

Melting Point (°C): 94.6 – 97.9

^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (3H, t), 1.24 – 1.34 (16H, m), 1.40 (2H, quint), 1.75 (2H, quint), 3.97 (2H, t), 5.50 (1H, s, Broad), 6.63 (1H, ddd, J = 7.9, J = 6.8, J = 2.6), 6.90 (2H, d), 8.05 (2H, d)

MS m/z 453 (M^+ + 1)

1-[4-(4-Dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,3,4-trifluoro-5-(4-octyloxyphenylcarbonyloxy)benzene (119)

Quantities: Compound 10 (1.06 g, 0.0025 mol), compound 117 (1.04 g, 0.0026 mol), DCC (0.59 g, 0.0029 mol), DMAP (0.10 g, 0.00078 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.75 g (37 %)

Transitions (°C): Cr 51.0 (N 35.7) I

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (6H, 2 x t), 1.22 – 1.42 (28H, m), 1.48 (4H, 2 x quint), 1.83 (4H, 2 x quint), 4.06 (4H, 2 x t), 6.98 (4H, 2 x d), 7.10 (1H, ddd, J = 6.8, J = 6.8, J = 2.3), 7.40 (2H, d), 8.13 (2H, d), 8.16 (2H, d), 8.28 (2H, d)

^{13}C NMR (100 MHz, CDCl3) 14.1 (x2), 22.6, 22.7, 26.0, 29.0, 29.1, 29.2, 29.3, 29.5, 29.6 (x3), 31.8, 31.9, 62.4 (x2) (alkyl chains, 20 required, 18 found); 113.0, 114.4, 114.5, 119.7, 120.7, 122.4, 125.2, 132.2, 132.4, 132.7, 155.9, 162.8, 163.2 (aromatic carbons, 17 required, 13 found); 163.8, 163.9, 164.1 (carbonyl carbons, 3 required, 3 found)

MS m/z 828 (M^+ + 1 + Na)

HPLC 99.8 %

Elemental analysis: $C_{47}H_{55}O_8F_3$ requires C 70.15 %, H 6.84 %; found C 70.31 %, H 7.10 %

1-(4-Dodecyloxyphenylcarbonyloxy)-2,3,4-trifluoro-5-[4-(4-octyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzene (120)

Quantities: Compound 9 (0.93 g, 0.0025 mol), compound 118 (1.18 g, 0.0026 mol), DCC (0.59 g, 0.0029 mol), DMAP (0.10 g, 0.00078 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.45 g (22 %)

Transitions (°C): Cr 64.2 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (3H, t), 0.84 (3H, t), 1.16 – 1.34 (24H, m), 1.41 (4H, 2 x quint), 1.75 (4H, 2 x quint), 3.98 (2H, t), 3.99 (2H, t), 6.90 (2H, d), 6.92 (2H, d), 7.02 (1H, ddd, J = 6.8, J = 6.8, J = 2.6), 7.32 (2H, d), 8.05 (2H, d), 8.08 (2H, d), 8.20 (2H, d)

^{13}C NMR (100 MHz, CDCl3) 14.1 (x2), 22.6, 22.7, 26.0 (x2), 29.0 (x2), 29.2, 29.3 (x2), 29.5, 29.6 (x3), 31.8, 31.9, 68.4 (x2) (alkyl chains, 20 required, 19 found); 113.0, 114.4, 114.5, 119.6, 120.7, 122.3, 125.1, 132.1, 132.4, 132.7, 134.5 (dd, J = 36.1, J = 13.1), 141.4 (ddd, J = 252.9, J = 14.6, J = 14.6), 142.1 (ddd, J = 252.1, J = 27.7, J = 11.5), 155.9, 162.8, 163.2 (aromtic carbons, 18 required, 16 found); 163.9, 164.1, 164.2 (carbonyl carbons, 3 required, 3 found)

MS m/z 828 (M^+ + 1 + Na)

HPLC 87 %

Elemental analysis: $C_{47}H_{55}O_8F_3$ requires C 70.15 %, H 6.84 %; found C 70.40 %, H 7.04 %

Scheme 22

Octyl 4-[4-(5-benzyloxy-2,3,4-trifluorophenylcarbonyloxy)phenylcarbonyloxy]benzoate (121)

Quantities: Compound 48 (0.89 g, 0.0031 mol), compound 28 (1.20 g, 0.0032 mol), DCC (0.73 g, 0.0035 mol), DMAP (0.12 g, 0.00096 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield colourless crystals.

Yield: 0.80 g (41 %)

Melting Point (°C): 112.0 – 114.0

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.40 (8H, m), 1.45 (2H, quint), 1.77 (2H, quint), 4.33 (2H, t), 5.21 (2H, s), 7.31 (2H, d), 7.35 – 7.48 (7H, m), 7.52 (1H, ddd, J = 8.3, J = 6.1, J = 2.3), 8.14 (2H, d), 8.30 (2H, d)

MS m/z 634 (M^+)

1-Propylbutyl 4-[4-(5-benzyloxy-2,3,4-trifluorophenylcarbonyloxy)phenylcarbonyloxy]benzoate (122)

Quantities: Compound 48 (2.21 g, 0.0078 mol), compound 29 (2.88 g, 0.0081 mol), DCC (1.84 g, 0.0089 mol), DMAP (0.30 g, 0.0024 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 3.43 g (71 %)

Melting Point (°C): 113.0 – 118.2

^{1}H NMR (400 MHz, $CDCl_3$) 0.94 (6H, t), 1.41 (4H, m), 1.67 (4H, m), 5.18 (1H, m), 5.20 (2H, s), 7.30 (2H, d), 7.52 (1H, ddd, J = 8.3, J = 6.1, J = 2.4), 8.14 (2H, d), 8.30 (2H, d)

MS m/z 620 (M^+)

Octyl 4-[4-(2,3,4-trifluoro-5-hydroxyphenylcarbonyloxy)phenylcarbonyloxy]benzoate (123)

Quantities: Compound 121 (0.80 g, 0.0013 mol), 10% Pd/C (0.20 g), ethyl acetate (150 ml). The experimental procedure was as described in the preparation of compound 24, to yield an off-white solid.

Yield: 0.67 g (95 %)

Melting Point (°C): 149.1 – 154.3

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.23 – 1.39 (8H, m), 1.44 (2H, quint), 1.78 (2H, quint), 4.33 (2H, t), 5.73 (1H, s, broad), 7.30 (2H, d), 7.40 (2H, d), 7.56 (1H, ddd, J = 8.6, J = 6.1, J = 2.4), 8.13 (2H, d), 8.29 (2H, d)

1-Propylbutyl 4-[4-(-2,3,4trifluorophenylcarbonyloxy)phenylcarbonyloxy]benzoate (124)

Quantities: Compound 122 (3.43 g, 0.0055 mol), 10% Pd/C (0.50 g), ethyl acetate (300 ml). The experimental procedure was as described in the preparation of compound 106, to yield an off-white solid.

Yield: 2.77 g (95 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.93 (6H, t), 1.40 (4H, m), 1.65 (4H, m), 5.18 (1H, m), 6.28 (1H, s, broad), 7.26 (2H, d), 7.38 (2H, d), 7.57 (1H, ddd, J = 8.8, J = 6.1, J = 2.4), 8.14 (2H, d), 8.29 (2H, d)

Octyl 4-{4-[5-(4'-dodecyloxyphenylcarbonyloxy)-2,3,4-trifluorophenylcarbonyloxy]phenylcarbonyloxy}benzoate (126)

Quantities: Compound 125 (0.45 g, 0.0012 mol), compound 123 (0.67 g, 0.0012 mol), DCC (0.22 g, 0.0013 mol), DMAP (0.04 g, 0.00036 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.55 g (50 %)

Transitions (°C): Cr 87.2 SmX_1 136.0 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (3H, t), 0.82 (3H, t), 1.15 – 1.32 (24H, m), 1.38 (4H, 2 x quint), 1.72 (4H, 2 x quint), 3.94 (2H, t), 4.26 (2H, t), 6.94 (2H, d), 7.23 (2H, d), 7.34 (2H, d), 7.53 (2H, d), 7.66 (2H, d), 7.83 (1H, ddd, J = 8.4, J = 6.4, J = 2.2), 8.06 (2H, d), 8.16 (2H, d), 8.22 (2H, d)

^{13}C NMR (100 MHz, CDCl3), 14.1 (x2), 22.6, 22.7, 26.0, 28.7, 29.2 (x3), 29.3, 29.4, 29.6 (x4), 31.8, 31.9, 65.3, 68.2 (Alkyl chains, 20 required, 19 found); 114.0 (dd, J = 7.7, J = 3.1), 115.0, 120.8 (d, J = 1.5), 121.7, 121.9, 125.3, 126.8, 127.2, 128.3, 128.4, 131.1, 131.2, 131.5, 132.0, 135.3 (dd, J = 10.0, J = 3.8), 141.5, (ddd, J = 256.0, J = 16.1, J = 13.8), 147.0, 148.0 (ddd, J = 263.7, J = 10.8, J = 2.3), 150.0 (ddd, J = 266.0, J = 11.5, J = 2.3), 154.3, 154.4, 159.8 (aromatic carbons, 22 required, 22 found); 160.0, 163.5, 163.7, 165.9 (carbonyl carbons, 4 required, 4 found)

MS m/z 908 (M^+)

HPLC 98.2 %

Elemental analysis: $C_{54}H_{59}O_9F_3$ requires C 71.37 %, H 6.50 %; found C 71.09 %, H 6.65 %

1-Propylbutyl 4-{4-[5-(4'-dodecyloxyphenylcarbonyloxy)-2,3,4-trifluorophenylcarbonyloxy]phenylcarbonyloxy}benzoate (127)

Quantities: Compound **125** (0.85 g, 0.0024 mol), compound **124** (1.31 g, 0.0025 mol), DCC (0.57 g, 0.0028 mol), DMAP (0.10 g, 0.00075 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound **84**, to yield colourless crystals.

Yield: 1.12 g (52 %)

Transitions (°C): Cr 95.5 (SmX_2 88.6) I

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 0.95 (6H, t), 1.24 – 1.53 (22H, m), 1.58 – 1.76 (4H, m), 1.83 (2H, quint), 4.03 (2H, t), 5.19 (1H, m), 7.02 (2H, d), 7.31 (2H, d), 7.42 (2H, d), 7.61 (2H, d), 7.73 (2H, d), 7.92 (1H, ddd, J = 8.6, J = 6.4, J = 2.2), 8.15 (2H, d), 8.25 (2H, d), 8.31 (2H, d)

^{13}C NMR (100 MHz, CDCl3) 16.2, 16.3, 20.8, 24.9, 28.2, 31.4, 31.5, 31.6, 31.7, 31.8 (x3), 34.1, 38.6, 70.3, 77.0 (alkyl chains, 20 required, 16 found); 116.2 (dd, J = 7.7, J = 3.8), 117.2, 123.0, 123.8, 124.0, 124.3, 127.5, 129.0, 129.4, 130.6, 130.8, 133.3, 133.4, 133.7, 134.2, 137.4 (dd, J = 10.8, J = 3.8), 149.2, 156.4, 156.6, 162.0, 162.2 (aromatic carbons, 22 required, 21 found); 163.5, 163.8, 165.6 (carbonyl carbons, 3 required, 3 found)

MS m/z 894 (M^+)

HPLC 88.6 %

Elemental analysis: $C_{53}H_{57}O_9F_3$ requires C 71.14 %, H 6.38 %; found C 71.37 %, H 6.64 %

3.3.3 Chiral Products

Scheme 23

(*S*)-1-Methylheptyl 3-benzyloxybenzoate (128)

Quantities: Compound 82 (8.50 g, 0.037 mol), compound 30 (5.00 g, 0.038 mol), DCC (8.61 g, 0.042 mol), DMAP (1.39 g, 0.011 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless oil.

Yield: 10.40 g (83 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.24 – 1.44 (11H, m, includes 3H, d), 1.62 (1H, m), 1.75 (1H, m), 5.11 (2H, s), 5.15 (1H, sext), 7.18 (1H, ddd, J = 7.9, J = 2.6, J = 1.3), 7.32 – 7.48 (6H, m), 7.65 – 7.68 (2H, m)

MS m/z 340 (M^+)

(*S*)-1-Methylheptyl 3-hydroxybenzoate (129)

Quantities: Compound 128 (10.40 g, 0.031 mol), 10% Pd/C (1.50 g), ethyl acetate (250 ml). The experimental procedure was as described in the preparation of compound 86, to yield a colourless oil.

Yield: 7.33 g (95 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 1.20 – 1.42 (11H, m, includes 3H, d), 1.60 (1H, m), 1.72 (1H, m), 5.15 (1H, sext), 6.78 (1H, s, broad), 7.09 (1H, ddd, J = 8.1, J = 2.5, J = 1.1), 7.31 (1H, dd, J = 8.1, J = 8.1), 7.60 (1H, ddd, J = 8.1, J = 2.5, J = 1.1), 7.67 (1H, dd, J = 2.5, J = 1.1)

MS m/z 250 (M^+)

(*S*)-1-Methylheptyl 3-[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]benzoate (130)

Quantities: Compound 10 (1.29 g, 0.0030 mol), compound 129 (0.77 g, 0.0031 mol), DCC (0.70 g, 0.0034 mol), DMAP (0.12 g, 0.0010 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, except 100% ethanol was used for recrystallisation, to yield colourless crystals.

Yield: 1.41 g (71 %)

Transitions (°C): Cr 48.0 SmC* 47.1 SmA* 52.5 I

$[\alpha]^{25}$: + 15.61 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 0.88 (3H, t), 1.22 – 1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.60 (1H, m), 1.73 (1H, m), 1.83 (2H, quint), 4.05 (2H, t), 5.15 (1H, sext), 6.99 (2H, d), 7.38 (2H, d), 7.42 (1H, ddd, *J* = 7.9, *J* = 2.1, *J* = 1.2), 7.52 (1H, dd, *J* = 7.9, *J* = 7.9), 7.87 (1H, dd, *J* = 2.1, *J* = 1.2), 7.98 (1H, ddd, *J* = 7.9, *J* = 1.2, *J* = 1.2), 8.16 (2H, d), 8.29 (2H, d)

^{13}C NMR (100 MHz, CDCl3), 14.0, 14.1, 20.0, 22.6, 22.7, 25.4, 26.0, 29.1 (x2), 29.3, 29.5, 29.6 (x3), 31.7, 31.9, 36.0, 68.4, 72.2 (Alkyl chains, 20 required, 19 found); 114.4, 120.9, 122.2, 122.8, 126.2, 126.5, 127.1, 129.4, 131.9, 132.4, 132.6, 150.8, 155.5, 163.8 (Aromatic carbons, 14 required, 14 found); 164.3 (x2), 165.2 (Carbonyl carbons, 3 required, 3 found)

MS m/z 682 (M^+ +1 + Na)

HPLC 99.5 %

Elemental analysis: $C_{41}H_{54}O_7$ requires C 74.77 %, H 8.21 %; found C 75.01 %, H 8.46 %

(*S*)-1-Methylheptyl 3-(4'-dodecyloxybiphenyl-4-carbonyloxy)benzoate (131)

Quantities: Compound 125 (1.12 g, 0.0029 mol), compound 129 (0.74 g, 0.0030 mol), DCC (0.68 g, 0.0033 mol), DMAP (0.11 g, 0.00090 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 1.12 g (63 %)

Transitions (°C): Cr 44.8 SmC* 45.4 SmA* 55.2 I

$[\alpha]^{25}$: + 17.16 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 0.88 (3H, t), 1.22 – 1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.60 (1H, m), 1.72 (1H, m), 1.81 (2H, quint), 4.02 (2H, t), 5.17 (1H, sext), 7.01 (2H, 8.8), 7.43 (1H, ddd), 7.51 (1H, dd), 7.60 (2H, d), 7.70 (2H, d), 7.88 (1H, dd), 8.24 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (x2), 20.1, 22.6, 22.7, 25.4, 26.0, 29.1, 29.2, 29.4 (x2), 29.6 (x3), 29.7, 31.7, 31.9, 36.0, 68.1, 72.2 (Alkyl chains, 20 required, 20 found); 115.0, 122.9, 126.3, 126.6, 127.0, 127.1, 128.4, 129.4, 130.8, 131.9, 132.6, 146.2, 150.9, 159.6 (Aromatic carbons, 14 required, 14 found); 165.0, 165.3 (Carbonyl carbons, 2 required, 2 found)

MS m/z 615 ($M^+ + 1$)

HPLC 100 %

Elemental analysis: $C_{40}H_{54}O_5$ requires C 78.18 %, H 8.79 %; found C 78.20 %, H 9.04 %

Scheme 24

(*S*)-1-Methylheptyl 5-benzyloxy-2,3,4-trifluorobenzoate (132)

Quantities: Compound 48 (6.28 g, 0.022 mol), compound 30 (2.95 g, 0.023 mol), DCC (5.21 g, 0.025 mol), DMAP (0.84 g, 0.0069 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless oil.

Yield: 6.96 g (80 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.80 (3H, t), 1.20 – 1.40 (11H, m, includes 3H, d), 1.52 (1H, m), 1.64 (1H, m), 5.06 (2H, s), 5.06 (1H, sext), 7.24 – 7.38 (6H, m)

(*S*)-1-Methylheptyl 5-hydroxy-2,3,4-trifluorobenzoate (133)

Quantities: Compound 132 (6.96 g, 0.018 mol), 10% Pd/C (1.00 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 86, except that the product was not dried over phosphorus pentoxide, to yield a colourless solid.

Yield: 5.38 g (98 %)

Melting Point (°C): 49.1 – 53.6

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 1.22 – 1.42 (11H, m, includes 3H, d), 1.59 (1H, m), 1.70 (1H, m), 5.15 (1H, sext), 5.50 (1H, d, J = 2.7), 7.37 (1H, ddd, J = 8.6, J = 6.2, J = 2.5)

(*S*)-1-Methylheptyl 5-[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,3,4-trifluorobenzoate (134)

Quantities: Compound 10 (1.07 g, 0.0025 mol), compound 133 (0.79 g, 0.0026 mol), DCC (0.59 g, 0.0029 mol), DMAP (0.10 g, 0.00078 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield a colourless solid.

Yield: 0.81 g (46 %)

Transitions (°C): Cr 42.4 (SmC* 32.5) SmA* 58.5 I

$[\alpha]^{26}$: + 11.9 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 0.89 (3H, t), 1.22 – 1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.61 (1H, m), 1.72 (1H, m), 1.83 (2H, quint), 4.06 (2H, t), 5.17 (1H, sext), 6.98 (2H, d), 7.40 (2H, d), 7.67 (1H, ddd, J = 8.1, J = 6.5, J = 2.3), 8.15 (2H, d), 8.28 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.1, 14.2, 20.0, 22.6, 22.7, 25.3, 26.0, 29.1, 29.4, 29.6, 29.7, 31.7, 32.0, 68.5, 73.5 (Alkyl chains, 20 required, 15 found); 114.5, 120.1, 120.8, 122.4,

125.1, 132.2, 132.5, 156.1, 161.9 (Aromatic carbons, 14 required, 9 found); 163.0, 164.0, 164.3 (Carbonyl carbons, 3 required, 3 found)

MS m/z 712 (M^+)

HPLC 99.4 %

Elemental analysis: $C_{41}H_{51}O_7F_3$ requires C 69.07 %, H 7.23 %; found C 69.30 %, H 7.52 %

(*S*)-1-Methylheptyl 5-(4'-dodecyloxybiphenyl-4-carbonyloxy)-2,3,4-trifluorobenzoate (135)

Quantities: Compound 125 (1.14 g, 0.0030 mol), compound 133 (0.94 g, 0.0031 mol), DCC (0.70 g, 0.0034 mol), DMAP (0.11 g, 0.00093 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 84, except that only ethanol was used for the recrystallisation, to yield colourless crystals.

Yield: 1.39 g (69 %)

Transitions (°C): Cr 40.6 (SmC* 30.6) SmA* 64.2 I

$[\alpha]^{26}$: + 13.2 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (6H, 2 x t), 1.22 – 1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.61 (1H, m), 1.72 (1H, m), 1.82 (2H, quint), 4.02 (2H, t), 5.18 (1H, sext), 7.01 (2H, d), 7.60 (2H, d), 7.68 (1H, ddd, J = 7.7, 6.5, 2.6), 7.71 (2H, d), 8.22 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.0, 14.1, 19.9, 22.5, 22.7, 25.2, 26.0, 29.1, 29.2, 29.3, 29.4, 29.6 (x3), 29.7, 68.1, 73.4 (alkyl chains, 20 required, 17 found); 115.0, 115.9 (d), 120.1, 125.5, 126.7, 128.4, 131.0, 131.6, 134.8 (dd, J = 10.0, J = 3.8), 141.1 (J = ddd, J = 257.5, J = 16.9, J = 13.8), 145.6 (dd, J = 11.5, J = 3.1), 146.8 (ddd, J = 259.1, not possible to measure additional J values), 159.8 (aromatic carbons, 12 required, 12 found), 161.9, 163.6 (carbonyl carbons, 2 required, 2 found)

MS m/z 668 (M^+)

HPLC 99.8 %

Elemental analysis: $C_{40}H_{51}O_5F_3$ requires C 71.86 %, H 7.63 %; found C 72.15 %, H 7.90 %

Scheme 25

(*S*)-1-Methylheptyl 4-bromobenzoate (137)

Quantities: Compound 136 (6.42 g, 0.032 mol), compound 30 (4.24 g, 0.033 mol), DCC (7.48 g, 0.036 mol), DMAP (1.20 g, 0.0099 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless oil.

Yield: 9.16 g (92 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22 – 1.44 (11H, m, includes 3H, d), 1.61 (1H, m), 1.73 (1H, m), 5.15 (1H, sext), 7.58 (2H, d), 7.91 (2H, d)

(*S*)-1-Methylheptyl 3'-benzyloxybiphenyl-4-carbonyloxylate (138)

Quantities: Compound 137 (4.50 g, 0.014 mol), compound 42 (3.88 g, 0.017 mol), tetrakis(triphenylphosphine) palladium (0) (0.46 g, 0.0004 mol), sodium carbonate (1.80 g, 0.017 mol), DME (100 ml), water (20 ml). The experimental procedure was as described in the preparation of compound 16, with the exception of the recrystallisation, to yield a colourless oil.

Yield: 5.35 g (92 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.26 -1.52 (11H, m, includes 3H, d), 1.67 (1H, m), 1.79 (1H, m), 5.14 (2H, s), 5.21 (1H, sext), 7.03 (1H, ddd, J = 7.6, J = 2.3, J = 1.5), 7.22 – 7.28 (2H, m), 7.34 – 7.54 (6H, m), 7.67 (2H, d), 8.13 (2H, d)

(*S*)-1-Methylheptyl 3'-hydroxybiphenyl-4-carbonyloxylate (139)

Quantities: Compound 138 (5.35 g, 0.013 mol), 10% Pd/C (1.00 g), ethyl acetate (250 ml). The experimental procedure was as described in the preparation of compound 106, to yield a colourless oil. NMR analysis revealed an incomplete reaction, so the procedure was repeated, and then hydrogen applied at atmospheric pressure for 1 week. The crude product was then purified *via* column chromatography (silica gel, hexane with the introduction of DCM), to yield a colourless oil.

Yield: 2.46 g (58 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.45 (11H, m, includes 3H, d), 1.63 (1H, m), 1.75 (1H, m), 5.20 (1H, sext), 5.86 (1H, s, broad), 6.91 (1H, ddd, J = 7.4, J = 1.8, J = 1.1),

7.14 (1H, dd, J = 1.8, J = 1.8), 7.18 (1H, ddd, J = 7.4, J = 1.8, J = 1.1), 7.34 (1H, dd, J = 7.4, J = 7.4), 7.63 (2H, d), 8.10 (2H, d)

MS m/z 326 (M^+)

(*S*)-1-Methylheptyl 3'-(4'-dodecyloxybiphenyl-4-carbonyloxy)-4-carbonyloxylate (140)

Quantities: Compound 125 (1.00 g, 0.0026 mol), compound 139 (0.88 g, 0.0027 mol), DCC (0.61 g, 0.0030 mol), DMAP (0.10 g, 0.00081 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 1.04 g (58 %)

Transitions (°C): Cr 88.0 I

$[\alpha]^{25}$: + 18.94 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (6H, 2 x t), 1.22 – 1.42 (27H, m, includes 3H, d), 1.47 (2H, quint), 1.62 (1H, m), 1.74 (1H, m), 1.81 (2H, quint), 4.01 (2H, t), 5.17 (1H, sext), 7.01 (2H, d), 7.27 (1H, ddd), 7.48 – 7.54 (3H, m), 7.60 (2H, d), 7.67 (2H, d), 7.70 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (x2), 20.1, 22.6, 22.7, 25.4, 26.0, 29.2 (x2), 29.3, 29.4, 29.6 (x3), 29.7, 31.7, 31.9, 36.1, 68.1, 71.8 (Alkyl chains, 20 required, 20 found); 115.0, 120.7, 121.4, 124.8, 126.6, 127.1, 127.3, 128.4, 130.0, 130.1, 130.7, 131.9, 141.7, 144.3, 146.1, 151.5, 159.6 (Aromatic carbons, 18 required, 17 found); 165.I, 166.0 (Carbonyl carbons, 2 required, 2 found)

MS m/z 691 (M^+ + 1)

HPLC 100.0 %

Elemental analysis: $C_{46}H_{58}O_5$ requires C 79.95 %, H 8.48 %; found C 80.04 %, H 8.76 %

Scheme 26

(*S*)-1-Methylheptyl 5-benzyloxy-2,3,4-trifluorobiphenyl-4'-carbonyloxylate (141)

Quantities: Compound 137 (4.50 g, 0.014 mol), compound 46 (4.87 g, 0.017 mol), tetrakistriphenylphosphine palladium (0) (0.46 g, 0.0004 mol), sodium carbonate (1.80 g, 0.017 mol), DME (100 ml), water (20 ml). The experimental procedure was as described in the preparation of compound 16, with the exception of the recrystallisation, to yield a colourless oil.

Yield: 6.43 g (98 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.22 – 1.45 (11H, m, includes 3H, d), 1.65 (1H, m), 1.78 (1H, m), 5.19 (2H, s), 5.19 (1H, sext), 6.84 (1H, ddd, J = 8.7, J = 7.0, J = 2.8), 7.34 – 7.48 (5H, m), 7.52 (2H, dd = 8.7, J = 1.5), 8.13 (2H, d, J = 8.7)

(*S*)-1-Methylheptyl 5-hydroxy-2,3,4-trifluorobiphenyl-4'-carbonyloxylate (142)

Quantities: Compound 141 (6.43 g, 0.014 mol), 10% Pd/C (1.00 g), ethyl acetate (250 ml). The experimental procedure was as described in the preparation of compound 9, except that the product was recrystallised from a mixture of hexane / ethanol, 5:1, to yield colourless crystals.

Yield: 4.02 g (76 %)

Melting Point (°C): 93.3 – 97.4

^{1}H NMR (400 MHz, $CDCl_3$) 0.86 (3H, t), 1.22 – 1.42 (11H, m, includes 3H, d), 1.65 (1H, m), 1.75 (1H, m), 5.19 (1H, sext), 5.52 (1H, d, J = 3.0), 6.88 (1H, ddd, J = 8.9, J = 6.7, J = 2.4), 7.55 (2H, dd, J = 8.6, J = 1.5), 8.11 (2H, d, J = 8.6)

MS m/z 380 (M^+)

(*S*)-1-Methylheptyl 5-(4'-dodecyloxybiphenyl-4-carbonyloxy)-2,3,4-trifluorobiphenyl-4'-carbonyloxylate (143)

Quantities: Compound 125 (0.92 g, 0.0024 mol), compound 142 (0.93 g, 0.0025 mol), DCC (0.57 g, 0.0028 mol), DMAP (0.09 g, 0.00075 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 1.12 g (63 %)

Transitions (°C): Cr 48.7 (SmC* 28.9 SmA* 31.9) I

$[\alpha]^{26}$: + 18.40 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (6H, 2 x t), 1.23 – 1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.62 (1H, m), 1.74 (1H, m), 1.82 (2H, quint), 4.02 (2H, t), 5.18 (1H, sext), 7.01 (2H, d), 7.19 (1H, ddd, J = 7.2, J = 7.2, J = 1.9), 7.60 (2H, d), 7.72 (2H, d), 8.13 (2H, d), 8.24 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (x2), 20.1, 22.6, 22.7, 25.4, 26.0, 29.1, 29.2, 29.3, 29.4, 29.6 (x3), 29.7, 31.7, 31.9, 68.2, 72.1 (alkyl carbon, 20 required, 19 found); 115.0, 118.2, 124.6 (dd, J = 11.5, J = 3.8), 125.7, 126.7, 128.4, 128.8 (x2), 129.9, 130.9, 131.0, 131.6, 135.3 (dd, J = 9.2, J = 3.8), 137.5, 141.5 (ddd, J = 265.4), 146.7, 159.7 (aromatic carbons, 18 required, 17 found); 163.8, 165.7 (carbonyl carbons, 2 required, 2 found)

MS m/z 714 (M^+)

HPLC 100.0 %

Elemental analysis: $C_{46}H_{55}O_5F_3$ requires C 74.15 %, H 7.46 %; found C 74.41 %, H 7.76 %

(*S*)-1-Methylheptyl 5-[4-(4-dodecyloxyphenylcarbonyloxy)phenylcarbonyloxy]-2,3,4-trifluorobiphenyl-4'-carbonyloxylate (144)

Quantities: Compound **10** (0.97 g, 0.00023 mol), compound **142** (0.89 g, 0.0023 mol), DCC (0.52 g, 0.0025 mol), DMAP (0.08 g, 0.00069 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound **84**, except that only ethanol was used for the recrystallisation, to yield colourless crystals.

Yield: 1.23 g (68 %)

Transitions (°C): Cr 79.5 I

$[\alpha]^{26}$: + 15.55 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.80 (3H, t), 0.81 (3H, t), 1.14 – 1.34 (27H, m, includes 3H, d), 1.40 (2H, quint), 1.55 (1H, m), 1.68 (1H, m), 1.76 (2H, quint), 3.98 (2H, t), 5.11 (1H, sext), 6.91 (2H, d), 7.10 (1H, ddd, J = 6.9, J = 6.9, J = 2.2), 7.32 (2H, d), 7.52 (2H, dd, J = 8.8, J = 1.1), 8.05 (2H, d), 8.08 (2H, d), 8.21 (2H, d)

MS m/z 788 (M^+)

HPLC 100 %

Elemental analysis: $C_{47}H_{55}O_7F_3$ requires C 71.54 %, H 7.04 %; found C 71.62 %, H 7.28 %

Scheme 27

Ethyl 4''-dodecyloxy-[1,1':4',1'']-terphenyl-3-carboxylate (146)

Quantities: Compound 145 (1.31 g, 0.0057 mol), compound 13 (2.73 g, 0.0071 mol), tetrakis(triphenylphosphine) palladium(0) (0.18 g, 0.00017 mol), sodium carbonate (0.75 g, 0.071 mol), DME (100 ml), water (20 ml). The experimental procedure was as described in the preparation of compound 141, to yield a colourless solid.

Yield: 1.72 g (62 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.22 – 1.45 (16H, m), 1.45 (3H, t), 1.48 (2H, quint), 1.83 (2H, quint), 4.02 (2H, t), 4.43 (2H, quart), 7.01 (2H, d), 7.54 (1H, dd, J = 7.6, J = 7.6), 7.58 (2H, d), 7.67 (2H, d), 7.70 (2H, d), 7.84 (1H, ddd, J = 7.4, J = 1.2, J = 1.2), 8.04 (1H, ddd, J = 7.4, J = 1.2, J = 1.2), 8.34 (1H, dd, J = 1.2, J = 1.2)

4''-Dodecyloxy-3-[1,1':4',1'']-terphenylcarboxylic acid (147)

Compound 146 (1.72 g, 0.0035 mol), potassium hydroxide (0.40 g, 0.0071 mol), ethanol (100 ml) and water (20 ml) were heated under reflux overnight. 10% HCl (50 ml) was then added to form a colourless precipitate. The reaction mixture was poured onto crushed ice, the precipitate filtered off and dried in vacuo to yield colourless crystals.

Yield: 1.41 g (88 %)

Melting Point: 223.9 – 232.8 °C

^{1}H NMR (400 MHz, DMSO-D6)[b] 0.87 (3H, t), 1.22 – 1.39 (16H, m), 1.44 (2H, quint), 1.75 (2H, quint), 4.03 (2H, t), 7.04 (2H, d), 7.51 (1H, dd, J = 7.4, J = 7.4), 7.67 (2H, d), 7.72 – 7.76 (4H, m), 7.81 (1H, ddd, J = 7.4), 7.90 (1H, ddd, J = 7.4), 8.21 (1H, dd)

MS m/z 458 (M^+)

[b] NMR analysis of compound 147 proved problematic due to solubility issues. Therefore it was not possible to measure all relevant coupling constants.

(*S*)-1-Methylheptyl 4-(3-carbonyloxy-4''-dodecyloxy-[1,1':4',I'']-terphenyl)benzoate (148)

Quantities: Compound 147 (1.20 g, 0.0026 mol), compound 34 (0.67 g, 0.0027 mol), DCC (0.61 g, 0.0030 mol), DMAP (0.01 g, 0.10 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.42 g (24 %)

Transitions (°C): Cr 109.8 I

$[\alpha]^{26}$: + 15.23 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (6H, 2 x t), 1.14 – 1.34 (27H, m, includes 3H, d), 1.41 (2H, quint), 1.56 (1H, m), 1.67 (1H, m), 1.74 (2H, quint), 3.94 (2H, t), 5.10 (1H, sext), 6.92 (2H, d), 7.25 (2H, d), 7.50 (2H, d), 7.54 (1H, dd, J = 7.6, J = 7.6), 7.60 (2H, d), 7.65 (2H, d), 7.85 (1H, ddd, J = 7.6, J = 1.9, J = 1.2), 8.07 (2H, J = 8.8), 8.11 (1H, ddd, J = 7.6, J = 1.9, J = 1.2), 8.40 (1H, dd, J = I.9, J = 1.9)

^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (x2), 20.1, 22.6, 22.7, 25.4, 26.1, 29.2, 29.4 (x3), 29.6, 31.8, 32.0, 36.1, 68.2, 72.0 (Alkyl chains, 20 required, 17 found); 114.9, 121.8, 127.2, 127.5, 128.1, 128.7, 129.0, 129.2, 129.7, 131.2, 132.3, 132.8, 137.4, 138.0, 140.6, 141.5, 154.4, 159.0 (Aromatic carbons, 18 required, 18 found); 164.8, 165.5 (Carbonyl carbons, 2 required, 2 found)

MS m/z 691 (M^+ + 1)

HPLC 100.0 %

Elemental analysis: $C_{46}H_{58}O_5$ requires C 79.95 %, H 8.48 %; found C 80.16 %, H 8.77 %

Scheme 28

4''-Dodecyloxy-2,3,4-trifluoro-5-[1,1':4',1'']-terphenylcarboxylic acid (149)

Quantities: Compound 80 (2.82 g, 0.010 mol), compound 13 (4.75 g, 0.012 mol), tetrakis(triphenylphosphine) palladium(0) (0.32 g, 0.00030 mol), sodium carbonate (1.27 g, 0.012 mol), DME (150 ml), water (50 ml). The experimental procedure was as described in the preparation of compound 141. However, when the $MgSO_4$ was removed, TLC analysis revealed no product in the ethereal extract. It was determined using a UV lamp that the product was present in the filtered solid. The $MgSO_4$ was then stirred in ethyl acetate and water overnight. 10% HCl (200 ml) was then added and the mixture stirred for 2 hours. The ethyl acetate layer was then taken and the solvent removed *in vacuo* to yield an-off-white sold, which was recrystallised from ethanol and dried *in vacuo* over phosphorus pentoxide, to yield colourless crystals. NMR analysis revealed that the ester linkage of the starting material (compound 80) had been hydrolysed during the reaction, and the resulting product was the unprotected carboxylic acid (compound 149).

Yield: 1.88 g (37 %)

Melting Point: 210.5 – 216.8 °C

^{1}H NMR (400 MHz, $CDCl_3$, plus few drops DMSO-D6) 0.73 (3H, t), 1.06 – 1.26 (16H, m), 1.33 (2H, quint), 1.66 (2H, quint), 3.86 (2H, t), 6.84 (2H, d), 7.38 – 7.42 (4H, m), 7.51 (2H, d), 7.77 (1H, ddd, J = 7.1, J = 7.1, J = 2.0), OH proton not revealed

MS m/z 512 (M^+)

(*S*)-1-Methylheptyl 4-(5-carbonyloxy-4''-dodecyloxy-2,3,4-trifluoro-[1,1':4',1'']-terphenyl)benzoate (150)

Quantities: Compound 149 (0.96 g, 0.0019 mol), compound 34 (0.48 g, 0.0019 mol), DCC (0.43 g, 0.0021 mol), DMAP (0.10 g, 0.00057 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.87 g (62 %)

Transitions (°C): Cr 84.6 I

$[\alpha]^{26}$: + 13.55 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.81 (6H, 2 x t), 1.15 – 1.33 (27H, m, includes 3H, d), 1.41 (2H, quint), 1.56 (1H, m), 1.67 (1H, m), 1.74 (1H, m), 3.94 (2H, t), 5.09 (1H, sext), 6.92 (2H, d),

7.25 (2H, d), 7.49 (2H, d), 7.53 (2H, dd, J = 8.9, J = 1.5), 7.61 (2H, d), 7.97 (1H, ddd, J = 7.6, J = 7.6, J = 2.2), 8.07 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.0, 14.1, 20.0, 22.6, 22.7, 25.4, 26.0, 29.1, 29.2, 29.3, 29.4, 29.6 (x4), 31.7, 31.9, 36.0, 68.0, 72.0 (alkyl chains, 20 required, 20 found); 114.8, 121.4, 126.5 (dd, J = 10.8, J = 3.8), 127.0, 128.0, 129.0, 129.1, 129.2, 130.8, 131.2, 132.2, 140.9, (ddd, J = 253.7, J = 15.4, J = 15.4), 141.4, 150.8 (ddd, J = 266.7, J = 11.5, J = 3.1), 152.2 (ddd, J = 258.3, J = 10.8, J = 2.3), 153.7, 159.1, 160.8 (aromatic carbons, 18 required, 18 found); 165.2 (carbonyl carbons, 1 required, 1 found)

MS m/z 745 (M^+ + 1)

HPLC 100.0 %

Elemental analysis: $C_{46}H_{55}O_5F_3$ requires C 74.15 %, H 7.46 %; found C 74.42 %, H 7.70 %

Scheme 29

(*S*)-1-Methylheptyl 3-(4-benzyloxyphenylcarbonyloxy)benzoate (151)

Quantities: Compound **19** (2.87 g, 0.013 mol), compound **129** (3.00 g, 0.012 mol), DCC (2.72 g, 0.013 mol), DMAP (0.44 g, 0.0036 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound **7**, to yield a colourless oil.

Yield: 5.18 g (92 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 1.22 – 1.42 (11H, m, includes 3H, d), 1.61 (1H, m), 1.72 (1H, m), 5.15 (3H, s + sext), 7.07 (2H, d), 7.33 – 7.48 (6H, m), 7.49 (1H, dd, J = 7.7, J = 7.7), 7.85 (1H, dd, J = 1.7, J = 1.7), 7.95 (1H, ddd, J = 7.7, J = 1.7, J = 1.7), 8.17 (2H, d)

(*S*)-1-Methylheptyl 3-(4-hydroxyphenylcarbonyloxy)benzoate (152)

Quantities: Compound **151** (5.18 g, 0.011 mol), 10% Pd/C (2 g), ethanol (300 ml). The experimental procedure was as described in the preparation of compound **86**, to yield a colourless solid.

Yield: 3.54 g (87 %)

Melting Point (°C): 73.1-74.7

^{1}H NMR (400 MHz, $CDCl_3$) 0.84 (3H, t), 1.22 – 1.42 (11H, includes 3H, d), 1.59 (1H, m), 1.71 (1H, m), 5.15 (1H, sext), 6.47 (1H, s, broad), 6.92 (2H, d), 7.40 (1H, ddd, J = 7.8, J = 2.6, J = 1.8), 7.50 (1H, dd, J = 7.8, J = 7.8), 7.85 (1H, dd, J = 1.8, J = 1.8), 7.96 (1H, ddd, J = 7.8, J = 1.8, J = 1.8), 8.10 (2H, d)

MS m/z 370 (M^+)

(*S*)-1-Methylheptyl 3-[4-(4'-dodecyloxybiphenyl-4-carbonyloxy)phenylcarbonyloxy]benzoate (153)

Quantities: Compound **125** (1.30 g, 0.0034 mol), compound **152** (1.50 g, 0.0041 mol), DCC (0.77 g, 0.0037 mol), DMAP (0.15 g, 0.0012 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound **84** to yield colourless crystals.

Yield: 1.20 g (48 %)

Transitions (°C): Cr 37.9 SmC^*_{ferro} 143.5 SmA^*_{hel} 156.5 I

$[\alpha]^{25}$: + 15.05 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (6H, 2 x t), 1.22-1.40 (27H, m, includes 3H, d), 1.47 (2H, quint), 1.60 (1H, m), 1.74 (1H, m), 1.81 (2H, quint), 4.00 (2H, t), 5.17 (1H, sext), 7.00 (2H, d), 7.39 (2H, d), 7.43 (1H, ddd, J = 7.9, J = 1.8, J = 1.2), 7.50 (1H, dd, J = 7.9, J = 7.9), 7.59 (2H, d), 7.70 (2H, d), 7.89 (1H, dd, J = 1.8, J = 1.2), 7.98 (1H, ddd, J = 7.9, J = 1.2, J = 1.2), 8.24 (2H, d), 8.30 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.0, 14.1, 20.0, 22.6, 22.7, 25.4, 26.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6 (x3), 31.7, 31.9, 36.0, 68.1, 72.2 (alkyl chains, 20 required, 20 found); 114.9, 122.1, 122.8, 126.2, 126.6, 126.7, 126.8, 127.1, 128.3, 129.4, 130.8, 131.7, 131.9, 132.6, 146.3, 150.7, 155.4, 159.6 (aromatic carbons, 18 required, 18 found); 164.2, 164.4, 165.2 (carbonyl carbons, 3 required, 3 found)

MS m/z 734 (M^+)

HPLC 100 %

Elemental analysis: $C_{47}H_{58}O_7$ requires C 76.81 %, H 7.95 %; found C 76.74 %, H 7.91 %

Scheme 30

(*S*)-1-Methylheptyl 5-(4-benzyloxyphenylcarbonyloxy)-2,3,4-trifluorobenzoate (154)

Quantities: Compound 19 (1.46 g, 0.0064 mol), compound 133 (2.00 g, 0.0066 mol), DCC (1.50 g, 0.0073 mol), DMAP (0.24 g, 0.0020 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7 to yield a colourless oil.

Yield: 2.96 g (90 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22-1.44 (11H, m), 1.60 (1H, m), 1.72 (1H, m), 5.16 (1H, sext), 5.17 (2H, s), 7.08 (2H, d), 7.33-7.47 (5H, m), 7.65 (1H, ddd, J = 7.8, J = 5.9, J = 2.0), 8.14 (2H, d)

(*S*)-1-Methylheptyl 2,3,4-trifluoro-5-(4-hydroxyphenylcarbonyloxy)benzoate (155)

Quantities: Compound 154 (2.81 g, 0.0055 mol), 10% Pd/C (0.50 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 24, except that the product was purified *via* column chromatography (silica gel, DCM / Hexane, 1:1), to yield a colourless solid.

Yield: 2.07 g (89 %)

Melting Point: 96.0 – 103.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 1.23-1.42 (11H, m, includes 3H, d), 1.61 (1H, m), 1.73 (1H, m), 5.17 (1H, sext), 6.11 (1H, s, broad), 6.94 (2H, d), 7.65 (1H, ddd, J = 8.1, J = 6.6, J = 2.6), 8.10 (2H, d)

MS m/z 424 (M^+)

(*S*)-1-Methylheptyl 5-[4-(4'-dodecyloxy-4-carbonyloxybiphenyl)phenylcarbonyloxy]-2,3,4-trifluorobenzoate (156)

Quantities: Compound 125 (0.97 g, 0.0025 mol), compound 155 (1.09 g, 0.0026 mol), DCC (0.59 g, 0.0029 mol), DMAP (0.10 g, 0.00078 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 84 to yield colourless crystals.

Yield: 0.81 g (41 %)

Transitions (°C): Cr 70.0 SmC* 137.9 SmA* 165.3 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (6H, 2 x t), 1.22-1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.61 (1H, m), 1.73 (1H, m), 1.82 (2H, quint), 4.02 (2H, t), 5.17 (1H, sext), 7.01 (2H,

d), 7.43 (2H, d), 7.61 (2H, d), 7.68 (1H, ddd, J = 7.9, J = 6.4, J = 2.4), 7.72 (2H, d), 8.25 (2H, d), 8.29 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 17.6 (x2), 23.4, 26.1, 26.2, 28.8, 29.6, 32.6, 32.8, 32.9 (x2), 33.1 (x2), 33.2 (x2), 35.2, 35.4, 39.4, 71.7, 77.0 (alkyl chains, 20 required, 20 found); 118.5, 119.4 (ddd, J = 8.5, J = 3.8), 123.5, 125.9, 128.7, 130.2 (x2), 131.9, 134.4, 135.2, 135.7, 138.2 (dd, J = 10.8, J = 3.8), 144.5 (ddd, J = 253.7, J = 16.9, J = 13.1), 149.6, 150.1, 153.0 (ddd, J = 261.4, J = 11.5, J = 2.3), 159.4, 163.2 (aromatic carbons, 18 required, 18 found), 165.4, 166.4, 167.9 (carbonyl carbons, 3 required, 3 found)

MS m/z 788 (M^+)

HPLC 98.3 %

Elemental analysis: $C_{47}H_{55}O_7F_3$ requires C 71.57 %, H 6.98 %; found C 71.79 %, H 7.09 %

Scheme 31

(*S*)-1-Methylheptyl 4-(3-benzyloxyphenylcarbonyloxy)benzoate (157)

Quantities: Compound 82 (0.91 g, 0.0040 mol), compound 34 (0.95 g, 0.0038 mol), DCC (0.86 g, 0.0042 mol), DMAP (0.14 g, 0.0011 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 7 to yield a colourless oil.

Yield: 1.74 g (99 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.22-1.45 (11H, m, includes 3H, d), 1.61 (1H, m), 1.74 (1H, m), 5.14 (2H, s), 5.16 (1H, sext), 7.26 (1H, ddd), 7.28 (2H, d), 7.32-7.48 (6H, m), 7.81 (1H, ddd), 7.81 (1H, dd), 8.14 (2H, d)

(*S*)-1-Methylheptyl 4-(3-hydroxyphenylcarbonyloxy)benzoate (158)

Quantities: Compound 157 (1.74 g, 0.0038 mol), 10% Pd/C (0.80 g), THF (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless oil.

Yield: 1.50 g (100 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.85 (3H, t), 1.20-1.42 (11H, m, includes 3H, d), 1.60 (1H, m), 1.71 (1H, m), 5.11 (1H, sext), 6.73 (1H, s, broad), 7.06 (1H, ddd), 7.19 (2H, d), 7.29 (1H, dd), 7.59 (1H, dd), 7.68 (1H, ddd), 8.06 (2H, d)

(*S*)-1-Methylheptyl 4-[3-(4'-dodecyloxy-4-carbonyloxybiphenyl)phenylcarbonyloxy]benzoate (159)

Quantities: Compound 125 (1.32 g, 0.0034 mol), compound 158 (1.50 g, 0.0041 mol), DCC (0.78 g, 0.0038 mol), DMAP (0.13 g, 0.0010 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.63 g (25 %)

Transitions (°C): Cr 81.5 I

$[\alpha]^{25}$: + 14.03 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (6H, 2 x t), 1.22-1.42 (33H, m, includes 3H, d), 1.47 (2H, quint), 1.61 (1H, m), 1.74 (1H, m), 1.82 (2H, quint), 4.03 (2H, t), 5.17 (1H, sext), 7.01 (2H, d), 7.30 (2H, d), 7.55 (1H, ddd), 7.61 (3H, d + dd), 7.72 (2H, d), 8.08 (1H, dd), 8.14 (3H, d + ddd), 8.25 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (x2), 20.1, 22.6, 22.7, 25.4, 26.1, 29.2 (x2), 29.4 (x2), 29.6 (x3), 29.7, 31.7, 31.9, 36.1, 68.2, 72.0 (alkyl chains, 20 required, 20 found); 115.0, 121.6, 123.7, 126.7, 126.9, 127.5, 127.7, 128.4, 128.7, 129.8, 130.7, 130.8, 131.2, 131.8, 146.3, 151.2, 154.3, 159.7 (aromatic carbons, 18 required, 18 found); 163.8, 164.9, 165.4 (carbonyl carbons, 3 required, 3 found)

MS m/z 735 ($M^+ + 1$)

HPLC 98.9 %

Elemental analysis: $C_{47}H_{58}O_7$ requires C 76.84 %, H 7.90 %; found C 77.05 %, H 8.17 %

Scheme 32

(*S*)-1-Methylheptyl 4-[4-(4'-dodecyloxybiphenyl-3-carbonyloxy)phenylcarbonyloxy]benzoate (160)

Quantities: Compound 17 (1.66 g, 0.0044 mol), compound 38 (1.77 g, 0.0048 mol), DCC (1.10 g, 0.0053 mol), DMAP (0.20 g, 0.0016 mol), DCM (150 ml). The experimental procedure was as described in the preparation of compound 84, except that a mixture of acetonitrile / ethyl acetate (10:1) was used for the recrystallisation, to yield colourless crystals.

Yield: 1.78 g (55 %)

Transitions (°C): Cr 85.0 I (recryst. 60)

$[\alpha]^{25}$: + 17.08 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.91 (6H, 2 x t), 1.22-1.42 (27H, m, includes 3H, d), 1.49 (2H, quint), 1.63 (1H, m), 1.76 (1H, m), 1.83 (2H, quint), 4.03 (2H, t), 5.19 (1H, sext), 7.03 (2H, d), 7.33 (2H, d), 7.44 (2H, d), 7.60 (1H, dd), 7.61 (2H, d), 7.86 (1H, ddd), 8.16 (3H, d + ddd), 8.33 (2H, d), 8.42 (1H, dd)

^{13}C NMR (100 MHz, $CDCl_3$) 14.0, 14.1, 20.0, 22.6, 22.7, 25.4, 26.0, 29.1, 29.2, 29.3, 29.4, 29.6 (x4), 31.7, 31.9, 36.0, 68.1, 71.9 (alkyl chains, 20 required, 20 found); 114.9, 121.6, 122.1, 126.7, 128.1, 128.3 (x2), 128.6, 129.1, 129.4, 131.1, 131.9, 132.0, 141.5, 154.3, 155.3, 159.2 (aromatic carbons, 18 required, 17 found); 163.9, 164.6, 165.4 (carbonyl carbons, 3 reuired, 3 found)

MS m/z 735 (M^+ + 1)

HPLC 98.9 %

Elemental analysis: $C_{47}H_{58}O_7$ requires C 76.84 %, H 7.90 %; found C 77.12 %, H 8.19 %

Scheme 33

(*S*)-1-Methylheptyl 4-[4-(5-benzyloxy-2,3,4-trifluorophenylcarbonyloxy)phenylcarbonyloxy]benzoate (161)

Quantities: Compound 48 (0.97 g, 0.0034 mol), compound 38 (1.30 g, 0.0035 mol), DCC (0.79 g, 0.0039 mol), DMAP (0.13 g, 0.0011 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 1.34 g (62 %)

Melting Point (°C): 96.5 – 104.3

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.24-1.45 (11H, m, includes 3H, d), 1.62 (1H, m), 1.74 (1H, m), 5.15 (1H, sext), 5.20 (2H, s), 7.31 (2H, d), 7.35-7.47 (7H, m), 7.52 (1H, ddd, J = 8.4, J = 6.1, J = 2.2), 8.13 (2H, d), 8.30 (2H, d)

MS m/z 634 (M^+)

(±)-1-Methylheptyl 4-[4-(5-benzyloxy-2,3,4-trifluorophenylcarbonyloxy)phenylcarbonyloxy]benzoate (162)

Quantities: Compound 48 (1.70 g, 0.0060 mol), compound 39 (2.34 g, 0.0063 mol), DCC (1.43 g, 0.0069 mol), DMAP (0.23 g, 0.0019 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 7, to yield a colourless solid.

Yield: 1.02 g (26 %)

Melting Point (°C): 87.8 – 89.9

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.25-1.44 (11H, includes 3H, d), 1.62 (1H, m), 1.74 (1H, m), 5.17 (1H, sext), 5.21 (2H, s), 7.32 (2H, d), 7.36-7.48 (7H, m), 7.53 (1H, ddd, J = 8.4, J = 6.1, J = 2.4), 8.14 (2H, d), 8.31 (2H, d)

MS m/z 634 (M^+)

(*S*)-1-Methylheptyl 4-[4-(2,3,4-trifluoro-5-hydroxyphenylcarbonyloxy)phenylcarbonyloxy]benzoate (163)

Quantities: Compound 161 (1.34 g, 0.0021 mol), 10% Pd/C (0.50 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless solid.

Yield: 1.07 g (94 %)

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.24-1.45 (11H, m, includes 3H, d), 1.63 (1H, m), 1.74 (1H, m), 5.16 (1H, sext), 6.06 (1H, s, broad), 7.28 (2H, d), 7.39 (2H, d), 7.57 (1H, ddd, J = 8.8, J = 6.2, J = 2.4), 8.13 (2H, d), 8.29 (2H, d)

MS m/z 544 (M^+)

(±)-1-Methylheptyl 4-[4-(2,3,4-trifluoro-5-hydroxyphenylcarbonyloxy)phenylcarbonyloxy]benzoate (164)

Quantities: Compound 162 (1.00 g, 0.0015 mol), 10% Pd/C (0.20 g), ethyl acetate (200 ml). The experimental procedure was as described in the preparation of compound 24, to yield a colourless solid.

Yield: 0.81 g (96 %)

Melting Point (°C): 119.4 – 125.1

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.24-1.46 (11H, m, includes 3H, d), 1.64 (1H, m), 1.76 (1H, m), 5.17 (1H, sext), 5.79 (1H, s, broad), 7.29 (2H, d), 7.40 (2H, d), 7.58 (1H, ddd, J = 8.8, J = 6.0, J = 2.3), 8.14 (2H, d), 8.30 (2H, d)

MS m/z 562 (M^+)

(*S*)-1-Methylheptyl 4-{4-[5-(4'-dodecyloxybiphenyl-4-carbonyloxy)-2,3,4-trifluorophenylcarbonyloxy]phenylcarbonyloxy}benzoate (165)

Quantities: Compound 125 (0.34 g, 0.00090 mol), compound 163 (0.50 g, 0.00092 mol), DCC (0.21 g, 0.0010 mol), DMAP (0.03 g, 0.00028 mol), DCM (100 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.35 g (43 %)

Transitions (°C): Cr 92.2 SmC* 103.8 I

$[\alpha]^{25}$: + 13.33 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (6H, 2 x t), 1.22-1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.62 (1H, m), 1.74 (1H, m), 1.82 (2H, quint), 4.02 (2H, t), 5.16 (1H, sext), 7.01 (2H, d), 7.30 (2H, d), 7.41 (2H, d), 7.60 (2H, d), 7.72 (2H, d), 7.91 (1H, ddd, J = 7.7, J = 6.4, J = 2.2), 8.13 (2H, d), 8.23 (2H, d), 8.30 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.0, 14.1, 20.1, 22.6, 22.7, 25.4, 26.0, 29.1, 29.2, 29.3, 29.4, 29.6 (x4), 31.7, 31.9, 36.0, 68.1, 72.0 (alkyl chains, 20 required, 20 found); 114.0 (dd, J = 7.7, J = 3.1), 115.0, 120.8, 121.6, 121.9, 125.3, 126.8, 127.2, 128.4, 128.7, 131.1, 131.2,

131.5, 132.0, 135.2 (dd, J = 10.0, J = 3.8), 146.9, 154.2, 154.4, 159.8, 160.0 (aromatic carbons, 22 required, 20 found); 163.5, 163.7, 165.4 (carbonyl carbons, 3 requird, 3 found)

MS m/z 908 (M^+)

HPLC 100 %

Elemental analysis: $C_{54}H_{59}O_9F_3$ requires C 71.37 %, H 6.50 %; found C 71.44 %, H 6.73 %

(±)-1-Methylheptyl 4-{4-[5-(4'-dodecyloxybiphenyl-4-carbonyloxy)-2,3,4-trifluorophenylcarbonyloxy]phenylcarbonyloxy}benzoate (166)

Quantities: Compound 125 (0.51 g, 0.0013 mol), compound 164 (0.79 g, 0.0014 mol), DCC (0.32 g, 0.0015 mol), DMAP (0.05 g, 0.00042 mol), DCM (200 ml). The experimental procedure was as described in the preparation of compound 84, to yield colourless crystals.

Yield: 0.69 g (57 %)

Transitions (°C): Cr 75.9 SmC* 103.5 I

$[\alpha]^{25}$: + 0 °

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (6H, 2 x t), 1.22-1.42 (27H, m, includes 3H, d), 1.48 (2H, quint), 1.62 (1H, m), 1.74 (1H, m), 1.82 (2H, quint), 4.02 (2H, t), 5.15 (1H, sext), 7.01 (2H, d), 7.29 (2H, d), 7.41 (2H, d), 7.60 (2H, d), 7.72 (2H, d), 7.90 (1H, ddd, J = 8.1, J = 5.5, J = 2.2), 8.13 (2H, d), 8.24 (2H, d), 8.30 (2H, d)

^{13}C NMR (100 MHz, $CDCl_3$) 14.0, 14.1, 20.0, 22.6, 22.7, 25.4, 26.0, 29.1, 29.2, 29.3, 29.4, 29.6 (x4), 31.7, 31.9, 36.0, 68.1, 71.9 (alkyl chains, 20 required, 20 found); 114.0 (dd, J = 6.9, J = 3.8), 115.0, 120.8, 121.6, 121.8, 125.2, 126.7, 127.2, 128.4, 128.7, 131.1 (x2), 131.5, 132.0, 135.2 (dd, J = 10.8, J = 3.1), 141.4 (ddd, J = 262.9, J = 13.5, J = 15.4), 146.9, 147.9 (ddd, J = 263.7, J = 13.1, J = 2.3), 149.9 (ddd, J = 265.2, J = 11.5, J = 2.3), 154.2, 154.4, 159.8, 160.0, 163.5, 163.7, 165.4 (aromatic carbons + carbonyl carbons, 26 required, 26 found)

MS m/z 908 (M^+)

HPLC 100 %

Elemental analysis: $C_{54}H_{59}O_9F_3$ requires C 71.38 %, H 6.49 %; found C 71.51 %, H 6.78 %

4. Experimental Discussion

The synthetic schemes and experimental section can be broadly broken into two parts, each of which can then be further sub-categorised:

1) Synthesis of intermediate compounds
   a) 'Arms' of the resultant final products (Schemes 1 – 5)
   b) The 'bent-core' of the resultant final products (Schemes 6 – 13)

2) Use of intermediate compounds to synthesise desired final products
   a) Achiral Products (Schemes 14 – 22)
   b) Chiral Products (Schemes 23 – 33)

Due to many of the final products being comprised of multi-ester moieties, it was necessary to employ extensive use of reaction procedures such as benzyl-protection / de-protection and esterification. This section will therefore not discuss in detail every reaction step, but will provide an overview of the experimental work carried out, highlighting appropriate interesting / unusual results and observations.

4.1 Required Intermediate Compounds

Scheme 1 shows the synthesis of the two-ring carboxylic acids (compounds 9 and 10). 4-Hydroxybenzoic acid (1) is *O*-alkylated with the appropriate 1-bromoalkane (2 and 3) to yield the 4-alkoxybenzoic acids 4 and 5. During the reaction, sodium hydroxide abstracts the acidic proton (of the carboxylic acid group), in addition to the phenolic proton, resulting in the formation of the corresponding alkyl-ester. A saponification step is then required in order to reform the carboxylic acid. Particularly in the case of the dodecyl compound (5), initial saponification did not result in complete hydrolysis of the ester (as shown in the NMR spectrum) possibly as a result of solubility problems. Therefore a second saponification step was carried out, this time using potassium hydroxide, providing an excellent yield (>80 %). Esterification with compound 6 using the DCC / DMAP esterification method developed by Steglich[99] yielded the benzyl-protected, alkyloxy 2-ring esters (7 and 8), again in excellent yields. The benzyl protecting group was then removed *via* hydrogenolysis using 10% palladium on carbon as catalyst, affording the carboxylic acids 9 and 10, which were used in further esterification reactions to add to appropriate phenolic bent-cores. Ethanol and ethyl acetate are common solvents to be used for hydrogenolysis, but in this instance the product is sparingly soluble and therefore the better solvent THF was employed.

Scheme 2 again begins with an *O*-alkylation, but this time with the more familiar conditions of potassium carbonate in butanone (Williamson ether synthesis[100]) to give the dodecyloxy-bromo-biphenyl (12). In order to generate the boronic acid (13) from the bromo-compound (12), it would be possible to use two methods, a Grignard reaction using magnesium, or a lithiation using *n*-butylithium (*n*-BuLi). However, treating compound 12 with *n*-BuLi requires low temperature (–78 °C) to prevent addition of a butyl chain and therefore it was decided that a Grignard reaction should be employed to prevent problems with solubility at the lower temperature. Although Grignard reactions themselves can sometimes be problematic with regard to initiating the reaction and possible dimerisation through homocoupling, a moderate yield of the boronic acid 13 was obtained.

Scheme 3 is slightly different to other 'intermediate' schemes, as the product (compound 17) represents an 'arm' of a target molecule, combined with the bent-core, due to the incorporation of the carboxylic acid group at the 3-position of the biphenyl unit. The Suzuki cross-coupling reaction is an extremely common tool in synthetic chemistry, particularly in the liquid crystal field, due to the common presence of biphenyl and terphenyl moieties within liquid crystalline systems[9]. Although it is more common to use a boronic acid as the

starting material, it is also possible to use a boronate ester, as is used in scheme 3 (compound 14) to generate the biphenyl aldehyde (16). Oxidation of aldehyde 16 with potassium permanganate resulted in the desired carboxylic acid (17), in moderate yield.

Scheme 4 represents a much more involved synthetic route, making use of the protection / de-protection strategy in order to build up the multi-ester units. The first step is a benzyl protection of the hydroxyl group of 4-hydroxybenzoic acid, using the same reaction conditions as the first step of scheme 1. The resulting benzyl-protected benzoic acid (19) was then esterified with an appropriate alcohol to yield the benzyl-protected esters (22 and 23). De-protection using hydrogenolysis re-afforded the hydroxyl group that was protected at the beginning of the scheme and therefore allows further esterification, with compound 19, which is benzyl-protected. Thus building up the molecule to incorporate the two ester groups, the alkyl chain, and a remaining hydroxyl group, protected by a benzyl group. Once again, the benzyl group is removed *via* hydrogenolysis to yield the phenols 28 and 29, which can then be used in esterification reactions to generate final products.

Scheme 5 represents an extremely similar pathway to that of scheme 4, as the benzyl-protected ester (19) was used as the starting material. However, in this case, the chiral moiety was incorporated with the first esterification through the reaction of compound 19 with (*S*)-2-octanol and (±)-2-octanol, to generate the corresponding ester compounds, 36 and 37 respectively. The remainder of the scheme follows as did scheme 4, in order to build up the similar phenolic target compounds 38 and 39.

Schemes 6 – 13 show the synthesis of the various bent-core units, based upon the 1,3-disubstituion of a phenyl ring. Once again, a protection / deprotection strategy is employed to permit the synthesis of unsymmetrical final compounds, where the two arms of the molecule are added sequentially to the bent-core (as will be discussed in section 4.2).

Scheme 6 begins with the benzyl-protection of 3-bromophenol to generate the benzyl-protected compound 41. Treatment with *n*-BuLi generated the aryllithium intermediate *via* halogen exchange, which upon quenching with trimethyl borate yielded the boronic acid (42). At this point, the scheme effectively makes two bent-cores. Compound 42 can be used in Suzuki-coupling reactions to form rigid carbon-carbon bonds between two phenyl rings, as is carried out in scheme 25, whilst oxidation of compound 42 using hydrogen peroxide generates the phenol 43. Compound 43 also has the benzyl-protected hydroxyl group which was introduced in the first step and facilitates subsequent syntheses of unsymmetrical products.

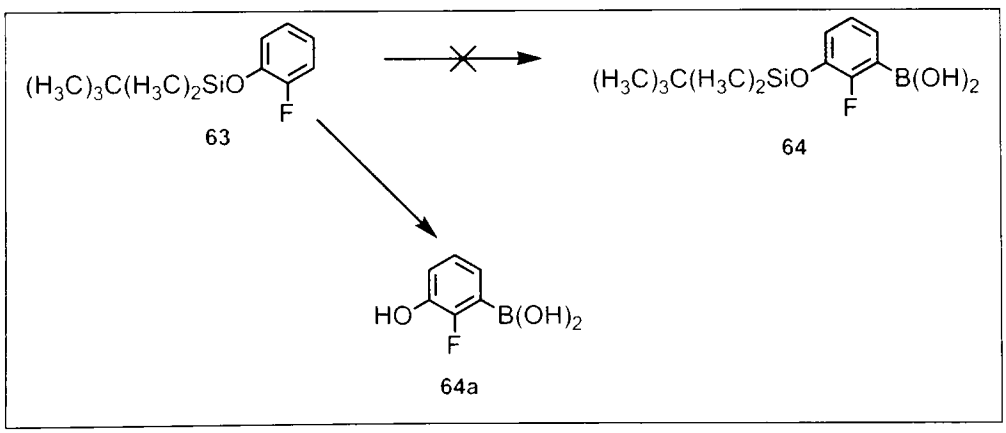
Scheme 7 employs a similar strategy to that of scheme 6, although now incorporating the three fluoro-substituents. 2,3,4-Trifluorphenol was first protected, again with a benzyl group to yield the protected compound 45. At this point, the scheme then splits into two parts. The proton *ortho* to the fluoro of compound 45 is acidic and therefore an *ortho*-directed metallation (using *n*-BuLi) can be carried out to abstract the proton. At this point, two differing products were formed, dependent upon the reagent used to quench the resultant arylllithium intermediate. Quenching with trimethyl borate generates the boronic acid (46), which as seen in scheme 6 can then be used either in a coupling reaction (Scheme 26), or oxidised to the corresponding phenol (compound 47) for use in esterification reactions. If, however, compound 45 is treated with *n*-BuLi and then the reaction mixture is poured onto solid carbon dioxide, the carboxylic acid (48) is generated (after acidification), which can then also undergo esterification reactions, but will result in the ester group emanating away from the bent-core, rather than towards the bent-core, as is the case in compounds such as 43 or 47.

The boronic acid (49) in scheme 8 was available in the laboratory from a previous project[101] and was oxidised to the corresponding phenol (50). A benzyl-protection was then utilised to protect the hydroxyl group and permit the treatment of compound 51 with *n*-BuLi to generate the benzyl-protected, boronic acid (52). A further oxidation provided the phenol (53), which was then deprotected *via* hydrogenolysis to yield the diphenol (54). By de-protecting the hydroxyl group at this stage, the synthesis of unsymmetrical final products was thus prevented, but it was decided to only synthesise a symmetrical target compound based upon this mono-fluoro core, which therefore reduced the number of reaction steps in the overall synthetic pathway.

Scheme 9 shows the synthesis of the benzyl-protected, difluorophenol (58), using similar methods as previously described. Again, an *ortho*-directed mettallation is employed to remove the proton in between the two fluoro-substituents. This proton is removed selectively due to the reinforced effect of both fluoro-substituents rendering the proton the most acidic.

Scheme 10 represents a more challenging synthetic pathway in order to achieve the synthesis of the target bent-core compound (69). Compound 59 was available in the laboratory, and was treated with *n*-BuLi (attempted synthesis a), with the aim of abstracting the proton *ortho* to the fluoro-substituent. However, after quenching with trimethyl borate and the associated ethereal workup, no characterisable product was acquired. It has been found in other similar systems that upon treating with *n*-BuLi, the protons of the benzyl group can sometimes be removed, causing failure of the reaction[102]. The procedure was repeated again, but this time

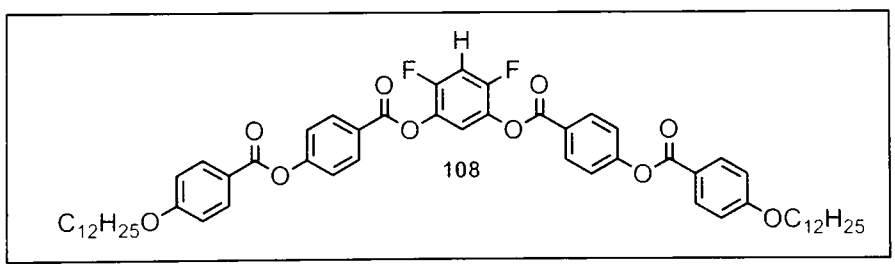
with the sterically-hindered and less nucleophilic base, lithium diisopropylamide (LDA) (synthesised *in situ via* the addition of *n*-BuLi to diisopropylamine). However, once again no characterisable product was acquired. It is not possible to detect whether the LDA was not a strong enough base to remove the (relatively) weakly acidic proton, or whether again there were problems with the benzylic protons, as no characterisable product was afforded. Due to the suspicion of problems with the benzyl group, it was decided to attempt the lithiation step using a different protecting group. Therefore, the hydroxyl group of 2-fluorophenol (61) was protected with the *t*-butyldimethylsiloxy group to yield compound 63, which was then treated with *sec*-BuLi (used due to the consideration that *n*-BuLi and LDA were not strong enough to remove the proton in the attempted syntheses a and b). However, the intended product was not acquired. The NMR spectra suggested that the correct proton had been removed by the *sec*-BuLi, to form a boronic acid, but that the *t*-butyldimethylsilyl protecting group had also been removed, therefore also re-generating the hydroxyl group, and giving the undesired compound 64a (shown below). It is possible that the *t*-butyldimethylsilyl protecting group was removed either during the lithiation step, or later when the reaction mixture was acidified to afford the boronic acid.



If the intended final products based upon this bent-core were going to be symmetric in molecular structure then this outcome would have been acceptable, as oxidation of the boronic acid would have led to the diphenol, allowing synthesis of the symmetric products in the single next step of the synthetic pathway (as shown in scheme 8). However, as unsymmetrical final products were desired as an end result, an alternative method of synthesis of this bent-core was therefore required. This was achieved by treating 1-bromo-2-fluorobenzene (compound 65) with LDA, and quenching with trimethyl borate to yield the intended boronic acid 66, in a very good yield (88 %). Upon inspection of the NMR, it did

not provide conclusive evidence that the product was as desired, instead seemingly a mixture of unknown products. As it was hard to distinguish the actual nature of the potential mixture, and that NMR spectrums of boronic acids can often be difficult to interpret[102, 103], the reaction scheme was continued, with the aim of being able to clarify the mixture of products once the boronic acid(s) had been oxidised to their corresponding phenols. However, after carrying out the experimental procedure and the associated ethereal work-up, NMR analysis revealed the single desired product, compound 67. The remainder of the scheme followed a similar route to those that have already been described, to achieve the desired benzyl-protected-fluorophenol (69).

Scheme 11 shows the interesting synthesis of the difluoro, chloro bent-core unit (77). Synthesis of this compound provided the most challenging experience within the work, as an element of method development was required in order to successfully synthesise the desired intermediates. The overall intention for the bent-core (77) was to synthesise difluoro final products such as compound 108. In order to generate the bent-core with the two fluoro substituents in the 2- and 4- positions, it is necessary to 'block' the site in between both fluoro-substituents, as this proton is particularly acidic, due to the electron-withdrawing effect of the two fluoro units and would therefore be removed in the two required lithtiation steps.



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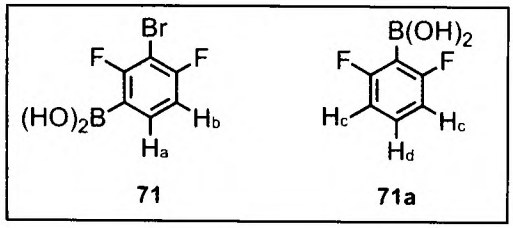
1-Bromo-2,6-difluorobenzene (70) was chosen as a starting material, as it was envisaged that the protons *ortho* to each of the fluoro-substituents could be removed successively using LDA, without removing the bromo-substituent, which would 'block' the position until the bromo-substituent could be removed (*via* a subsequent hydrogenolysis step). The synthesis of compound 71 was attempted using two sets of reaction conditions. Firstly, the reaction was carried out at the common temperature for carrying out lithiation reactions of −78 °C. After carrying out the reaction and the ethereal work-up, NMR analysis (figure 4-1) revealed that the material was a mixture of two products, the intended boronic acid (71) and a second

product acquired as a result of the bromo-substituent being removed (**71a**), in an approximate ratio of 1:0.7.



71 **71a**

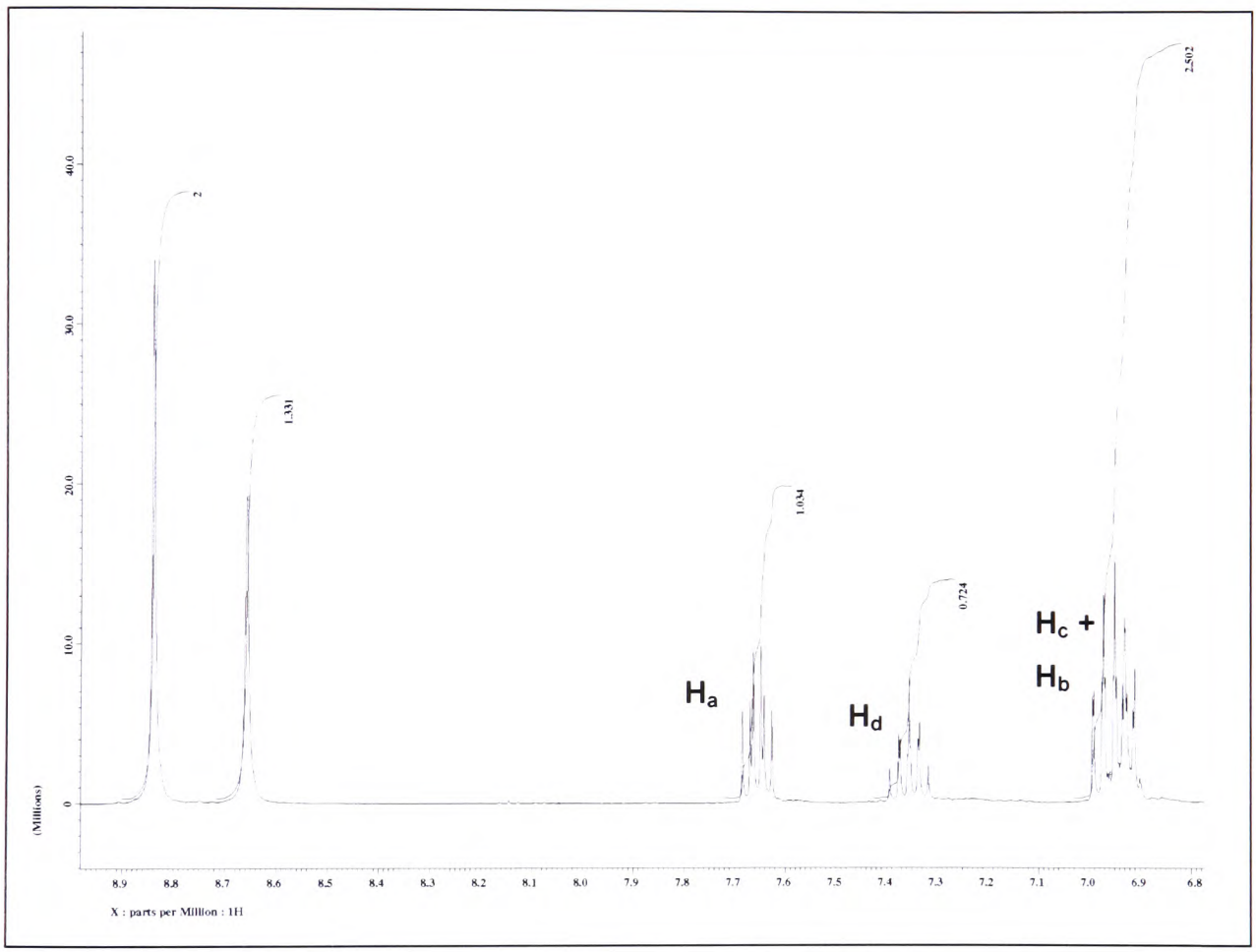
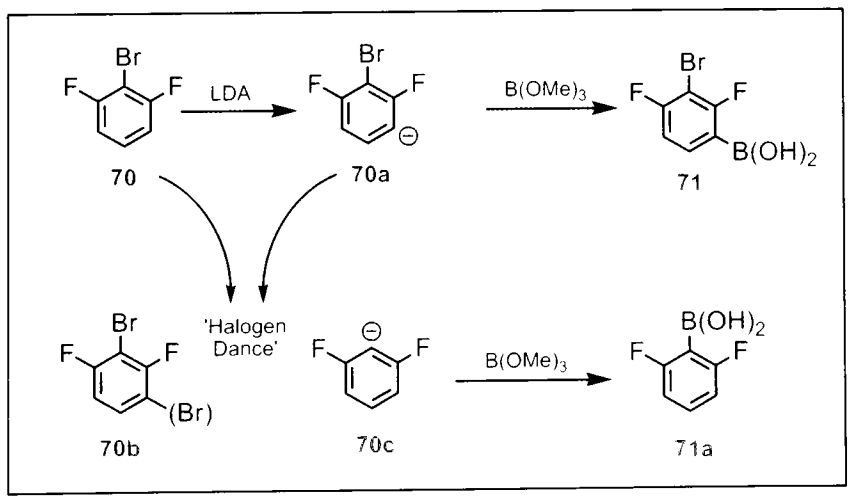


Figure 4-1. NMR Spectrum of compound **71**, attempted synthesis (Method A).

The presence of the two compounds in the mixture is confirmed by the observed peak responses and their associated splitting patterns. When considering the expected splitting patterns for the protons of compounds such as **71**, the effect of the fluoro-substituents must also be taken into account, as the signal for a proton will also be split by fluoro-substituents and it is common to find meta-fluoro substituents coupling with protons, with a similar *J*-value to that of an *ortho* hydrogen (approximately 7-8 Hz). Therefore, the splitting pattern

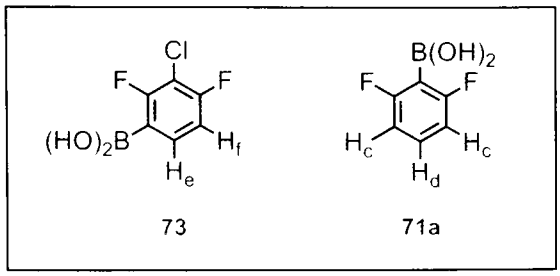
expected for H_a on compound 71, would be close to a quartet, as the *J*-values for H_b and the two fluoro-substituents would be similar. As can be seen in figure 4-1, a near-quartet is indeed observed, although there is a small degree of additional splitting resulting from the fact that, although similar, the *J*-values will vary slightly between the three substituents (H_b and both fluoro units). The equivalent proton on compound 71a (H_d) would potentially split with both hydrogen units and both fluoro units to a similar degree, and therefore a near-quintet would be expected, as is observed in figure 4-1. Again, the slight variation in the actual *J*-values observed for each of the units causes a slight additional splitting. It is important to note that using LDA to remove a proton in this way would not be expected to remove the bromo substituent instead. One possible explanation for the observation of this phenomenon is a 'Halogen-Dance' (HD) reaction[104-108]. In an HD reaction, the substitution pattern of a (hetero-)aryl bromide or iodide can undergo a rearrangement, when treated with an appropriate base[106]. Halogen units undergoing this rearrangement are particularly reactive when they are *ortho* to other halogen substituents[108], as is the case with compound 70. Early examples employed alkali amide bases such as sodium and potassium amide, although more recently, lithiating reagents such as LDA or *n*-BuLi have been employed[106]. The first step of the reaction is the formation of an anion, either through the abstraction of a proton, or through metal-halogen exchange[105, 106]. In the case of compound 70, LDA is employed to remove the acidic proton *ortho* to the fluoro-susbtituent, and therefore form the anion (70a).



Quenching of this anion (70a) with trimethyl borate yields the expected boronic acid (71). However, it is possible that *via* an HD reaction, the anion (70a) can react with the starting

material (70) to give the new anion (70c) and potentially 1,3-dibromo-2,6-difluorobenzene (70b), or regenerate the starting material (70) if the bromo unit removed from species 70a forms an *N*-bromo complex with the residual LDA in the reaction mixture[102]. The driving force behind this reaction is the formation of the most stable anion, with the lithium atom residing on the most acidic position of the phenyl ring[102, 105], which in the case of compound 70 is the 1-position where the bromo-substituent is initially residing. The newly formed anion (70c), with the negative charge *ortho* to both of the fluoro-substituents, as a result of the HD rearrangement, then forms the undesired boronic acid (71a), upon quenching with trimethyl borate. Any residual / regenerated starting material (70), or the potential compound 70b would most likely be washed out of the reaction mixture during the 'hexane-wash' at the end of the work-up procedure, and therefore would not be observed in the subsequent NMR spectrum. Alternatively, if a halogen dance mechanism is not the reason for the removal of the bromo substituent, the effect of the two fluoro substituents either side may render the bromo substituent sufficiently labile for the relatively weak nucleophilic nature of LDA to be able to abstract the bromide unit. In an attempt to eliminate or reduce the effect of the HD reaction, or the possible nucleophilic abstraction of bromide by LDA, causing the mixture of products, the temperature of the reaction was reduced to −100 °C (synthesis b), using a liquid nitrogen / ethanol bath. However, the result was again a mixture of the two boronic acids (71 and 71a), although a more promising result was ascertained. The 1:0.7 ratio obtained for synthesis a had been improved to approximately 5:1 in favour of the desired boronic acid (71), but separation would be difficult or impossible. As the attempted syntheses (a and b) of compound 71 had not produced the single desired boronic acid, 1-chloro-2,6-difluorobenzene (72) was employed. It was anticipated that the problem of mixed products would be eliminated due to the fact that *n*-BuLi, under normal circumstances, does not abstract a chloro-substituent. However, the attempted synthesis c of compound 73 once again revealed a mixture of the two boronic acids (73 and 71a), although unlike the attempted synthesis of compound 71, the ratio of boronic acid 73 to 71a was actually reversed, and a 5:1 ratio in favour of the undesired product (71a) was obtained. It is unlikely that this is as a result of a halogen dance mechanism, as it is assumed that this would probably result in a decrease in the amount of the side-product, when going from the bromo-compound to the chloro analogue, as chloro units do not normally undergo halogen dance reactions[104, 108]. Discounting the HD mechanism forces consideration of the *n*-BuLi causing a halogen-exchange, even though this does not normally occur with chloro units. As the chloro-

subsituent is between the two fluoro-substituents, it is potentially activated sufficiently to be removed by *n*-BuLi, which will therefore form the carbanion at the most stable place on the phenyl ring and subsequently form the corresponding boronic acid (71a), upon quenching with trimethyl borate.



73 71a

After discovering that the chloro-substituent of compound 72 was removed by *n*-BuLi, a second attempt at the synthesis of compound 73 was made, using LDA, a weaker, less nucleophilic and sterically hindered base, which combined with the lower temperature of −100 °C, prevented the removal of the chloro-substituent and instead removed the acidic proton *ortho* to the fluoro-substituent. NMR analysis (figure 4-2) of compound 73 revealed that the desired boronic acid had indeed been obtained, as a single product, in good yield.

As can be seen in figure 4-2, the response for H_e is again a near-quartet, similar to that observed in compound 71 (figure 4-1), again as a result of the two *meta* fluoro-substituents imparting a similar degree of coupling as that of the *ortho* hydrogen, H_f. The splitting expected for H_f would be a near-triplet due to the splitting with the *ortho* fluoro-substituent, and H_e, which is then doubled due to the *para*-splitting of the *para* fluoro-substituent, as is observed.

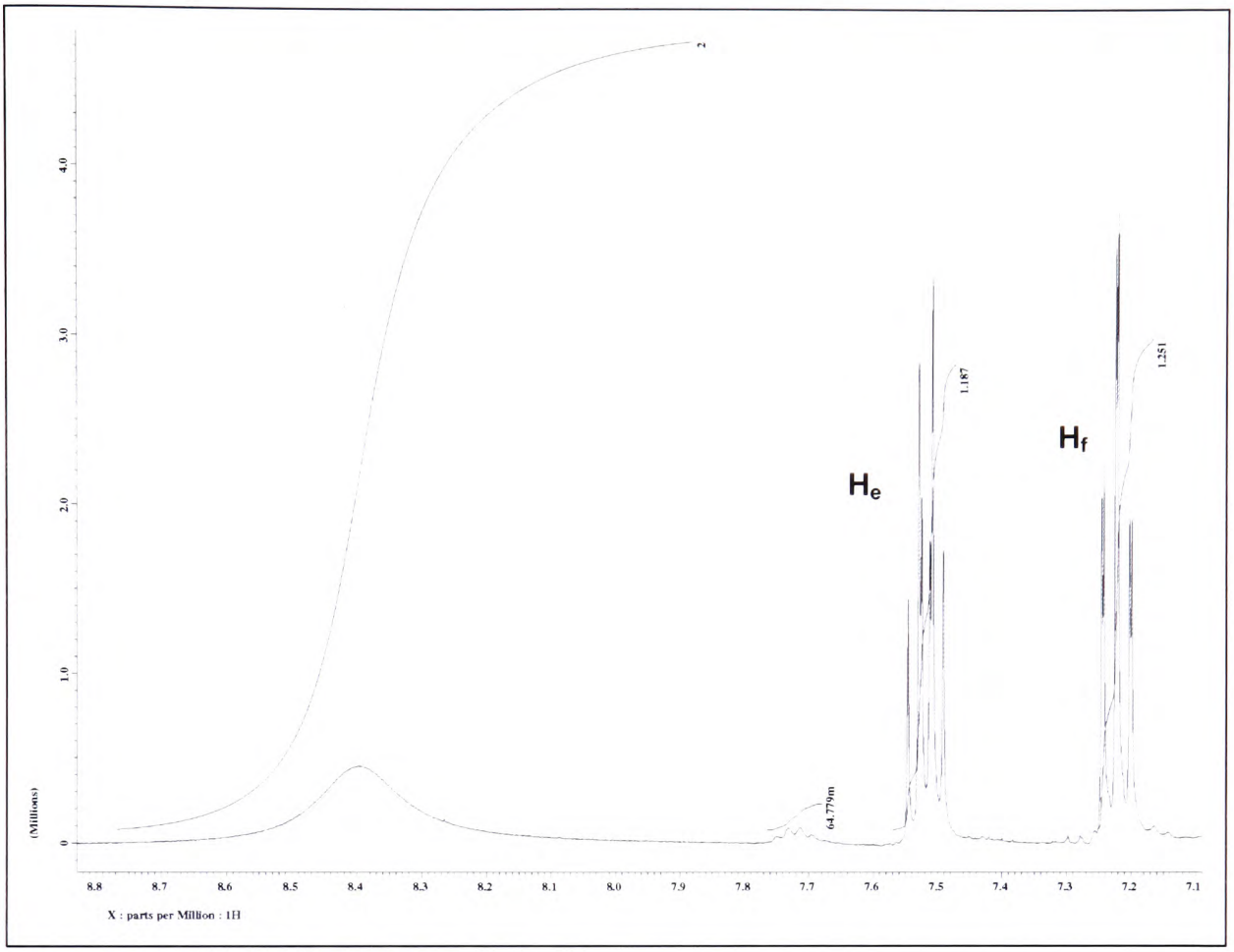


Figure 4-2. NMR spectrum of compound **73**.

After the successful synthesis of compound **73**, the remainder of the reaction scheme was able to proceed as illustrated. Oxidation of the boronic acid (**73**) yielded the phenol (**74**), which was then protected with a benzyl group (**75**). It was then possible to employ the same reaction conditions as in the synthesis of compound **73** to remove the second acidic proton, *ortho* to the fluoro-substituent of compound **75**. A second oxidation then afforded the desired phenol (**77**), which due to the potential two phenolic groups (one protected with a benzyl group) allows for the synthesis of unsymmetrical target compounds. It was anticipated that in the remaining reaction steps to the final compounds (scheme 19), the chloro-substituent would be removed when the benzyl group is removed during hydrogenolysis. However, this did not proceed as expected and will be discussed in section 4.2.

Scheme 12 illustrates the synthesis of the ethyl-protected benzoic acid (**80**). The acidic proton *ortho* to the fluoro-substituent of 1-bromo-2,3,4-trifluorobenzene (**78**) was removed using LDA, and the resulting aryllithium poured onto solid carbon dioxide to generate the lithium salt of the desired product (**79**), which was afforded by acidification. In order to allow

functionalisation using the bromo-unit (in subsequent Suzuki coupling reactions), the carboxylic acid group was then protected as the ethyl ester, by employing an acid-catalysed Fischer esterification[29].

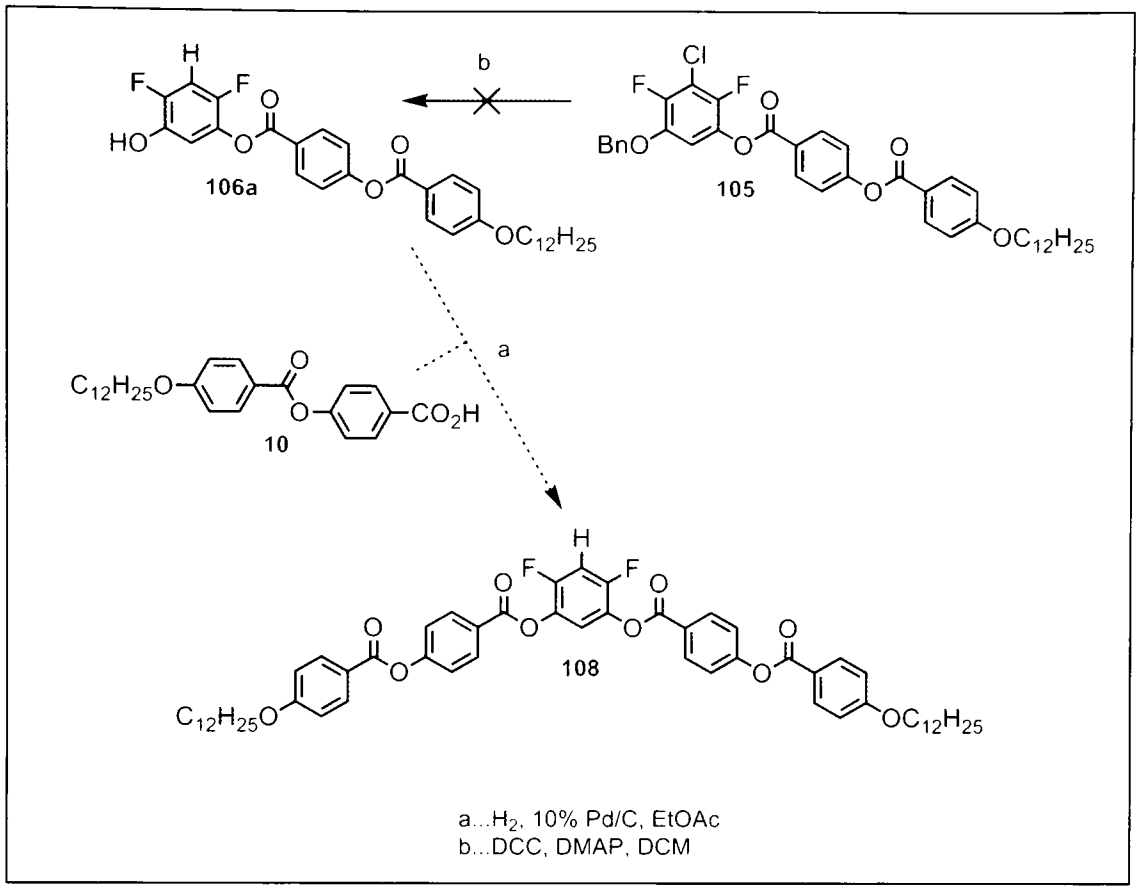
Scheme 13 is only a single reaction step, resulting in the synthesis of the benzyl-protected, bent-core benzoic acid (82), using the same reaction conditions as detailed in the first step of scheme 1.

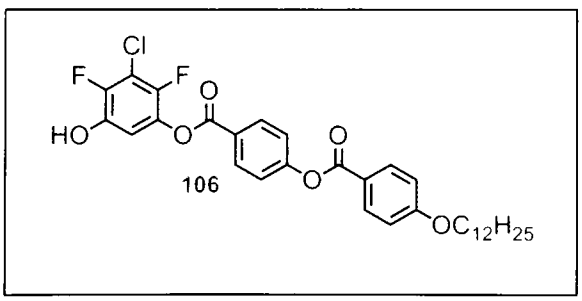
4.2 Achiral Products

Scheme 14 represents the simplest pathway employed, to generate the symmetrical product (84). A fairly low yield was obtained (22%), although as the reaction was a double esterification, purification by column chromatography, and then further purification by recrystalliation was employed, it is therefore not completely unexpected. However, in a similar, double esterification (scheme 16), a yield of 52 % was obtained. Such differences are often due to varying degrees of loss during recrystallisation.

Schemes 15, 17 and 18 illustrate clearly the protection / deprotection strategy employed to 'build-up' the multi-ester compounds. Choice of appropriate starting materials allows for the synthesis of highly unsymmetrical products (for example compound 87), where one 'arm' of the molecule is significantly shorter than the other, or products which are unsymmetrical only by virtue of incorporating differing alkoxy chain lengths on each of the two arms (for example compound 88).

Scheme 19 follows on from the interesting synthesis of compound 77 (scheme 11), in an attempt to synthesise the difluoro target compound 108. Esterification of compound 77 with the two-ring benzoic acid (10) provided the benzyl protected compound 105. It was expected that the subsequent hydrogenolysis, employed to remove the benzyl group of compound 105, would also result in the reductive abstraction of the chloro unit, as has been reported in the literature[109], and would therefore permit the following pathway to the desired product (108), esterifying compound 106a with compound 10. However, NMR analysis soon revealed that the afforded compound after hygrogenolysis was in fact compound 106, with the chloro-substituent remaining in the 5-position of the bent-core. This observation was also confirmed by mass spectrometry, where mass ion peaks of 678 and 680 were found in a 3:1 ratio.





Although this step of the reaction pathway had not proceeded as expected, it did allow the synthesis of compound **107**, which although an undesired product, did make for an interesting comparison with other target compounds (see section 5.1.1). An attempt was then made using a 'method for the reduction of chloroarenes' reported by Rahaim and Maleczka[110], using polymethylhydrosilane (PMHS). Although the quoted yields in the article are very good (many in excess of 90%), they are for relatively simple systems and it was therefore somewhat expected that the more complex structure of compound **107**, particularly with the chloro unit sterically hindered between the two fluoro units, would not readily undergo such a reaction. NMR analysis revealed only the starting material (**107**), easily

identifiable by the single signal for a proton on the bent-core, rather than the two that would be present should the chloro unit have been removed. The potential benefits upon the resultant mesophase morphology of compound **108** have been predicted and are discussed in section 5.1.1. Therefore compound **108** is a desired target for future work within the research group.

Scheme 20 is very similar to schemes 15, 17 and 18, where appropriate intermediate compounds were chosen to enable the synthesis of the desired symmetrical, or unsymmetrical products (**113** and **114**). The final step of the pathway (scheme 20) involved the esterification of the two ring benzoic acid (**9**) with the three-ring-trifluorophenol (**112**), to yield the unsymmetrical compound **114**. After purification of the reaction mixture by column chromatography and recrystallisation, NMR analysis indicated a 'pure' compound (within the limits of detection by NMR). However, when further analysis of the compound was carried out using HPLC, it was discovered that the compound was not pure, and was instead a mixture of three materials, as indicated by the three peaks from the HPLC chromatogram (figure 4-3).

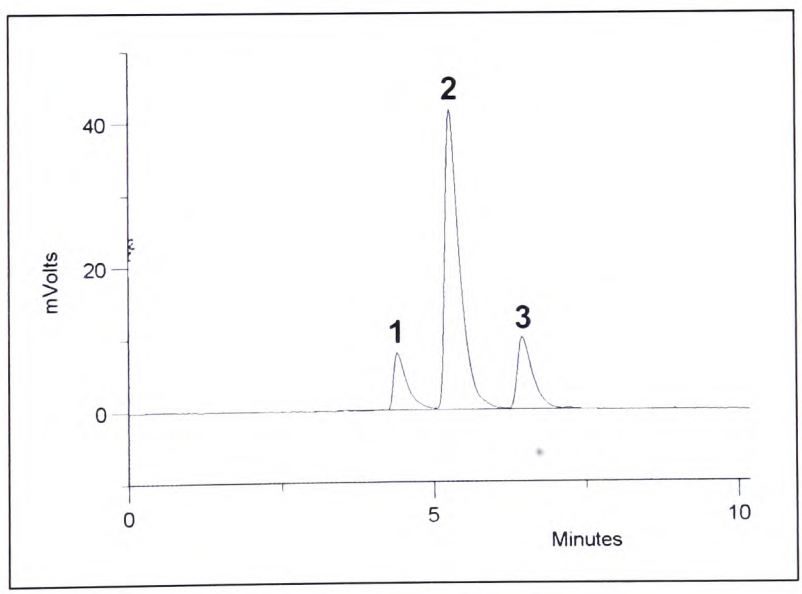


Figure 4-3. HPLC Spectrum of compound **114**.

As the peaks are so well resolved, compound **114** was then re-investigated by TLC, to assess the possibility of purification by further column chromatography. However, only one spot was observed, despite trialling a variety of eluents (DCM, DCM / hexane mixtures, ethyl acetate, ethyl acetate / hexane mixtures). This left only one option, to purify the material by

preparatory HPLC, a very effective but time consuming and relatively high cost method, but ideal for difficult purifications such as this. The preparatory HPLC was carried out using a solvent mixture of 60:40 acetonitrile / DCM, which provided the optimum resolution compared to the retention time on the column. At this point it was assumed that the largest peak in the spectrum (numbered **2** in figure 4-3) was indeed the intended product from the reaction, but fractions of the other two peaks were collected in order to establish the nature of the impurities. After purification by preparatory HPLC, the purity of each of the fractions collected was again tested analytically by HPLC, which showed just one component for each of the three solutions, corresponding to the three original peaks in compound **114**. NMR analysis of all three components gave exactly the same splitting patterns, although the values obtained for the integration of the alkyl regions differed significantly. The integration values obtained within the NMR spectrum of fraction **1** corresponded to the symmetrical, C_8, C_8 product (identical to compound **113**). For fraction **2**, the NMR spectrum corresponded to the expected unsymmetrical product, compound **114**. For fraction **3**, the NMR spectrum corresponded to the symmetrical C_{12}, C_{12} product (identical to compound **178**). To account for these findings, the mechanism of the DCC (Steglich) esterification must be considered. The Steglich esterification is a mild reaction[111, 112] and is ideally suited to the target structures, where the intermediate compounds already contain multiple ester units, which would undergo hydrolysis under standard Fischer esterification. In the first step of the reaction mechanism, the carboxylic acid is activated towards nucleophilic attack[103, 112] (figure 4-4), through the formation of the *O*-acylisourea (**171**), which offers a similar reactivity to that of the corresponding acid anhydride[112].

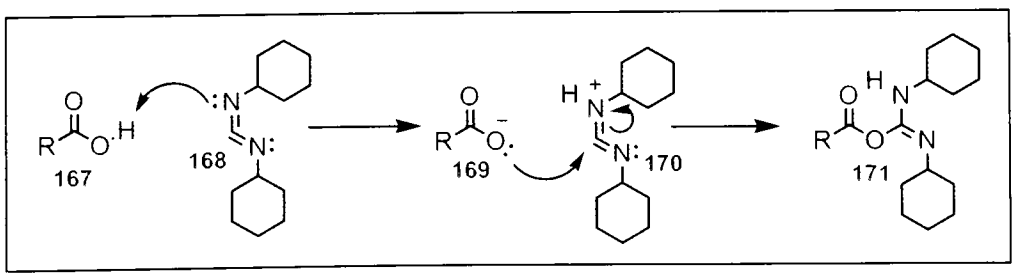


Figure 4-4. Formation of the activated carboxylic acid in the Steglich esterification[112].

The next step in the reaction mechanism is the nucleophilic attack of the alcohol (**172**) on the activated carboxylic acid (**173**), which forms the protonated ester (**174**). The ester product is then formed by deprotonation to give the desired product (**176**), whilst dicyclohexylurea

(DCU, 175a) is formed as a side-product (as shown in figure 4-5), which is easily removed by filtration, as it is insoluble in most common organic solvents.

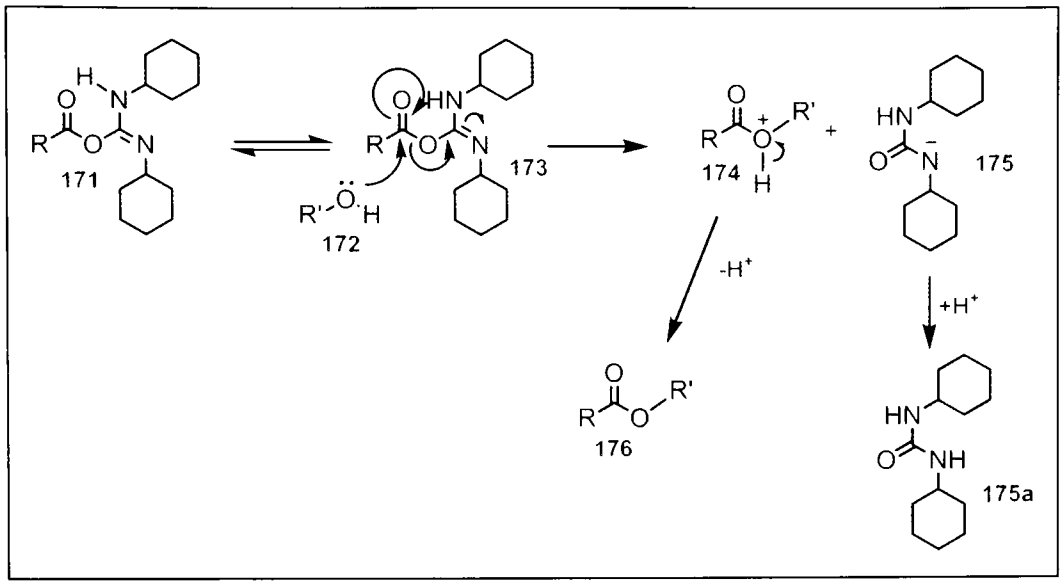


Figure 4-5. Nucleophilic attack on the activated carboxylic acid by the alcohol.

However, in the case of the synthesis of compound **114**, the result from the HPLC analysis shows that the mechanism cannot be as simple as shown above. As is shown in figure 4-6, the ester unit adjacent to the trifluoro bent-core of compound **112** is susceptible to nucleophilic attack from another molecule of compound **112**, due to the stabilisation imparted by the fluoro-susbtituents on the leaving group[102, 113], thus producing the C_{12}, C_{12} symmetrical product **178**, in 17% yield. Similar effects have also been experienced by Hird, as a result of trans-esterification involving bent-core molecules incorporating the trifluoro moiety[102, 113]. The mechanism shown in figure 4-6 provides an explanation for the third fraction in the mixture (as observed by HPLC, numbered 3 in figure 4-3), but does not account for the generation of the C_8, C_8 symmetrical product also observed (fraction **1**). To account for this, further nucleophilic attack on the desired product must be considered, as shown in figure 4-7.

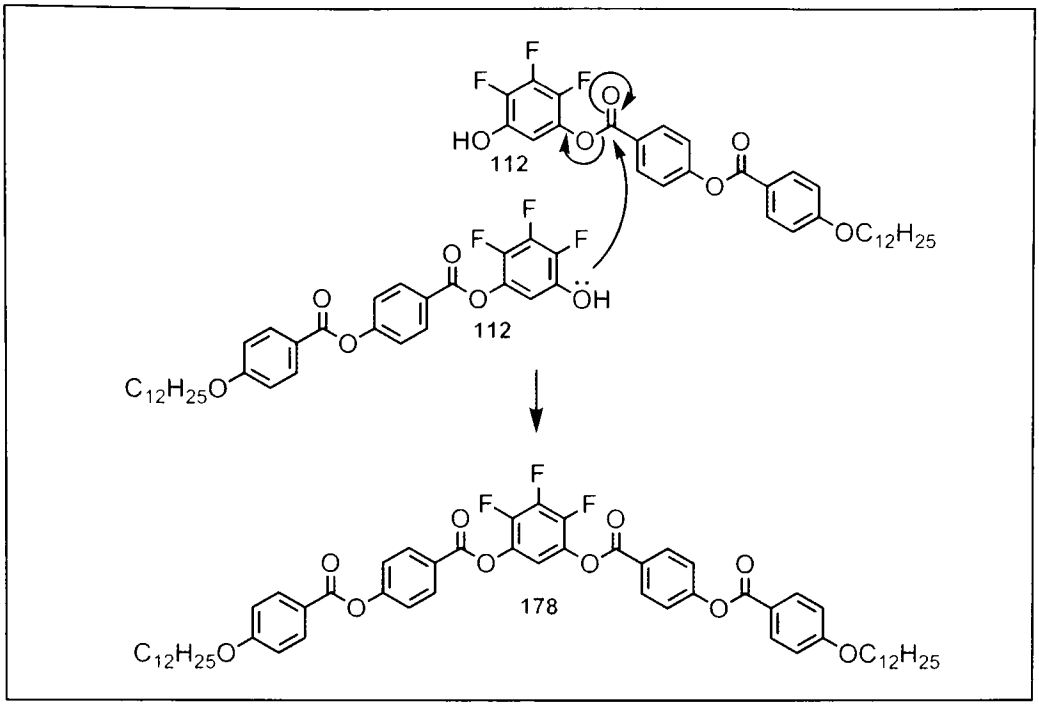


Figure 4-6. Nucleophilic attack on compound 112 by another molecule of the same compound, to yield the symmetrical product 178[102, 113].

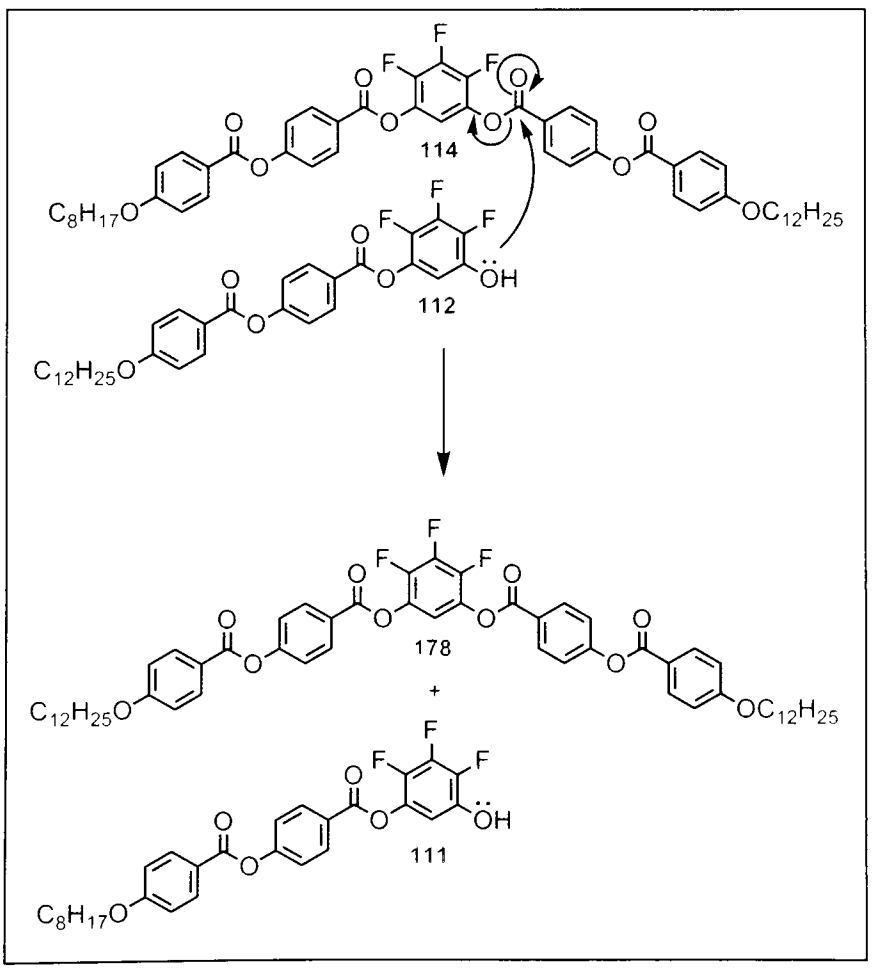


Figure 4-7. Nucleophilic attack on the desired product (114) by the intermediate phenol (112).

The ester unit(s) of compound **114** is (are) also susceptible to nucleophilic attack, in the same manner as compound **112** was in figure 4-6. If the ester unit on the 'C_{12}-arm' is attacked, then the result is also generation of the symmetrical product **178** (as depicted in figure 4-7). If however, compound **112** attacks the 'C_8-side' of compound **114**, the net result will be the regeneration of the starting materials, **114** and **112**, which therefore explains the reasoning behind the fact that the third fraction observed by HPLC consisted of the greater proportion, 17% compared with the 12% of the first fraction. Of more interest is the phenol generated as a result of being the leaving group, compound **111**. It should be noted that this compound was not a starting material (in the synthesis of compound **114**) and due to trans-esterification, it has been produced *in situ*. However, the formation of compound **111** in this way is crucial to the justification of obtaining the symmetrical C_8, C_8 compound **113** (fraction **1** from HPLC analysis). As shown in figure 4-8, compound **113** can be synthesised from the attack of compound **111** upon either the desired product (**114**), or the activated carboxylic acid ($9_{(activated)}$). Fraction one (compound **113**) from the original HPLC analysis equates to a 12% proportion of the overall mixture, 5% less than fraction three. This can be accounted for in two ways. Firstly, compound **113** can only be synthesised (as shown in figure 4-8) by attack of phenol **111** on the desired product (**114**), requiring compound **114** to be synthesised first in the reaction. Secondly, the generation of the C_8, C_8 symmetrical by-product (**113**) potentially promotes the synthesis of the C_{12}, C_{12} symmetrical by-product (**178**), as the phenol (**112**) is regenerated, as shown in figure 4-8, which is therefore able to attack either another molecule of compound **112**, or the unsymmetrical desired product (**114**), as shown in figures 4-6 and 4-7, respsectively. The example shown here, and the observations of Hird[102, 113], indicate that the trans-esterification is promoted by the fact that the trifluoro moiety on the bent-core acts to stabilise the leaving group when the phenolic compound attcks the ester unit of either itself, or the target compound of the reaction. The effect of a trans-esterifiction of this kind has also been recently observed by Stackhouse, whilst also working on a bent-core system[114]. However, in this case, the reaction did not involve fluoro units and occurred away from the bent-core. It is possibly not a surprise that the trans-esterification did not happen at the bent-core, as there would be no stabilisation as a result of the fluoro-substituents, which would potentially promote trans-esterification at the bent-core. Most surprisingly, however, was the observation of a quantitative yield of the trans-esterified product (no desired product isolated)[115], rather than just an impurity, as observed by Hird[102, 113], and described previously in this section. It does seem that compounds incorporating the trifluoro unit are much more

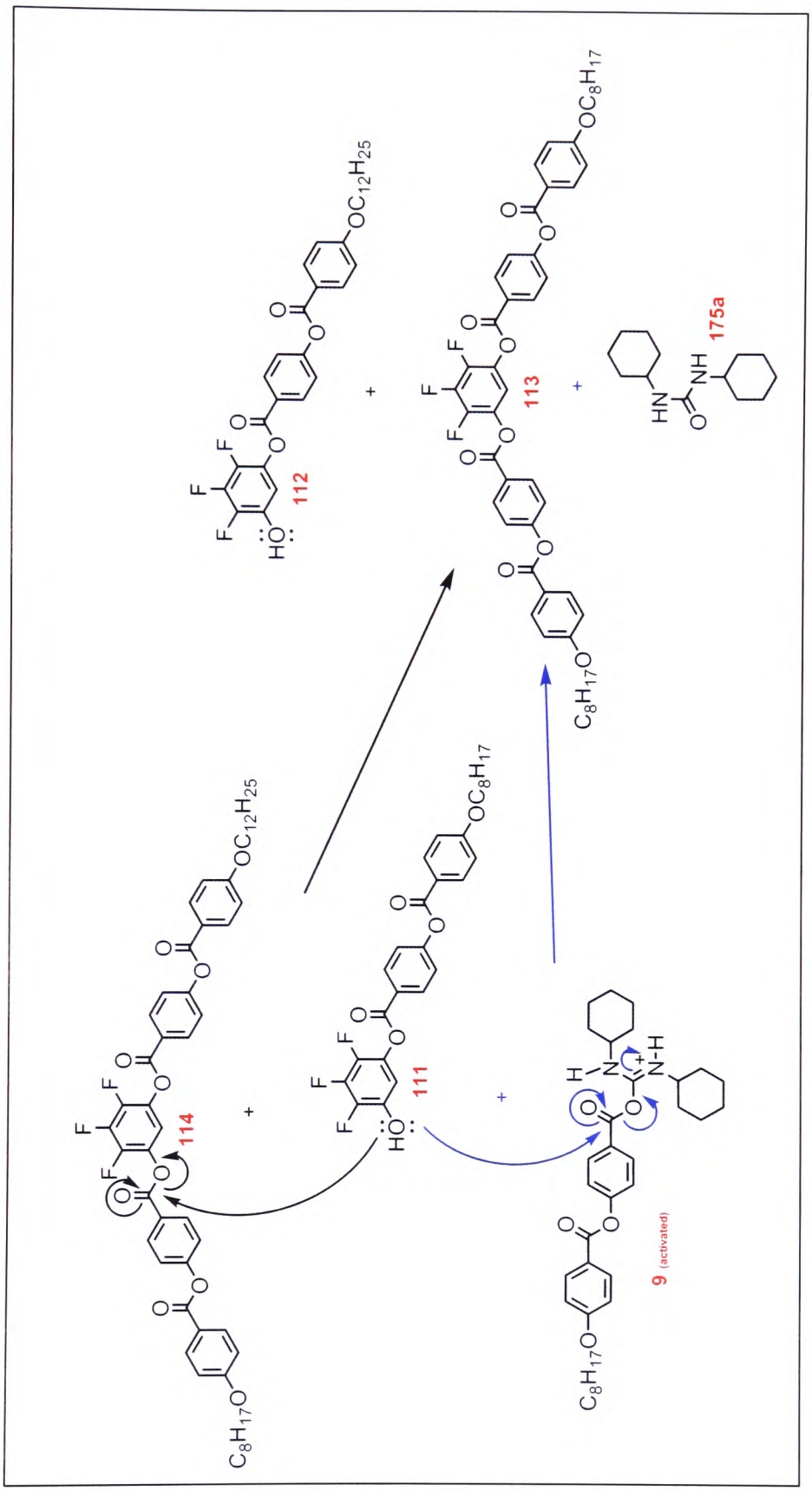


Figure 4-8. Mechanism for the formation of compound **113**, as a side-product in the synthesis of compound **114**.

susceptible to this phenomenon, as has been observed in subsequent post-doctoral work[116]. Recently, esterifications of this kind have been carried out at 0 °C using an ice / salt bath, to reduce the rate of the competing side-reactions. Of the systems tested in this way so far, the reaction has led to synthesis of only the desired product and no impurities as a result of trans-esterification[116].

Scheme 21 is very similar to scheme 20, as it shows the synthesis of the very unsymmetrical compounds **119** and **120**, which also incorporate the trifluoro bent-core. From HPLC analysis, it seems that the synthesis of compound **120** also resulted in a degree of trans-esterification, as again three peaks were observed in the HPLC spectrum and an overall purity of 87% was achieved. After purification of compound **114** *via* preparatory HPLC, it was found that the mesophase morphology and indeed the transition temperatures changed very little, due to the very similar nature of the impurities to the desired compound. As it was envisaged that the nature of the impurities in compound **120** would be of a similar nature to those in compound **114**, it was considered that little effect would be seen as a result of them in the resultant mesophase morphology. Therefore the decision was taken not to purify compound **120** in this way and to instead devote the time and effort to other areas of the project. Should the transition temperatures of compound **120** have proved to of particular importance or interest, then further purification would have been sought in order to fully investigate the pure compound.

Scheme 22 represents the last of the achiral systems, although they were synthesised for comparison with the chiral systems (see section 5.2.1). Whereas the achiral banana-shaped systems described previously are largely symmetrical about the bent-core, with the ester linking groups all pointing towards the core, compounds **126** and **127** have a structure where the ester groups are pointing in one direction along the molecule, rather than towards the core. In order to achieve this, the starting materials must be chosen appropriately so that the phenol and carboxylic acid units are on their respective opposites, compared with the previous achiral materials. The carboxylic acid unit is now incorporated onto the bent-core unit (compound **48**) and the phenolic unit is incorporated onto the 'arm' of the molecule (compounds **28** and **29**). The remainder of the scheme follows the similar route of de-protection and further esterification to yield the target compounds (**126** and **127**). Despite appearing to be pure by NMR, compound **127** was subsequently found to be impure by HPLC (88.6%) and it is therefore thought that the reaction may have been subject to a degree of trans-esterification also. As was the case with compound **120**, the decision was also taken to not purify compound **127** by preparatory HPLC. It is interesting to note that despite many

of these compounds being a similar chemical composition, they do not all undergo trans-esterification. Throughout the course of the project, a reason for this has not been forthcoming and a detailed investigation into the phenomenon is beyond the scope of this thesis.

4.3 Chiral Products

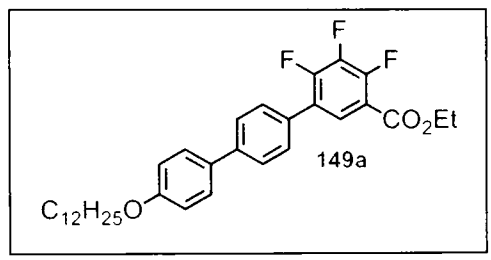
Scheme 23 represents the first of the chiral systems, incorporating the chiral (*S*)-2-octanol moiety. As chiral compounds such as (*S*)-2-octanol are very expensive to purchase, it is usual to combine them into the molecular architecture at the latest possible stage of the reaction pathway to minimise loss of the expensive compound at each step due to variation in reaction yields. However, in the case of compounds such as 131 and subsequent larger molecules, this would result in building up the compounds based upon carboxylic acid compounds, which would become increasingly difficult to work with, due to their relative insolubility, as the molecules were built up. By incorporating the chiral moiety in the first step of this pathway, it allows for the formation of a phenolic group each time a benzyl-group is removed, which therefore makes solubility issues of following reactions easier to overcome.

The DCC / DMAP method is used to esterify compounds 82 and 30, which, as has already been discussed, is ideal for building up multi-ester molecular architectures such as these. In the case of compound 128 (and other subsequent similar reactions), it is also of benefit to use this method as, unlike other procedures such as the Mitsonobu reaction[117], the reaction mechanism does not alter the stereochemistry of the chiral moiety. The resulting benzyl-protected compound 128 was then de-protected by hydrogenolysis to generate the phenol (129). A final esterification with either compound 10 or compound 125 yielded the target compounds 130 and 131.

Scheme 24 mirrors the pathway set out in scheme 23, but details the synthesis of the trifluoro analogues, compounds 134 and 135.

Schemes 25-28 all involve Suzuki cross-coupling reactions in order to synthesise biphenyl and terphenyl moieties within the structures, which therefore add significant rigidity to the molecular architecture. This has a profound effect upon the mesophase morphology and will be discussed in section 5.2.1.The reaction procedure for a Suzuki-coupling requires the use of sodium carbonate and it is therefore a potential problem concerning the ester groups incorporated into the starting materials for the coupling reactions in these schemes. However, sodium carbonate is a weak base and as can be seen for compounds 138 and 141, exceptionally good yields (92% and 98%, respectively) were obtained, confirming that the ester groups were able to tolerate the concentration of sodium carbonate within the reaction mixture. The synthesis of the terphenyl moieties in schemes 27 and 28 also employed the Suzuki-coupling procedure, this time to couple the bipenhyl boronic acid (13) to compounds 145 (scheme 27) and 80 (scheme 28). The yields for the two reactions, however, were

significantly lower than those obtained for compounds 138 and 141, with compound 149 being very low (37%). The synthesis of compound 149 in particular was unusual and presumably contributed to the low yield obtained. As was described in section 3.3.3, after the product was extracted into diethyl ether, the magnesium sulphate was removed *via* filtration, but the filtrate was found to not contain any of the expected product (149a), but instead the ester group being used as a protecting group on compound 80 had been removed during the coupling reaction. Although unexpected, this was not a serious problem, as the next step in the reaction pathway would have been to hydrolyse the ester to re-afford the carboxylic acid unit, to therefore permit the final step in the scheme to generate compound 150.



149a

Scheme 29 illustrates the first scheme to incorporate the four-ring structure. Compound 19 is esterified with the bent-core phenol (129), which already incorporates the chiral moiety (as shown in scheme 23). Similarly to compounds 130 and 131, this also causes the bend to be at one end of the molecule, with the remaining structure being largely linear, made *via* deprotection of the phenol group (152), and subsequent esterification to yield the target compound 153.

The remaining schemes all follow a similar strategy, that of esterification, de-protection and further esterification in order to build the multi-ester units into the molecular architecture. Scheme 33 actually forms two schemes within itself, as it also comprises of the racemic version of each compound, in order to synthesis both the enantiopure, and racemic compounds 165 and 166, respectively.

Schemes 23-33 all follow a similar pathway in order to build up the desired final products. Throughout each scheme, all products were purified by column chromatography and recrystallisation, affording moderate to good yields in most cases.

5. Results and Discussion

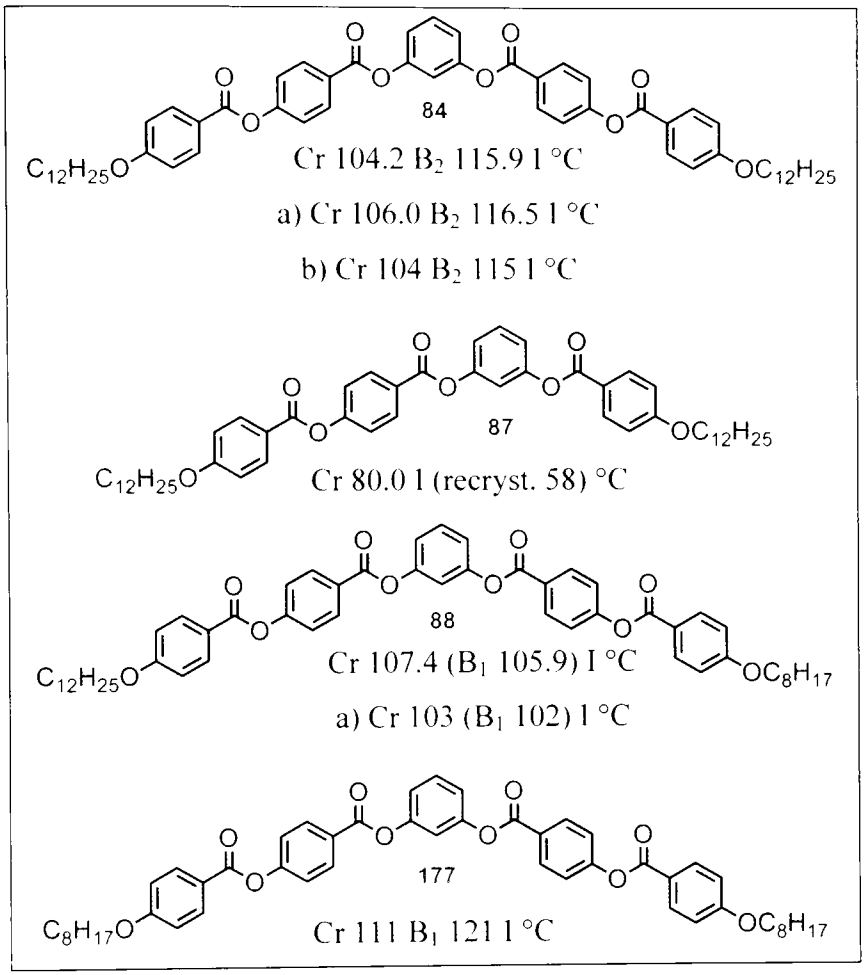
5.1 Achiral Compounds

The following section describes the results obtained after analysis of the achiral compounds by polarising optical microscopy (POM) and differential scanning calorimetry (DSC), drawing attention to any trends and interesting / unusual observations.

5.1.1 Melting Points, Transition Temperatures and Mesophase Morphologies

Many banana-shaped compounds reported in the literature are of a symmetrical structure, due to the relative ease of synthesis[44]. Compound 84 is such an example, comprising of five rings, connected by ester linking groups, and identical alkoxy chains. Although a known compound (transitions a)[97] and b)[98]), compound 84 was synthesised in order to gain experience of a fully characterised banana phase (in this case a B_2 phase), whilst also providing a useful parent compound for comparison of subsequent, varied molecular structures. In liquid crystalline systems, it is common to utilise an unsymmetrical molecular structure in order to reduce melting points, and thus generate mesophases at more accessible temperature ranges, which are both easier to analyse / characterise, and also provide a greater potential for applications such as displays, where the working temperature is of paramount importance[9]. Compound 87 is unsymmetrical to a large extent, as a result of reducing the number of phenyl rings to four. As expected, the melting point has been lowered compared to the parent system (84), but the asymmetry has also led to a complete loss of the B_2 phase, perhaps not surprising as the molecule is no longer banana-shaped, and yet is not sufficiently rod-like to exhibit conventional calamitic liquid crytal phases. Compound 88 is also unsymmetrical, but to a much less extent than compound 87, as the difference from the parent (84), is only in the length of the two alkoxy chains (C_8 and C_{12}). Despite the unsymmetrical nature of the compound, the melting point has actually risen compared to the parent compound (84), although this seems to contradict literature values (it was not known at the time of this synthesis that compound 88 had been previously reported by Achten et al., a)[44, 98]), which show a slight reduction in melting point. Melting points can be unpredictable, but comparison of compound 84 with 88 does reveal an unusual result, perhaps due to the shorter C_8 chain being stiffer than the longer C_{12} chain, therefore outweighing the effect of the asymmetry. Most significantly, compound 88 exhibits a B_1 phase, which would appear to be a logical

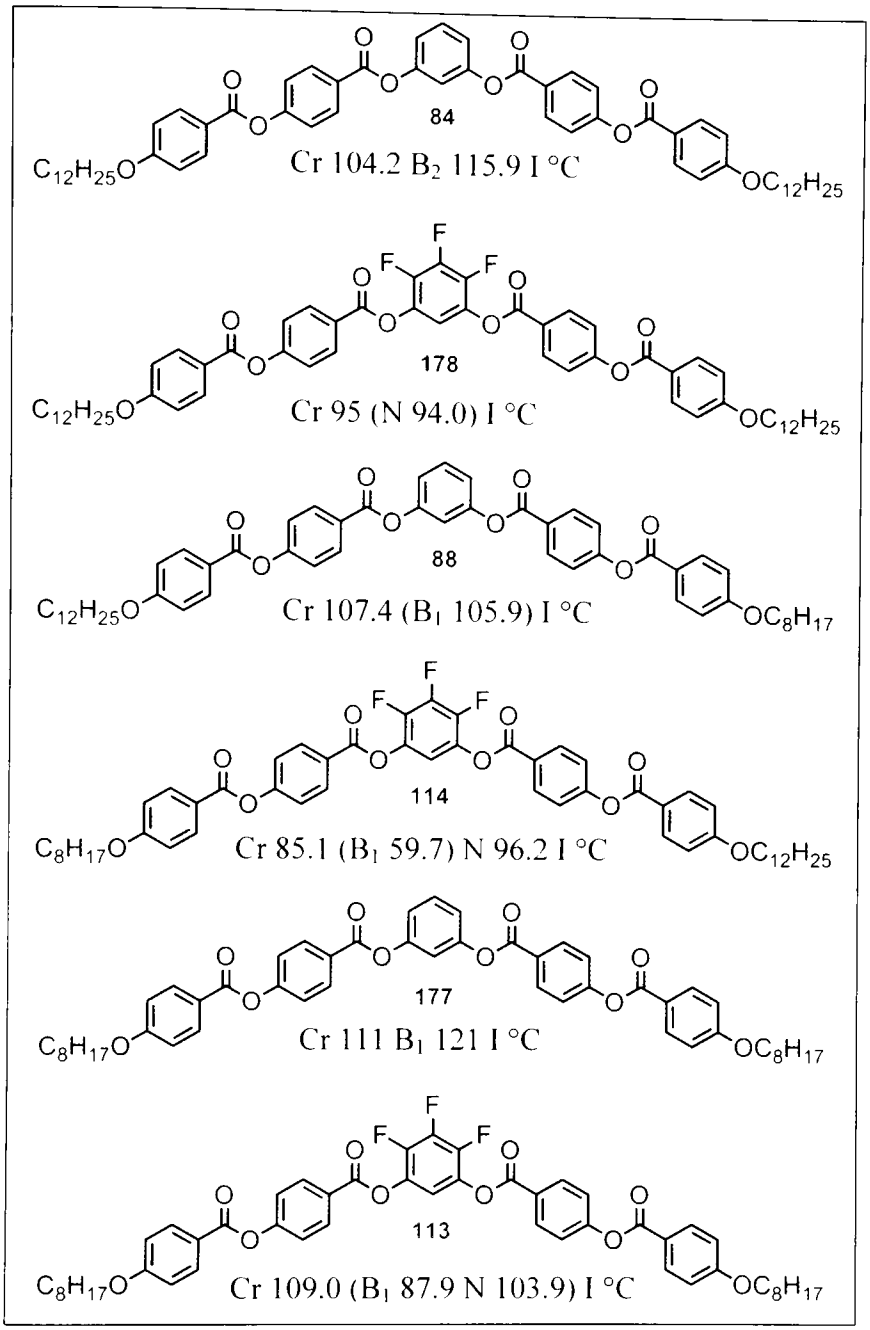
progression from the B_2 phase of compound 84, to the B_1 phase exhibited by the symmetrical (C_8, C_8) compound 177, reported in the literature[49, 98].



It is interesting to note that the clearing point of compound 88 is much lower than the clearing point of compound 84, despite a relatively small difference in the chain length of one of the alkyloxy chains, an observation that would be unlikely to be found in comparable calamitic systems. However, in the case of these banana-shaped systems, the asymmetry caused by the two differing alkoxy chain lengths renders the compound less banana-shaped, which therefore de-stabilises the banana phase. Compound 88 has also been subjected to electrooptical investigation by Hirst at the Florida State University, who found some interesting switching properties exhibited by the compound[118] and will be discussed in section 5.1.2.

The trifluoro bent-core unit has been previously utilised by Hird et al.[55], when assessing the influence of bend upon ferroelectric host materials, and a number of interesting properties

were found, including the generation of chiral mesophases, despite the molecules being achiral. These findings paralled the interesting chiral properties exhibited by some banana phases, despite the molecules themselves being achiral[44, 49]. Incorporating the trifluoro core into the banana-shaped structures 84 and 88 also presents interesting results. Compound 178 was previously synthesised by Hird[119, 120] and shows a remarkable change in mesophase morphology. As also seen in many calamitic systems, the addition of fluoro substituents has resulted in both a reduced melting and clearing point, due to the increased breadth of the molecules preventing molecular packing[9, 66]. Of substantial interest is the observation of conventional mesomorphism, in the form of a nematic phase, a dramatic change from the B_2 phase exhibited by compound 84. A rod-shaped molecule has long been regarded as a pre-requisite for the generation of a calamitic mesophase[9, 15, 44, 45] so it is therefore somewhat surprising that the bent-shape of compound 178 can also exhibit such a phase. These preliminary investigations confirm the fact that banana-shaped compounds, and their associated liquid crystalline phases, are very sensitive to small structural changes in molecular structure. Compound 114 was synthesised to continue investigating the effects of introducing asymmetry to banana-shaped molecules. Compound 114 is a five-ring structure, with differing alkoxy chain lengths (C_8 and C_{12}). The asymmetry of the molecule has had the expected effect of reducing the melting point compared to the symmetrical compound 178 and also exhibits a nematic phase with a slightly higher T_{N-I}, due to the shorter alkoxy chain.



Compound 178, along with examples in the literature have been reported to exhibit chiral domains[77] and this was also found during the analysis of compound 114 *via* polarising optical microscopy. Figure 5-1 shows two photomicrographs of the nematic phase of compound 114, and clearly shows the presence of the chiral domains, characterised by observing a reversal in colour of the two domains, upon rotation of the polariser.

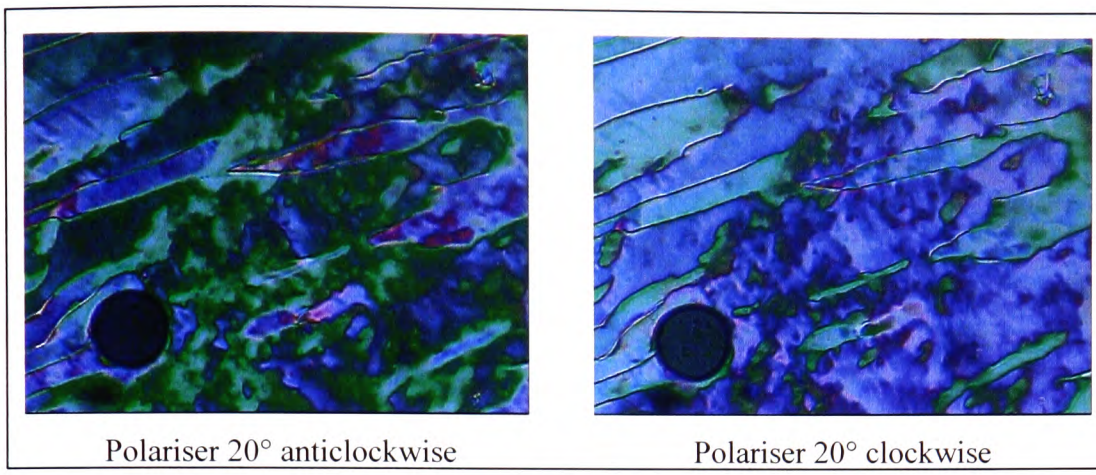


Figure 5-1. Photomicrographs of the nematic phase of compound **114**, 88 °C.

Of further significance is the observation of an underlying banana phase, below the nematic phase (Figure 5-2). Cooling the nematic phase results in a transition and the schliern texture of the nematic phase is quickly transformed into a mosaic-like texture, characteristic of the B_1 phase. The transition temperatures of compound **114** indicate that there is a delicate boundary between banana and conventional mesomorphism, and that the type of liquid crystalline phase generated is extremely sensitive upon the molecular structure, as can be seen by the change in mesophase within this small series of compounds.

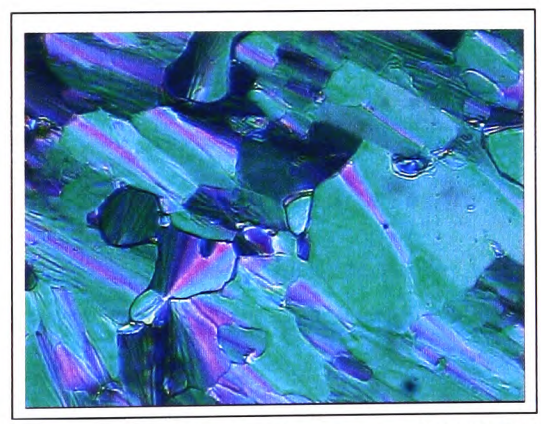


Figure 5-2. Photomicrograph of the B_1 phase of compound **114**, 58.5 °C.

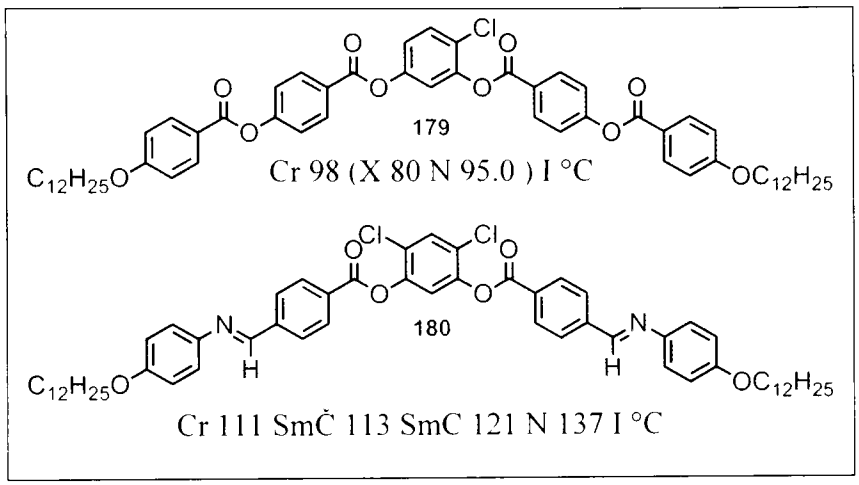
The observation of the B_1 phase in compound **114** prompted the synthesis of compound **113**, in order to further assess the effect of the alkoxy chain lengths upon the generation of the nematic and / or the B_1 phase, based upon the same trifluoro bent-core.

Compound **113** is symmetrical, hence more banana-like in shape, incorporating C_8 chains on each arm of the structure. The result is the generation of a nematic phase (again exhibiting chiral domains), with the underlying B_1 phase also being observed. As was also observed for

compound 114 (compared to compound 88), the stability of the banana-phase of compound 113 is significantly reduced compared to the unfluorinated system (177), again confirming the more rod-like shape of the trifluoro systems when compared to the more banana-shaped parent systems. However, the B_1 phase stability of compound 113 is enhanced by nearly 30 °C compared to compound 114, presumably as a result of the compound being of a symmetrical nature, therefore promoting the generation of a banana phase. Compound 178 does not exhibit a banana phase, possibly due to the combination of a high melting point and the two long dodecyloxy terminal chains. It would be interesting to know whether a potential B_1 phase of the symmetrical compound 178 would also be higher in stability than compound 114, or whether the change to the longer C_{12} chains would prohibit the B_1 phase and possibly exhibit a B_2 phase, as observed for compound 89 (discussed later in this section). In comparison to compounds 178 and 114, the nematic phase of compound 113 has been enhanced by approximately 10 and 8 °C, respectively, which is as would be expected for calamitic systems if the alkyl(oxy) chain lengths are reduced. The change in chain length, along with the now symmetrical nature of the molecules of compound 113 has resulted in the B_1 phase stability being enhanced by nearly 28 °C, although it is still substantially lower than for the unfluorinated parent compound (177); again confirming the more rod-like shape of the trifluoro systems.

All of these observations provide further evidence regarding the boundaries governing the class of liquid crystalline phase generated. In these particular examples, it is evident that the addition of the trifluoro substituents at the bent-core initiate the generation of a nematic phase, and suitably chosen alkoxy chain lengths can also give rise to the exhibition of an underlying banana phase (B_1). It is possibly of greater interest how a nematic phase is able to be generated from a banana-shaped molecule. In the past it has been accepted that a linear, or near-linear, molecular shape is a pre-requisite for the generation of a calamitic phase such as a nematic, and therefore, the significantly bent molecular shape of these compounds would not be expected to be conducive to the formation of such phases. Indeed this is the case in structures such as compounds 84 and 88, where only banana mesomorphism is observed. Therefore the trifluoro substituents must be having an effect upon the molecular shape which therefore permits the generation of a nematic (calamitic) phase. Other examples of apparently banana-shaped compounds exhibiting nematic phases have been reported in the literature[66, 77]. Compounds 179 and 180 were reported by Pelzl et al.[49, 77] and are of a similar five-ring construction to the structures already discussed, and also exhibit nematic phases, despite their bent shape.

Compound 179 shows the effect of adding a chloro-substituent to the 4-position of compound 84. As seen in the trifluoro compounds (178, 114 and 113), this also causes the compound to exhibit a nematic phase and also an underlying phase. As the phase has only been preliminary designated as 'X', it is not possible to say whether the stability of the B_2 phase of compound 84 has been reduced, or lost completely. Assuming the X phase is a B_2 phase, the chloro-substituent has caused a large reduction of 36 °C compared to compound 84. Obviously this value will be even greater if the B_2 phase has been lost completely.



Although compound 180 is of a differing chemical composition and therefore cannot be directly compared, it is interesting that the dichloro-core results in the generation of both smectic and nematic phases, with a clearing point substantially higher than those of compounds 178, 179, 114 or 113. Pelzl used NMR studies to show that the chloro substituents on the core cause a straightening of the molecule and therefore permit the generation of calamitic mesophases, as the molecule becomes less banana-shaped[49, 121]. In light of the straightening effect caused by the chloro-substituent, it is therefore logical to draw similar conclusions regarding the trifluoro analogues (178, 114, 113), as the fluoro substituents adjacent to the ester linking groups will be imparting a similar effect as the chloro substituents in compounds 179 and 180. Although a detailed investigation of this phenomenon is beyond the scope of this thesis, figure 5-3a depicts a schematic representation of the effect that the fluoro-susbtituents are having on the overall conformation of the molecule.

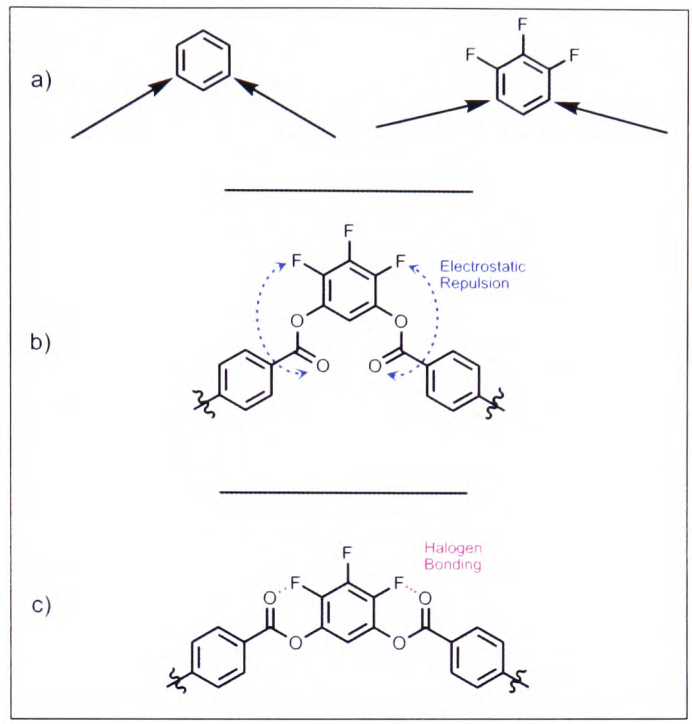


Figure 5-3. a) Schematic representation of the 'straightening effect' caused by the interaction of the fluoro-substituents with the adjacent ester groups; b) conformation caused by a repulsion between the fluoro unit(s) and neighbouring ester group(s); c) conformation favoured as a result of intramolecular halogen bonding between the fluoro unit(s) and the neighbouring ester group(s).

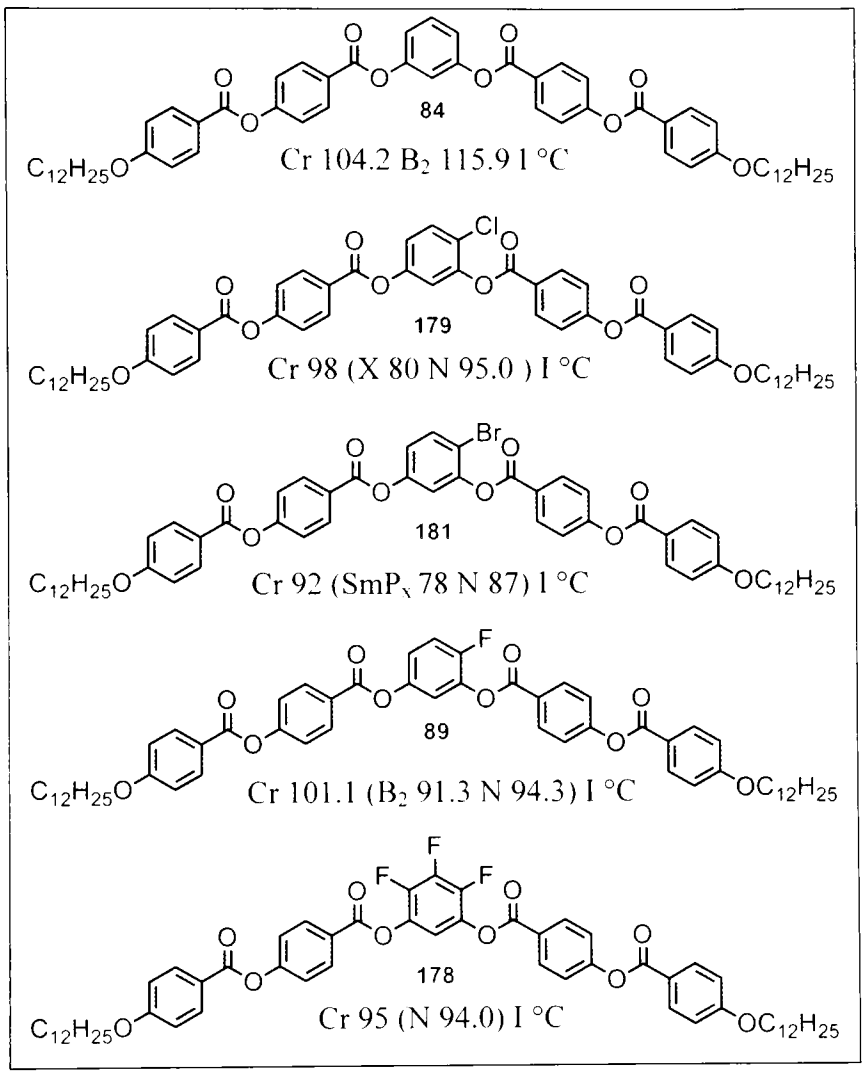
Instinctively, it would be expected that the electronegative fluoro unit will be imparting an electro-static repulsion between itself and the electron-rich carbonyl unit of the ester group. However, as depicted in figure 5-3b, this would result in a very bent conformer, which would therefore not be conducive to the generation of calamitic phases such as the nematic phase observed for compounds **178**, **114** and **113**. Although figure 5-3b shows the conformation of the bent-core to an extreme, any 'intermediate' conformers would result in substantially 'twisted' arms relative to the bent-core itself, which would therefore add to the breadth of the molecule, rendering the molecular shape neither rod-like or banana-like, therefore not conducive to the formation of the observed nematic phase. The second possible concept involves the potential for an intramolecular halogen bond between the fluoro unit(s) and the neighbouring ester group(s). A halogen bond is analogous to a hydrogen bond, and is the result of an interaction between an electron-rich moiety and a polarisable halogen unit. The phenomenon of halogen bonding within the field of liquid crystals has begun to receive some

interest in the literature, although the reported liquid crystalline structures are of a dimer configuration, with the two compounds being held together with a halogen bond[122, 123]. Like a hydrogen bond, a halogen bond is relatively weak, and the strength of the bond is also dependent upon the nature of the halogen unit employed. Therefore, the strongest halogen bond results from employing the most polarisable iodo unit, and the weakest from the least polarisable fluoro unit. Indeed, iodo and bromo units are the usual choice, as the chloro and fluoro units are only weakly polarisable and therefore only confer weak intermolecular forces[44, 102, 122, 123]. However, in the case of compounds 178, 114 and 113, the close proximity of the fluoro unit(s) to the neighbouring ester group(s) creates an intramolecular halogen bond. As this is an intramolecular force, rather than an intermolecular force, as reported in the literature[122, 123], the low polarisability of the fluoro unit will be of less significance, and the weak halogen bond would perhaps be sufficient enough to confer a favoured structural conformation of the bent-core, which in turn renders the structure more rod-like in shape. This is shown in figure 5-3c, where the halogen bond favours the conformation shown, rather than the inverted conformation shown in figure 5-3b. The fact that a calamitic phase, in the form of a nematic is observed for these compounds (178, 114 and 113) suggests that the molecule is indeed adopting a more linear conformation, as was proved for compounds 179 and 180 by Pelzl[77]. However, whilst it was reported in the literature that these compounds (179 and 180) exhibited a nematic phase as a result of being a linear conformation (confirmed by NMR evidence), an explanation for the linear conformation was not provided. It is therefore proposed that a possible reasoning for the linear structural conformation of such compounds is as a result of halogen bonding, with the relatively weak bond involving the fluoro unit being sufficient to favour the more linear conformation due to the bond being intramolecular rather than intermolecular, and the fact that the resultant structural conformation also provides a stable six-membered ring, as shown in figure 5-3c. However, at present this explanation remains speculative and requires further consideration and investigation.

The fact that in addition to the nematic phase, the B_1 phase is also observed in compounds 114 and 113 suggests that the molecule is being straightened enough to allow the nematic phase to be generated, but still has a sufficiently bent-shape (possibly due to conformational changes upon cooling) to allow the formation of the B_1 phase, although at much lower stability than the unfluorinated systems (177 and 88).

The position of substituents at the core of banana-shaped molecules has been shown to radically affect the mesogenic properties[49] and it is therefore a logical progression to evaluate

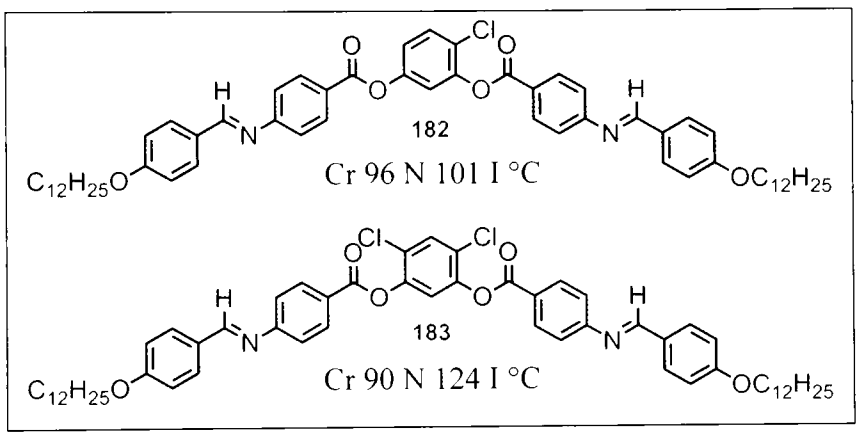
the effect of varying the molecular structure around the trifluoro core used so far, and to also vary the degree, and position of fluoro substitution on the bent-core.



Within these five compounds (84, 179, 181[124], 89 and 178), there are a number of interesting points for discussion, relating to small changes in the molecular structure. The unfluorinated system (84), termed the parent system at the start of this section, is a known compound exhibiting the B_2 phase, and it is interesting to see the change to the nematic phase in compound 178. It is of even greater interest that the mono-fluoro compound (89), which can be classed as somewhere in between the extremes of compound 84 and 178 in terms of fluoro-substitution, results in the exhibition of both the B_2 and the nematic phase (which also exhibits chiral domains).

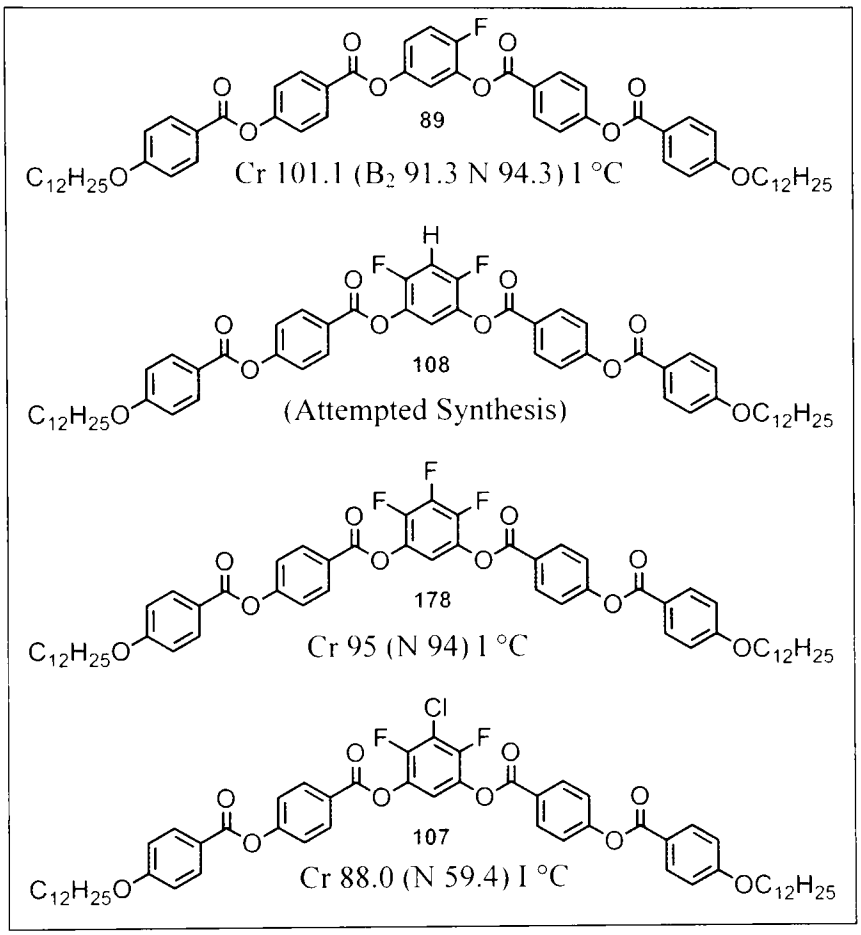
In a calamitic smectic C phase (to which the B_2 is closely related), the introduction of fluoro substituents usually results in a reduction of phase stability[9, 66] and this is exactly what is observed in compound 89 (compared to compound 84), where the addition of a fluoro-substituent has resulted in a reduction of the B_2 phase by approximate 22 °C. However, in the case of compound 89, this is presumably attributable to the straightening effect of the fluoro-substituent, which will disrupt the necessary packing of the B_2 phase, whereas in a calamitic system the resultant reduction in phase stability is due to the steric effect of a lateral substituent adding to the breadth of the molecule. The reduction in banana-phase stability (and therefore the clearing point of the compound) has been somewhat balanced out by the generation of the nematic phase above. It is interesting to note that the nematic phase of compound 89 confers a similar stability to that of compound 178, despite the degree of substitution being substantially different, a trend that would not be seen in rod-shaped systems, where the additional two lateral fluoro substituents would cause a large reduction in liquid crystalline phase stability. By replacing the chloro-substituent of compound 179 with the fluoro (89), there is very little difference in the stability of the nematic phase. However, increasing the size of the substituent even more by the addition of a bromo-substituent (compound 181) results in a reduction of the stability of the nematic phase compared to compounds 179 and 89. Whilst the bromo unit is obviously exerting a similar straightening effect on the molecule, which therefore allows the generation of the nematic phase, the increased size of the bromo unit results in an increase in the breadth of the molecule, which has a detrimental effect upon the stability of the phase. Although the melting point has also been lowered (compared to compound 179), the resultant phases are monotropic. The 'straightening' effect being imparted on the molecule by the bromo and chloro substituents of compounds 179 and 181 could also be attributable to the halogen bonding described previously. However, halogen bonding is stronger for more polarisable halogens, such as iodo and bromo, and weaker for chloro and fluoro. Hence, it would be expected that the straightening effect for the bromo compound (181) will be greater (as a result of the stronger halogen bond), and therefore a higher T_{N-I} would be anticipated (compared to the chloro and fluoro analogues, compounds 179 and 89, respectively). However, the much larger size of the bromo unit will have a detrimental steric effect upon the T_{N-I} due to the breadth of the molecule being increased. Such a reduction in T_{N-I}, caused by the large bromo substituent, would be much greater if only steric effects were present. Similarly, a higher T_{N-I} would be expected for the fluoro compound (89) compared to the chloro compound (179) based on steric effects, but the higher polarisability of the chloro unit just wins out and a slightly

higher T_{N-I} results. The larger chloro- and bromo-substituents have a greater effect on the lower temperature phases of the two compounds (179 and 181). As the lower temperature phases of compounds 179 and 181 are not fully characterised, it is not possible to say whether the B_2 phase of compound 89 has been de-stabilised, or whether it has been lost completely, resulting in the exhibition of a different liquid crystalline phase. However, the effect can be justified by considering the effect of the larger chloro- and bromo-substituents, which will disrupt the packing within the layer structure of the B_2 phase. Within this context, compounds 182 and 183, reported by Matsunaga et al.[47] are particularly interesting, although they were synthesised prior to the birth of banana-shaped liquid crystals research[44] as we now know it.



Compounds 182 and 183 both exhibit a nematic phase, but the phase is enhanced by 23 °C in 183, as a result of both arms being straightened by the effect of the two chloro-substituents, rather than the one substituent in compound 182. As has been previously discussed, there is very little difference in the stability of the nematic phase generated by compounds 89 and 178, despite the varied degree of fluoro-susbstitution. Comparison with compounds 182 and 183 suggests that the additional 'straightening effect' of the substituents of compound 178 should result in a much higher stability compared to the mono-fluoro derivative (89), however this is not observed. The two fluoro-substituents adjacent to the two ester groups will straighten the arms of the molecule, however, the third fluoro-substituent in the 5-position of the bent-core increases the breadth of the molecule and reduces the liquid crystalline capabilities of the compound. This is particularly relevant as the nematic phase is being generated from a bent molecular shape, as a rod-like molecule is normally associated

with the generation of such phases. These considerations led to the attempted synthesis of compound **108** and also an interesting comparison with compound **107**.

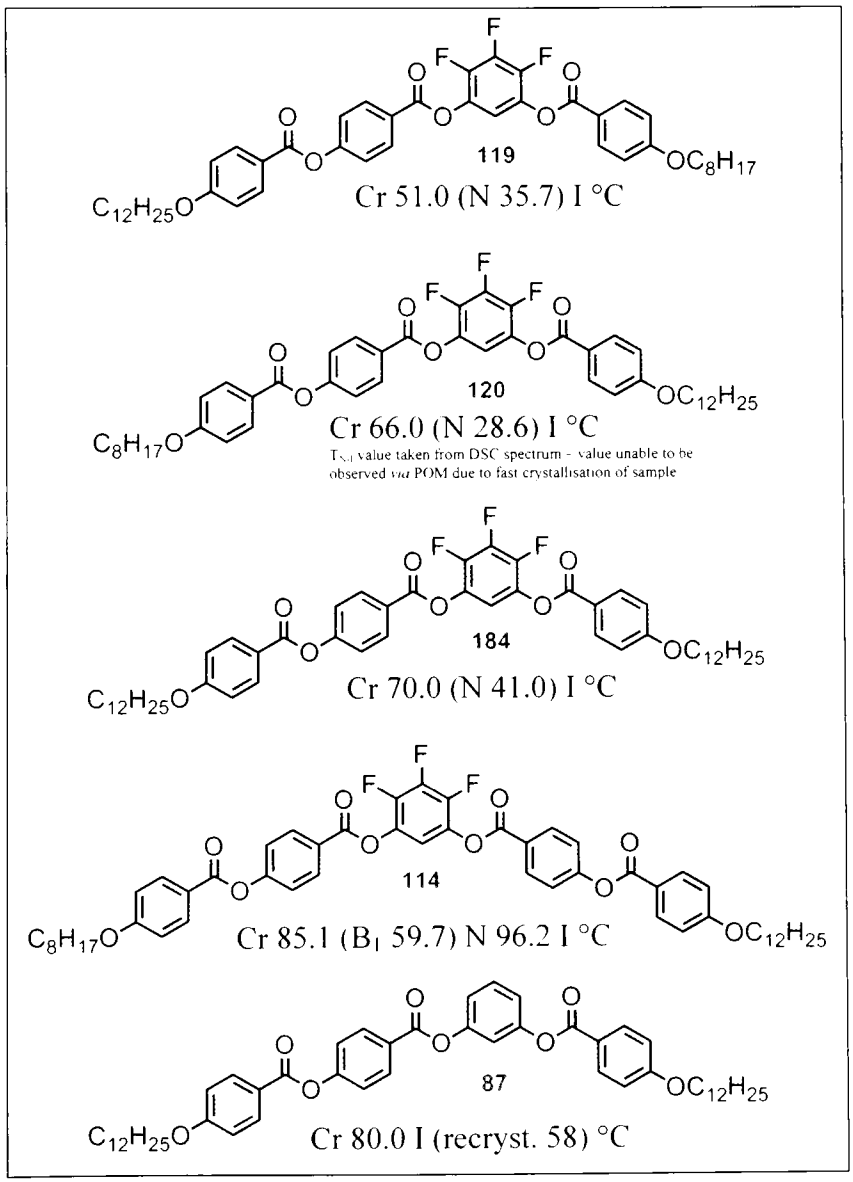


It is unfortunate that to date[c], compound **108** has not been synthesised[d], as it is expected that a similar trend to that seen for compounds **182** and **183** will be observed between compounds **89** and **108**. Despite this setback, the potential pre-cursor to compound **108**, compound **107**, has provided interesting information regarding the position and nature of substituents on the bent-core. Replacing the fluoro-substituent in the 5-position of compound **178** with the chloro-substituent (compound **107**) results in a large reduction in the T_{N-I}, comparable with similar trends in calamitic systems. This can be attributed to the fact that a chloro unit is

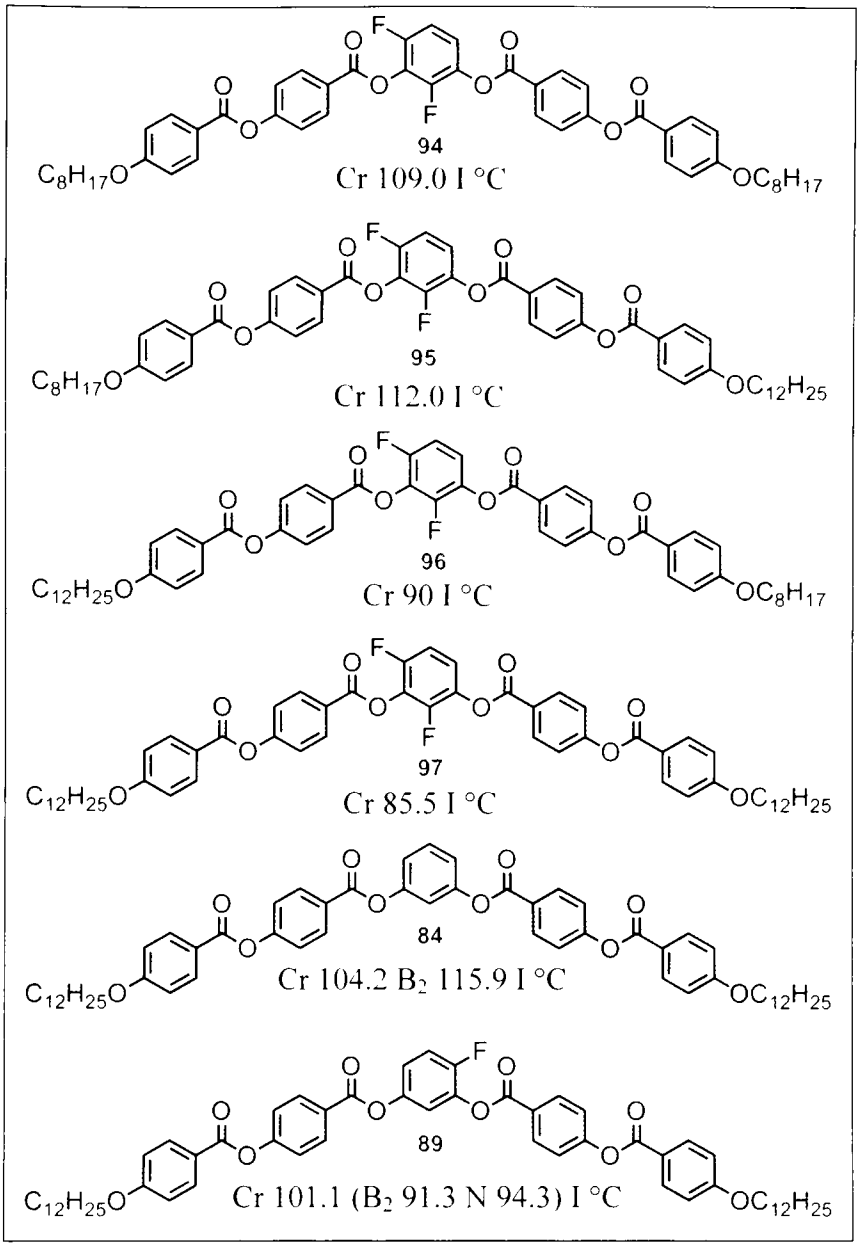
[c] The synthesis of compound **108** is a possible target for future projects within the research group, and will be published / presented upon its successful synthesis and characterisation

[d] Details of attempted synthesis can be found in section 4.2

substantially larger than a fluoro unit and will therefore add significant breadth to the molecule, further deviating from a rod-shape required for the nematic phase. It must also be considered that a fluoro-substituent in the 5-position of the bent-core should also have a derogatory effect on the generation of a nematic phase, compared to having a much smaller hydrogen substituent in the position and therefore it would be expected that the nematic phase stability of compound **108** will be markedly higher than that of compound **178**. In a calamitic system, the increase may be expected to be around 20 °C[102], so it will therefore allow further comparisons between the effect of various substituents on both calamitic and bent-core systems.

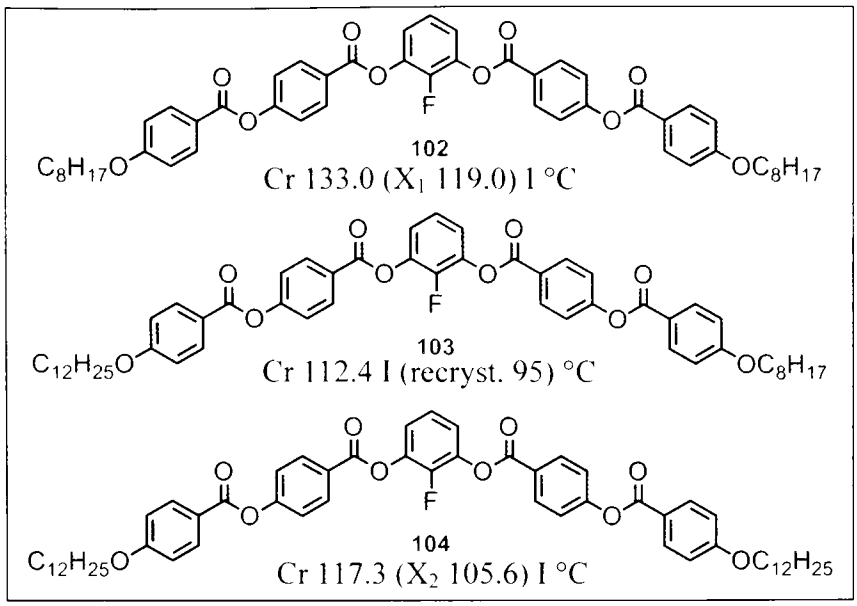


The unsymmetrical nature of compound **114**, compared to the symmetrical system (**178**) resulted in an interesting mesophase morphology. To further investigate the effect of such a structure being unsymmetrical, compounds **119** and **120** were synthesised where the 4-ring architecture, combined with differing alkoxy chain lengths, renders the molecules drastically unsymmetrical. Compound **184**, synthesised by Hird[119] is also a useful comparison. As could be expected for such an unsymmetrical structure, the melting points of compounds **119**, **120** and **184** (synthesised by Hird[119]) have been substantially reduced compared to the five-ring compound (**114**). However, the stability of the nematic phase has also been severely reduced, rendering the phases monotropic. Of the two unsymmetrical compounds, compound **119**, where the C_8 alkoxy chain is attached to the shorter 'arm' of the molecule, exhibits a nematic phase to the higher stability, although this is still a reduction of approximately 60 °C when compared with compound **114**. Where the C_{12} alkoxy chain is attached to the shorter arm of the molecule (compound **120**), the nematic phase is further reduced and is only seen transiently *via* POM. The formation of the nematic phase upon cooling the isotropic liquid also initiates crystallisation of the sample and therefore it was not possible to obtain a value for the T_{N-I} other than the onset value of the DSC thermogram. Compound **184**, with two dodecyloxy chains on its arms, has the highest T_{N-I} value, which would not be expected in calamitic systems, where the nematic phase is favoured by shorter chains. Despite the relatively low phase stabilities of the three compounds (**119**, **120** and **184**), it is interesting to note that they all exhibit a liquid crystalline phase as a result of the trifluoro substituents (an observation which has also been observed for other compounds in the literature[53]), whereas compound **87** (four-ring structure, although identical alkoxy chains), does not exhibit any phases. This indicates that not only do the fluoro-substituents have a positive effect on the melting point (ie. a large reduction), but also favour conventional mesomorphism over banana mesomorphism. Although the T_{N-I} transitions for the three compounds (**119**, **120** and **184**) are quite low, it is interesting to note that such compounds are actually liquid crystalline, given their apparent bent-shape, although this bend will be diminished by the straightening effect of the lateral fluoro-substituents. Any comparable four-ring linear calamitic structures would have an expected T_{N-I} in the region of 300 °C, or possibly even greater[102, 125]. In addition to this, subsequent post-doctoral work has found that employing shorter alkoxy chain lengths in such general structures seems to promote the generation of smectic phases, rather than nematic phases, and again this is not as would be expected in calamitic systems[116, 126].



The difluoro bent-core of compounds **94**, **95**, **96** and **97** were synthesised to explore the straightening effect of the fluoro-substituent in the 2 and 4 positions of the bent-core, adjacent to the ester linkage groups. It was envisaged that the straightening effect of the substituent in the 4-position may be cancelled out by the fluoro-substituent in the 2-position, resulting in a mesophase morphology similar to the parent system (**84**). However, this is not the case, as all four compounds are non-mesogenic. The 'cancelling' effect of the straightening effect may indeed be occurring, but there will also be steric influences relating to the extra fluoro-substituent. The relatively low melting point of compound **97**, compared to compound **89**, means that steric effects must be the decisive factor. If the molecule was

'straight', then a nematic phase would be likely to be seen. If the molecule was 'bent', then a B_2 phase would be the likely result. Although lack of mesomorphism prevents comparison of the mesomorphic properties with other compounds, the melting points of the four compounds do provide some interesting observations. Compounds 94 and 95 both have a C_8 alkoxy chain on the arm of the molecule within the two fluoro-substituents; the melting points are quite similar, and are both significantly higher (approx. 20 – 25 °C) than the melting points of compounds 96 and 97, where the arm of the molecule within the two fluoro-substituents has a C_{12} alkoxy chain. Despite the lower melting points, the two compounds remain non-mesogenic. With the benefit of hindsight, it is possibly not much of a surprise that the B_2 phase observed for compound 84 is no longer exhibited by the difluoro-analogue (97). The B_2 phase, as discussed in section 1.5.2.1 is a layered structure, where the bend of the molecule causes the polarisation to be directed perpendicular to the layers. The fluoro-susbstituents in the 2 and 4-positions of the bent-core will have an antagonistic effect on the polarisation of the molecule at the core, therefore causing a disruption in the packing of the molecules within the layers, in addition to the extra bulk / breadth associated with the substituents. Also, comparison with compound 89, where the single fluoro-substituent results in the formation of both a nematic and a B_2 phase, suggests that the straightening effect seen in compound 89 is indeed cancelled out by the addition of the second substituent in compound 97, resulting in the compound no longer being straight enough to generate a nematic phase, and unable to form a banana phase (B_2) due to the disruption caused by the fluoro-substituents.It is therefore not possible to completely assess the issue of whether one fluoro-substituent is cancelling out the straightening effect of the other one, as the presence of the second substituent inherently causes other polar and steric effects. Whilst the fluoro substituent in the 4-position of the bent-core will confer a similar straightening effect to the arms of the molecule as described previously, the fluoro-substituent in the 2-position of the bent-core will also potentially halogen bond to the carbonyl unit of the ester group, which will result in a similar conformation to that shown in figure 5-3b, particularly if any double halogen bonding between the two arms, and the fluoro substituent in the 2-position of the bent-core occurs. Any enhancement of the bend in this way will therefore further reduce the scope for calamitic (nematic) liquid crystalline phases in these compounds.



Compounds **102**, **103** and **104** were synthesised to investigate the effect of a single fluoro-substituent within the bend of the molecule, in the 2-position of the bent-core. The results observed for these compounds have proved to be some of the most interesting of the bent-core systems synthesised, although to date an exact and accurate characterisation of the liquid crystalline phases has not been able to be made. Synthesis of the three homologues (with variation of the two alkoxy chain lengths) allows for direct comparison with the unfluorinated systems (compounds **84**, **88** and **177**). Compound **102** exhibits a liquid crystalline phase (designated X_1) to a similar stability as compound **177**, although the increase in melting point has rendered the phase monotropic. Although it has not been possible to fully identify the nature of the phase, it does provide some very interesting optical textures, as shown in Figure 5-4. Upon cooling the isotropic liquid, the texture appears as filaments (Figure 5-4a), which upon first consultation look like the beginning of crystallisation. However, further investigation revealed that the phase is indeed reversible (confirmed by DSC measurements), proving the existence of the liquid crystalline phase. Further cooling results in many more filaments being formed, which join and give very straight edges. Throughout the slide there are a number of areas where the texture changes, resulting in the array of pictures seen in Figure 5-4. Picture b shows an area where a number of concentric lines have formed, reminiscent of the textures of the B_7 phase reported in the literature[53, 59, 63, 64]. However, a main characteristic of the B_7 phase is the observation of spiral and helical textures, these were not observed. The B_7 was also discounted as there were many areas of the slide where other textures were present which looked more Schlieren-like in

appearance particularly near the clearing point, such as picture c in Figure 5-4, but no point defects were found. Some areas of the slide such as picture d suggested a texture similar to the B_1 phase, although the jagged and sharp edges present do not coincide with the usual mosaic texture expected for a B_1 phase (such as observed for compound **114**, Figure 5-2). It therefore seems that the B_1 phase exhibited by compound **177** has been lost completely by the introduction of the fluoro-substituent (compound **102**).

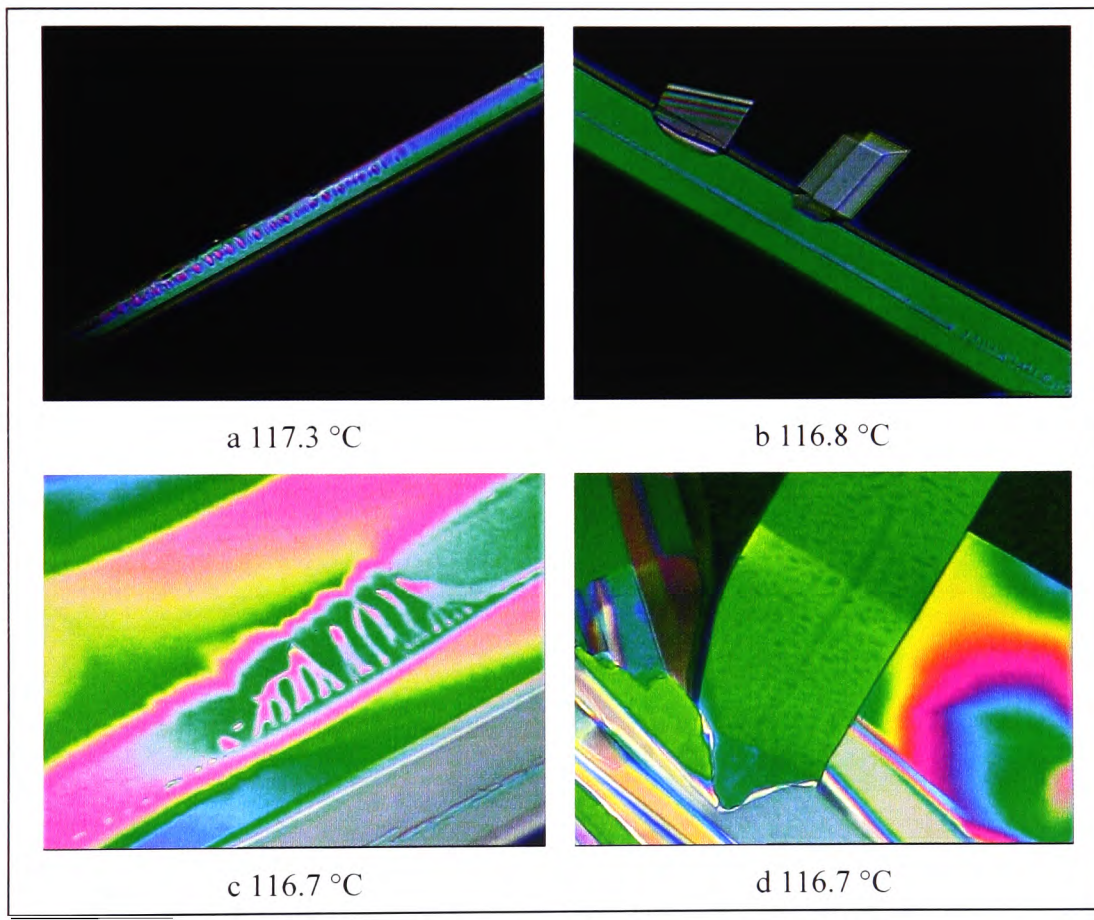


Figure 5-4. Photomicrographs of the unusual textures observed for compound **102**.

Repeated clearing and cooling of the sample provided a slightly different optical texture each time, although the overall appearance remained similar. When the sample was further cooled down, many filaments joined to form larger domains, which again looked almost crystal like in appearance, but were confirmed as a liquid crystalline phase, as they were completely reversible. Some of the larger areas of texture resulted in the observation of chiral domains, characterised *via* a swap in colour between the two domains (Figure 5-5) upon rotation of the

polariser. A sample of compound **102** was also sent to the Hirst research group at the Florida State University who are currently investigating the compound in order to identify and classify the phase. It is anticipated that the results will be published in due course.

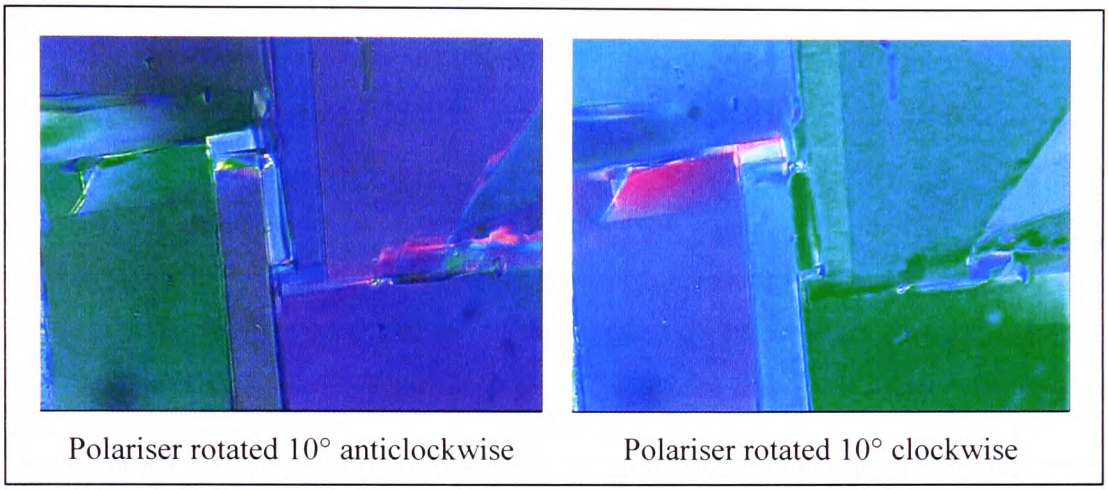


Figure 5-5. Photomicrographs of the chiral domains observed in the unknown phase of compound **102**, 112.9 °C.

Replacing one of the C_8 alkoxy chains of compound **102** with a C_{12} chain presents compound **103**, which despite having a lowered melting point, is non-mesogenic. The main reason for this may be that the compound does not supercool to a large extent, resulting in the sample crystallising before any potential liquid crystalline phase can be exhibited. However, the fact that there are no phases seen at the point of recrystallisation (95 °C) shows that the X_1 phase of compound **102** has at least been reduced in stability by at least 20 °C. The liquid crystalline stability of compound **102** was reduced by 3 °C compared to compound **177**, so therefore assuming a similar effect as observed for compound **103** compared with compound **88**, this would result in a potential liquid crystalline phase being exhibited near to 100 °C, the region where the crystallisation of the sample thus prevents the phase being observed. Again, the slight asymmetry in the two different alkoxy chains destabilises banana phase stability. The negative result obtained for compound **103**, however, is of some help in the assessment of the unkown phases (X_1 and X_2) of compounds **102** and **104**. It is interesting to note that of the three compounds, compound **103** is the only unsymmetrical compound and therefore does not constitute a true banana-shape, nor does it exhibit mesomorphism. Compounds **102** and **104** are both symmetrical and both exhibit, albeit unknown, liquid crystalline phases.

Therefore this would suggest that the unknown phases are 'banana (B) phases', whereas the B-phase is not supported by the unsymmetrical nature of compound **103**. Compound **104** is another very interesting compound, although unfortunately again it has not been possible to fully characterise the exhibited mesophase. As with compounds **102** and **103**, the fluoro-substituent has caused an increase in the melting point, compared to the analogous unfluorinated system (compounds **177**, **88** and **84**), which renders the liquid crystalline phase (designated X_2) monotropic, a reduction of 10 °C compared to the B_2 phase of compound **84**. Upon cooling the isotropic liquid, a very faint 'fog-like' texture is observed, which exhibits domains of opposite handedness when rotating the polarisers by an extremely small amount (< 5 °). However, as soon as the droplets are observed, the sample tends to re-crystallise. Due to this problem it was very hard to prove reversibility of the phase *via* optical microscopy, but a suitable heating / cooling cycle on the DSC provided proof of the reversibility (Figure 5-7). Upon cooling the compound from the isotropic liquid, a transition into the unknown phase is observed at 103 °C. Applying a heating scan just after this transition prevents recrystallisation (observed at 95 °C on the DSC thermogram) and therefore confirms the reversibility of the phase, shown by the peak observed at 105 °C, which does not coincide with the melting point peak. Due to the phase being so difficult to observe from the isotropic liquid, it was not possible to acquire photographs to illustrate the chiral domains. It was possible to take a poor quality picture, which shows the 'fog-like' texture reasonably well when brightened slightly using computer photographic software, as shown in Figure 5-6.

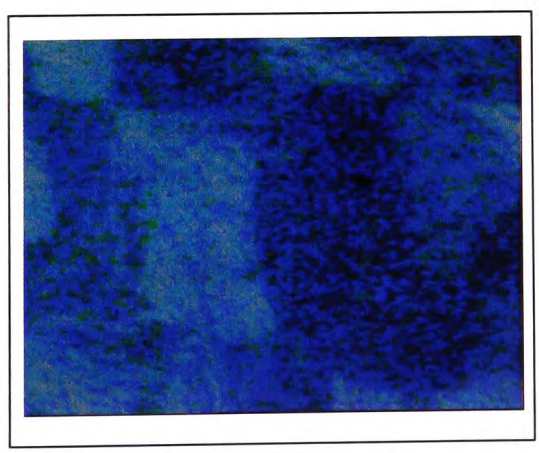
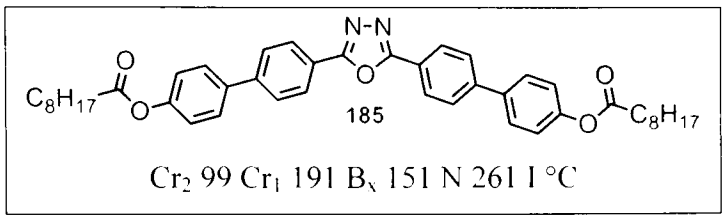


Figure 5-6. Photomicrograph of the 'fog-like' texture of compound **104**, 103.6 °C.

The texture is reminiscent of a blue or cubic phase, which exhibit pseudo-homeotropic textures[102], although this does not provide evidence as to the nature of the observed phase. The faint texture observed is also very similar to the texture and description reported by Kang et al. for compound **185**, where, similarly to compounds **102** and **104**, the phase was designated as B_x[127].



185

Cr_2 99 Cr_1 191 B_x 151 N 261 I °C

Due to the unusual nature, and the small range of the phase before recrystallisation (of compound **104**), it has not been possible to classify the exact phase and therefore can only be designated as X_2. It is hoped that further work may be able to establish the true nature of the phase, but the small range renders this very difficult indeed.

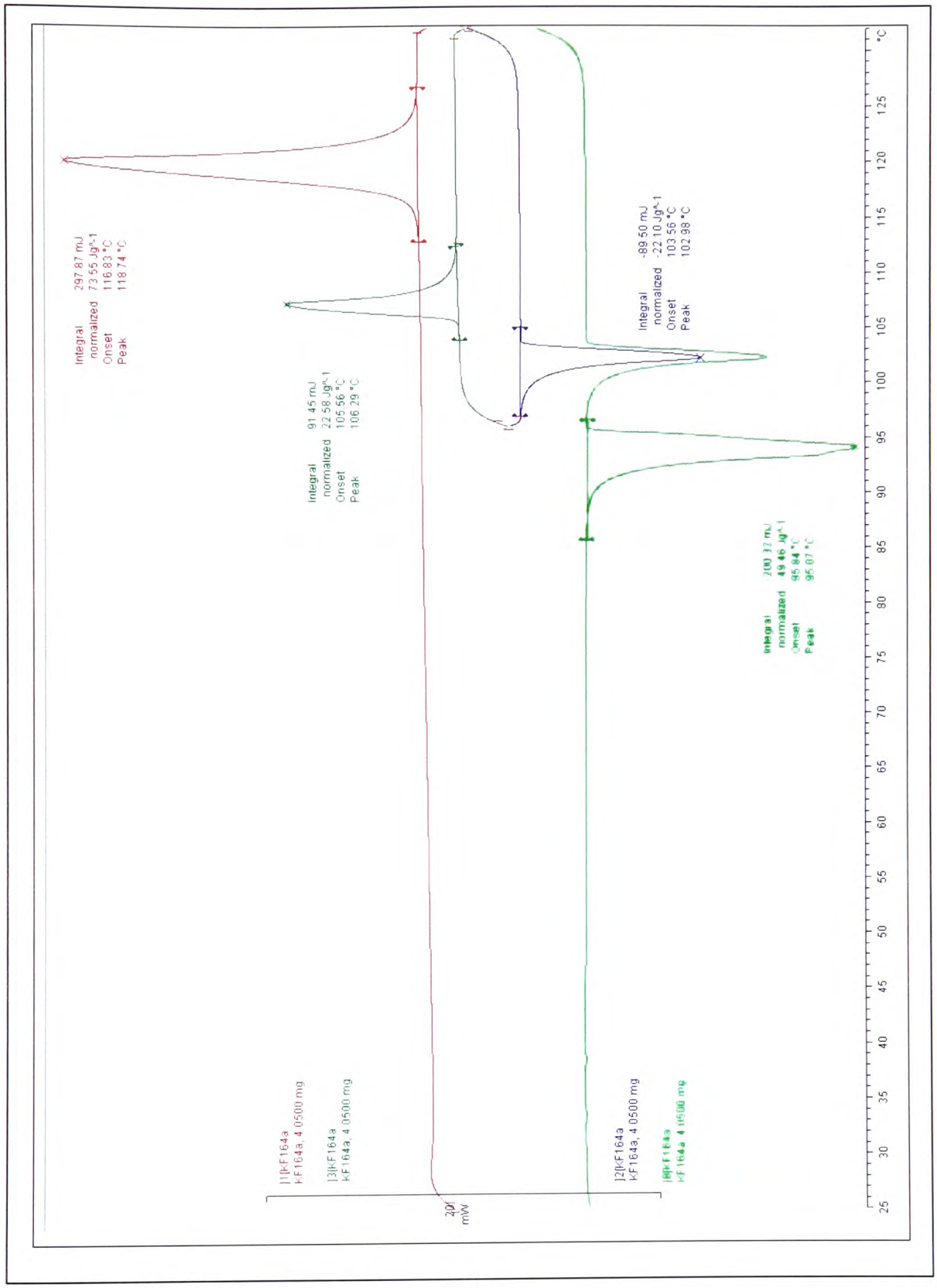
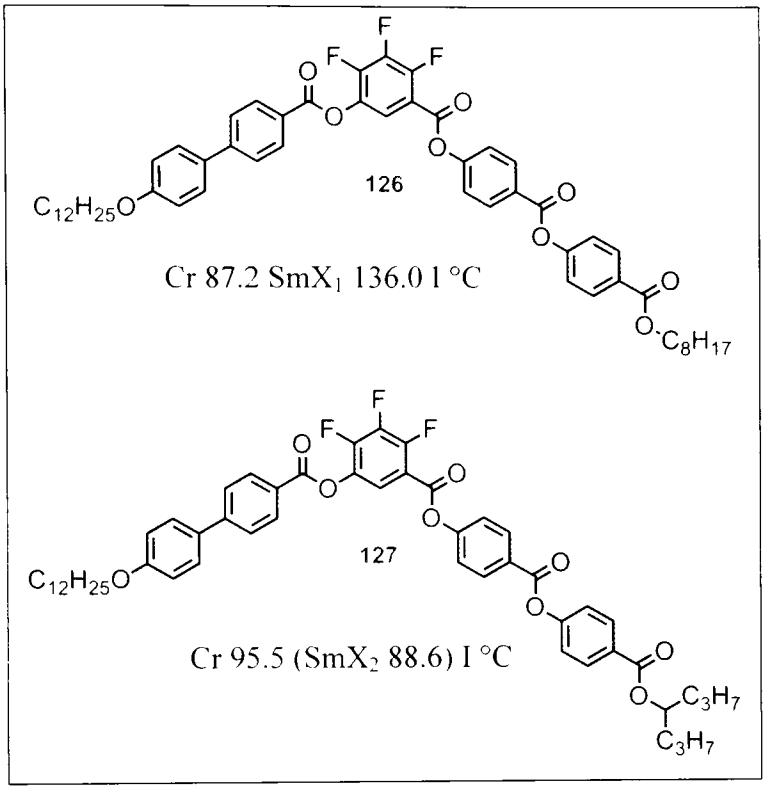


Figure 5-7. DSC Thermogram for compound **104**.

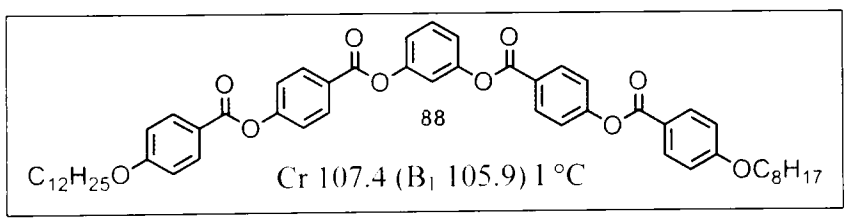
The final two achiral compounds synthesised were actually for comparison with the chiral compounds **165** and **166**, and will therefore be discussed in section 5.2.



Although compounds **126** and **127** are of a banana-like molecular structure, they are not a true banana configuration, as the ester linking groups point in the same direction along the molecule, rather than towards the bent-core, as is the case for the preceeding achiral systems. The phases exhibited appear to be of a smectic nature, which is very interesting, as it would not be expected that such a bent structure would permit the generation of a calamitic phase. However, the fact that a smectic phae is observed shows a link between conventional and banana mesomorphism, as the bent structure of true banana molecules is able to form layered phases (eg. B_2 phase), which is similar to the layered smectic (conventional) phase.

5.1.2 Evaluation by Electrooptic Methods

As discussed in section 1.5, there are eight characterised banana phases (B_1 – B_8), of which the 'smectic-like' B_2 phase has been widely investigated due to its ferro- and antiferro-electric switching properties[49, 118]. However, research and investigation into the properties concerning the other phases has continued and has begun to reveal some very interesting findings. There has been considerable interest in the columnar B_1 phase, as it has been reported that under the influence of relatively high electric fields (>25 V / μm[128]), the B_1 phase of certain compounds can undergo a transition into the B_2 phase, and exhibit ferroelectric switching[118, 128]. Applying electric fields of this magnitude to liquid crystal cells (2-5 μm thick) obviously presents problems concerning sample preparation and subsequent study[118]. It is therefore particularly interesting that Hirst et al., working at Florida State University, discovered a transition from the B_1 phase to a B_2 phase in compound 88, at a relatively low electric field (10 V / μm)[118].



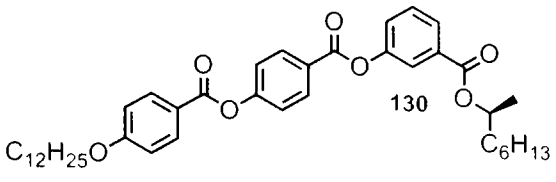
It was found that applying an electric field to compound 88 caused a major structural transition at 10 V / μm, where switching domains grow from the B_1 texture, and underwent ferroelectric switching between a light and a dark state. Of most interest is the observation that after the transition has taken place, the applied electric field can be substantially reduced (<1V / μm), and the material does not relax back into the B_1 texture, therefore producing an almost thresholdless field response. These interesting results provided the basis of a subsequent publication[118].

5.2 Chiral Compounds

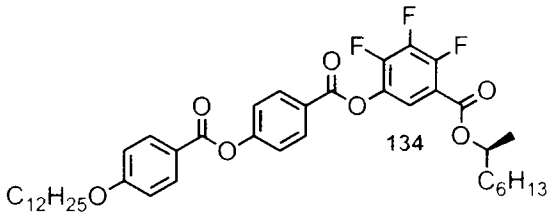
Whilst it has long been a preconception that a linear, rod-shaped molecule is required in order to generate a liquid crystalline phase, the advent of banana-shaped (bent-core) liquid crystals has begun to re-define these molecular constraints. As has been shown in section 5.1 and in thousands of published articles, a vast number of bent molecular shapes have resulted in an ever increasing number of new and exciting liquid crystalline phases, many with varied and interesting properties, such as chiral domains and electroopitcal switching, despite the molecules themselves being achiral. The following section aims to begin an investigation into how introducing a bend (based on the 1,3-disubstitution pattern, as utilised in the achiral compounds of section 5.1) into a more 'conventional' calamitic-type structure affects the resultant 'conventional' mesomorphism and will explore the developinig trends and interesting results / observations obtained.

5.2.1 Melting Points, Transition Temperatures and Mesophase Morphologies

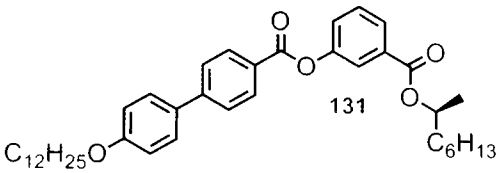
Compounds **130**, **131**, **134** and **135** were synthesised as a preliminary look into how introducing a bent-core into a typical 'calamitic-like' structure affects the generation and stability of potential liquid crystalline phases. Compounds **186** and **187** have been previously reported by Hird et al.[55, 113, 129, 130], and provide an effective starting point from which comparisons can be made. Compound **186** is the dodecyloxy-analogue of the well-known antiferroelectric compound, MHPOBC (discussed in section 1.4.2.1, compound V), and is a three-ring structure, combining rigidity (biphenyl unit) with a degree of flexibility (ester linking groups). The result of this is the exhibition of four smectic phases, over a reasonably large temperature range (~60 °C). Compound **131** is of the same composition as compound **186**, however, the phenyl unit now has a 1,3-disubstitution pattern rather than the 1,4-disubstitution pattern of **186**, which therefore confers a significant bend to the molecular structure. As could be expected, this deviation from a linear molecule results in a dramatic reduction (>70 °C) in the temperature of the SmA*-I transition, due to the bend of the molecule being less able to be accommodated in the layered phase structure. Despite this loss, the mesophase morphology is enantiotropic due to the accompanying reduction in melting point.



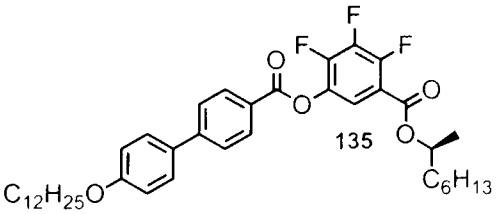
Cr 48.0 (SmC* 47.1) SmA* 52.5 I °C



Cr 42.2 (SmC* 32.5) SmA* 58.5 I °C

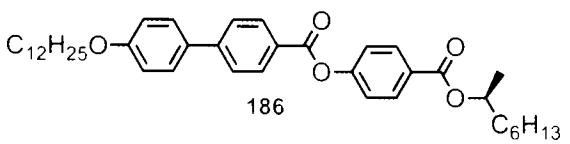


Cr 44.8 SmC* 45.4 SmA* 55.2 I °C

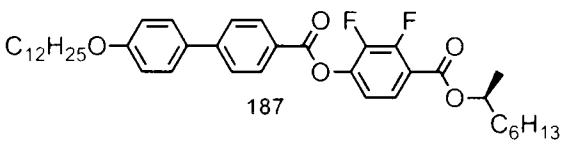


Cr 40.6 (SmC* 30.6[e]) SmA* 64.2 I °C

a) Cr 38.0 (SmX* 30.0) SmA* 70.0 I °C



Cr 72.5 SmC^*_{anti} 107.5 SmC^*_{ferri} 108.5 SmC^*_{ferro} 121.0 SmA* 131.5 I °C



Cr 52.8 SmC^*_{anti} 94.0 SmC^*_{ferri} 95.2 SmC^*_{ferro} 99.5 SmA* 110.0 I °C

Compound 130 has an extra ester linkage compared to compound 131, giving extra conformational flexibility, as the molecule no longer incorporates a biphenyl moiety. This flexibility, combined with the slight lengthening of the molecule results in a slight enhancement of the smectic C phase, but a slight reduction in the smectic A phase stability.

As has been previously discussed in section 5.1.1, the introduction of fluoro-susbstituents, in particular the 2,3,4-trifluoro bent-core unit, has a dramatic effect upon both the classification and stability, of the mesophase generated. Again, with the previous work of Hird et al.[55] in mind, the trifluoro- unit was incorporated into the bent-core chiral structures presented in this

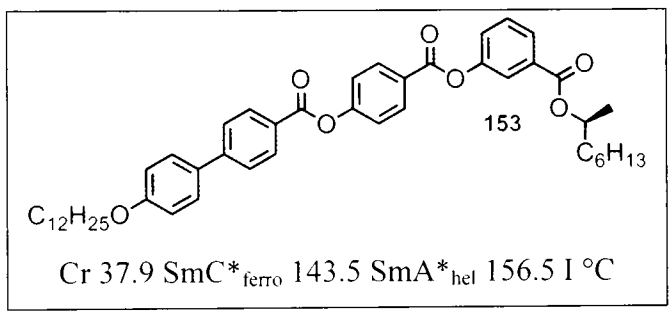
[e] Transition taken from DSC thermogram

chapter. Firstly, the effect of adding fluoro substituents to calamitic, rod-like compounds should be considered. For a calamitic system such as compound 186, the addition of one or more fluoro-substituents would be expected to result in both a reduction in melting point and a reduction in the stability of the smectic phases exhibited[66], due to the increased breadth of the molecule disrupting the packing within the smectic layers. This can be seen in compound 187, where a difluorophenyl unit replaces the unfluorinated phenyl unit of compound 186. The result is a lowered melting point, but also a reduction in the stability of each phase exhibited, particularly the SmA* and SmC^*_{ferro}. It would therefore be expected that adding a bent-core to such a structure, and incorporating a trifluoro- rather than a difluoro- core would result in a catastrophic effect upon the mesophase generation. Whilst the clearing points of compounds 134 and 135 (compound 130 has been previously reported[55], but a higher clearing point was recorded) have been significantly reduced compared to the linear systems 186 and 187, the result is not the catastrophic effect expected.

Comparison of compound 186 with 187 shows the expected reduction in phase stability when the fluoro-substituents are added to the structure. Compound 134 has a clearing point of 58.5 °C (6 °C higher than the unfluorinated system 130), but the SmC* phase has been reduced by nearly 15 °C. This effect is also observed for compound 135, which has an enhanced SmA*-I transition compared to compound 131, but a reduction in the SmC*-SmA* transition. It is interesting to observe that once again the addition of the trifluoro bent-core is having such a dramatic and unexpected effect upon the generation of liquid crystalline phases and it can therefore be assumed that the close proximity of the fluoro-substituents to the adjacent ester groups is again causing a straightening of the 'arms' of the molecule, causing the molecular shape to adopt a more linear conformation than that of the unfluorinated systems. In the case of these smectic systems, it is also of interest how the fluoro-substituents have an opposing effect upon the SmA and SmC phases. This can be rationalised by the considering the structure of the phase themselves. The smectic A phase is an orthogonal, layered structure (as discussed in section 1.3), and therefore it is relatively easy to envisage that a bent molecular shape will be unable to pack into the layers with as much as ease as an equivalent linear system. Therefore the straightening effect of the fluoro-substituents will favour the generation of the SmA phase, as observed in compounds 134 and 135 (compared to compounds 130 and 131, respectively). The SmC phase is also a layered structure, but the molecules are tilted with respect to the layer normal and therefore a bent molecular shape will cause less disruption to the tilted (helical) phase generated. This results in the tilted SmC phase being reduced when the fluoro-substituents are added, due to the 'straightened'

molecules causing a disruption in the tilted packing of the molecules, to a greater extent than for orthoganol molecules of the SmA phase.

The three-ring structures (compounds 130, 131, 134 and 135) provide a good insight into how introducing a bend within typical calamitic-type structure affects the associated mesophases, and in particular the relative abilities of orthogonal and tilted bent-core molecules in a layered liquid crystalline phase. However, the the relatively small (three-ring) molecule limits the potential scope for variation of molecular structure. Extending the work to incorporate a four-ring architecture provided greater potential for variation of structural features such as the position of bend, whilst also increasing the potential for the generation of liquid crystalline phases. Compound 153 is the first example of a four-ring architecture and offers some of the most interesting results.



Cr 37.9 SmC^*_{ferro} 143.5 SmA^*_{hel} 156.5 I °C

Compound 153 is a logical progression from compounds 130 and 131 and is largely of a linear conformation, with the bend being at one end of the molecule and comprising of an extra phenyl ring and ester group compared to compound 131, effectively extending the linear region of the molecule. The result of this structure is an extremely large increase in phase stability and perhaps more importantly for evalutation purposes, range of temperature. In comparison to compounds 130 and 131, the SmA* and SmC* phases of compound 153 are enhanced by just over 100 °C. The increase in clearing point is not solely responsible for the large temperature range, as the very low melting point is helpful in this respect. Indeed, for such a relatively large structure, the melting point is surprisingly low. Initial analysis of the compound *via* POM revealed what appeared to be a SmA* phase, upon cooling the isotropic liquid, followed by a SmC* phase when cooled further. The SmA* phase exhibits regions of focal conic texture, as well as homeotropic regions as would be expected (Figure 5-8a). When cooled below 143.5 °C, a phase transition occurs into the SmC phase, causing the focal

conics to appear 'broken', with dechiralization lines across the backs, and the homeotropic regions become birefringent, an effect that is more exaggerated as the temperature is cooled further (Figure 5-8b and figure 5-8c), again as would be expected for a SmC phase, as the molecules become more tilted within the layers. However, as can be seen in Figure 5-8a, the homeotropic texture of the SmA phase (of compound **153**) is not completely black and exhibits a slight 'mottled' texture (this is very subtle and is not prominent in the photomicrograph).

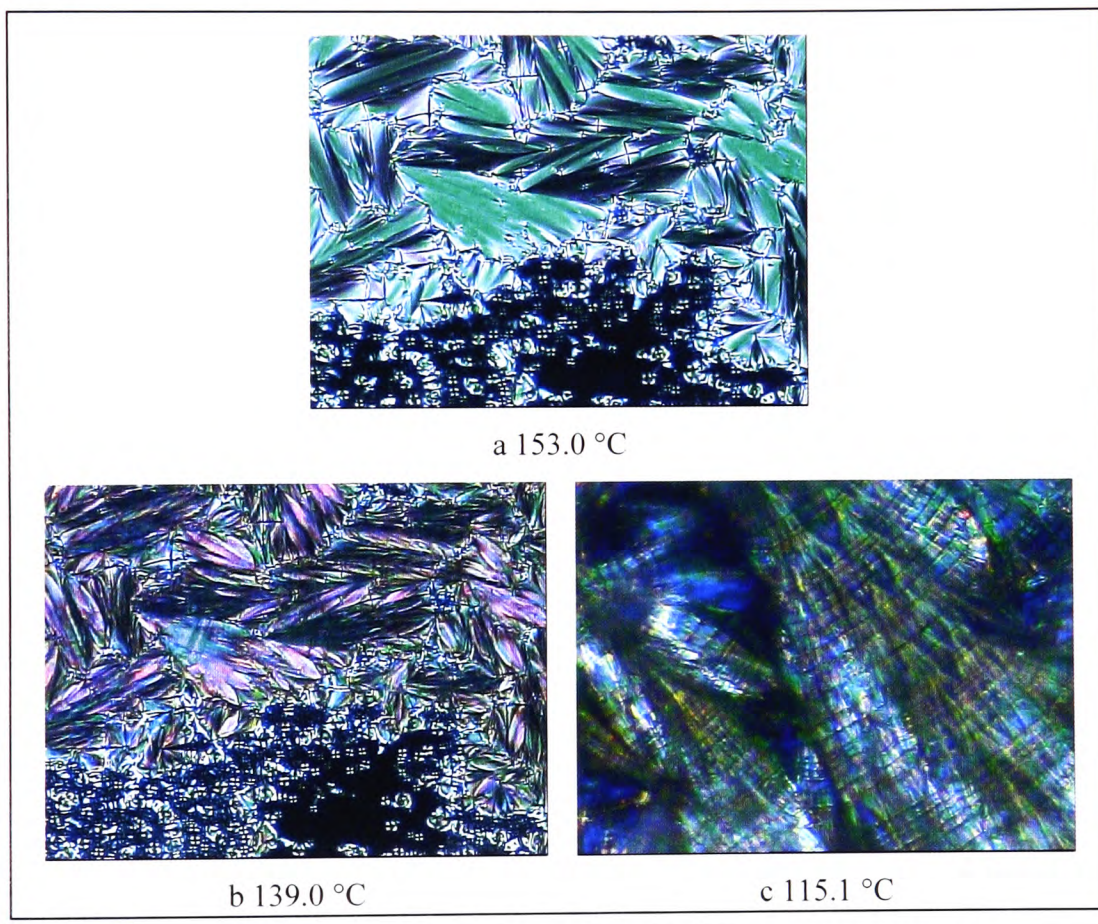


Figure 5-8. Photomicrographs of compound **153** – a) SmA^*_{hel}; b) and c) SmC^*_{ferro}.

Rotation of the polariser to the right by 10° causes the homeotropic texture to remain dark, but enhance the mottled texture. Rotating the polariser to the left by 10° returns a brighter appearance. This would indicate a helical nature to the phase. These effects are, however, very subtle, making a definitive classification of the phase difficult. These observations suggest that the SmA* phase could actually be a SmC* phase, and the transition observed is a

transition into either an antiferroelectric phase, or a second ferroelectric phase. Electrooptical measurements were performed (discussed in section 5.2.2) on compound 153 in order to establish the nature of the two phases. These measurements showed that the lower temperature phase is ferroelectric and that the higher temperature phase does not exhibit any switching, therefore confirming that the higher temperature phase is indeed a SmA* phase. Compound 153 was then reassessed by POM using a free standing film (Figure 5-9). As can be seen in the figure, when viewed with crossed polarisers (Figure 5-9a), the homeotropic region appears near-black in colour, with a slight mottled texture. Upon rotation of the polariser to the left (Figure 5-9b), the appearance is brighter, whereas when rotating the polariser to the right Figure 5-9c), the appearance remains dark. In both cases, however, the mottled texture remains. These observations would also support a helical nature to the phase, as originally thought using a microscope slide. Therefore the phase was designated as SmA*(helical). Figure 5-10 shows a proposed structure for the SmA^*_{hel} phase of compound 153, arrived at after careful consideration regarding the packing of the hockey-stick-shaped bent-core molecules of compound 153 within the layers of a SmA* phase. As can be seen in figure 5-10, it is proposed that the molecules are not packed orthogonal to the layer normal. Instead the longer section of each molecule is tilted, due to the molecular bend. In an achiral system, there would be two possible tilt types arising, therefore resulting in the overall macroscopic structure of a SmA phase (figure 5-10a). However, as is the case with compound 153, the molecule is chiral, and only one direction for the tilt of the longer section is possible, therefore effectively producing a SmC^*_{ferro} phase, along with the associated helical structure. However, as the tilt arises from the molecular bend, rather than the polarity issues normally associated with the SmC* phase and that the tilt will not be affected by variation of temperature, the phase must be of a different type to the SmC^*_{ferro}, and is therefore designated as SmA^*_{hel}. The helical nature of the SmA* phase, and the subsequent switching properties of the underlying SmC* phase (discussed in section 5.2.2), are of considerable interest and were therefore subsequently published[131].

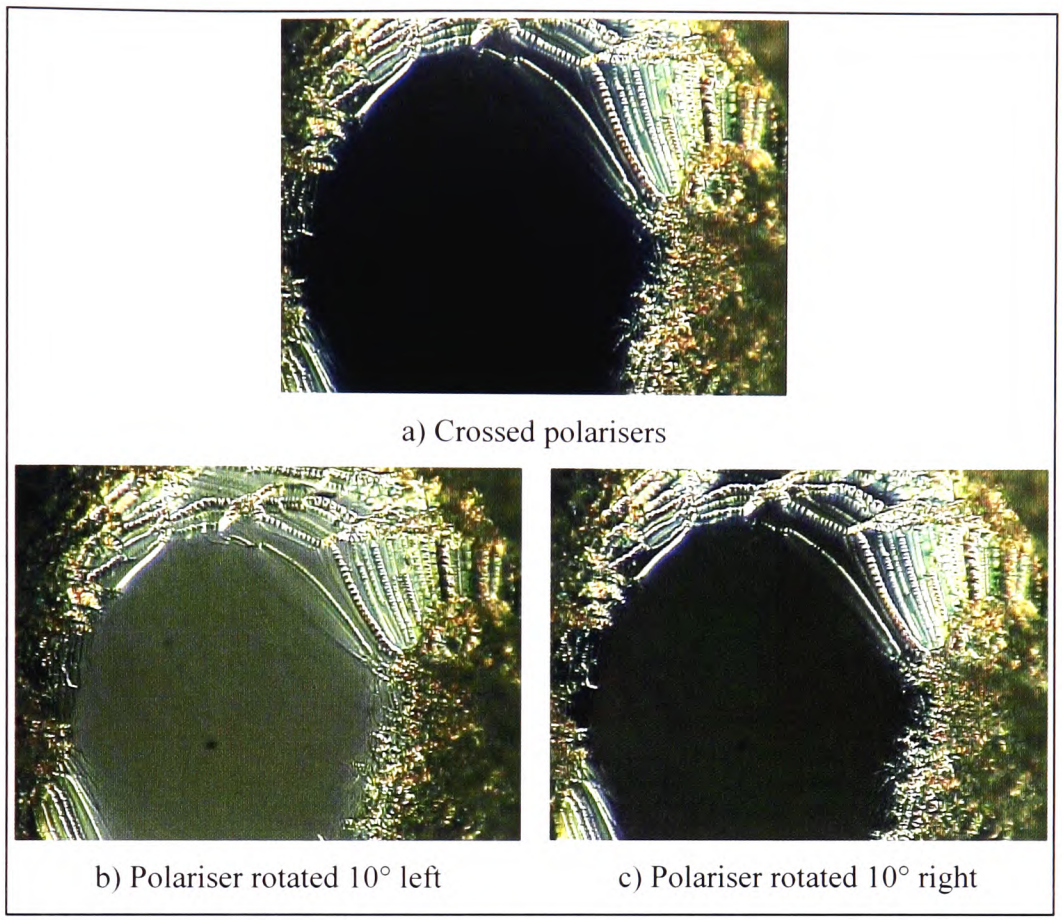


Figure 5-9. Photomicrographs of compound **153**, SmA*$_{hel}$, free standing film, 156.6 °C.

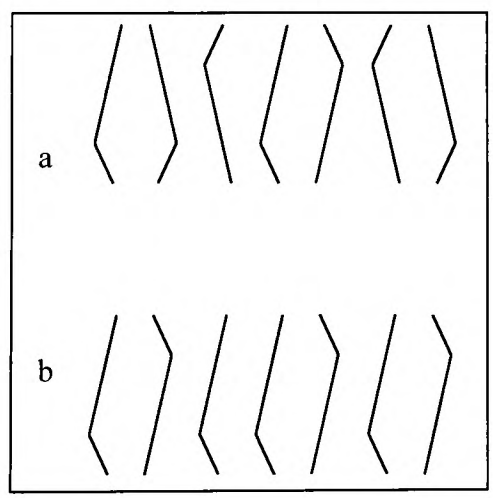
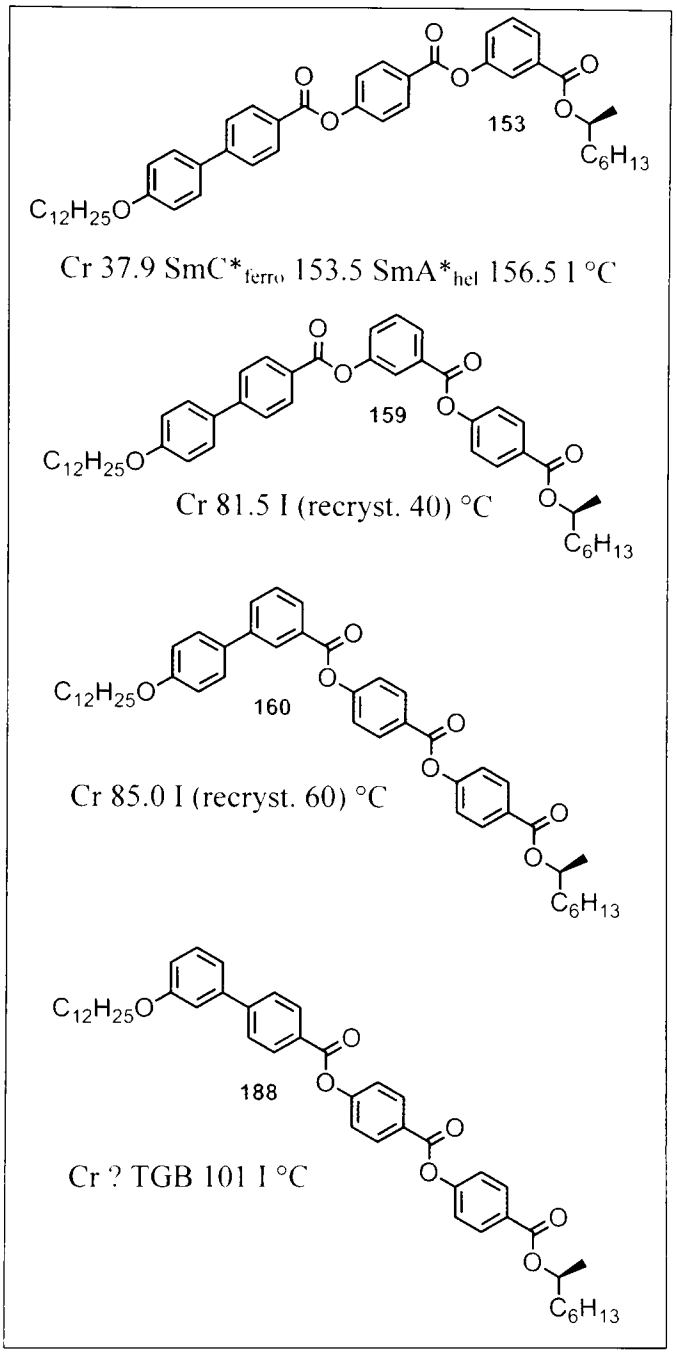


Figure 5-10. Schematic representation of a) conventional SmA phase; b) proposed structure of SmA*$_{hel}$ phase.



As previously mentioned, a motive behind incorporating a 4-ring architecture was the potential to vary the position of bend within the molecule and this was achieved *via* the synthesis of compound **153**, **159**, **160** and **188** (synthesised by Hird[119] at the University of Hull). The variation in position of bend is acquired by changing which of the four phenyl rings is substituted in the 1- and 3-positions, thus creating the 'bent-core'. The interesting mesomorphic behaviour of compound **153** has already been discussed, and makes an excellent compound to allow further comparison. Compound **159** has the bend closer to the

centre of the molecule and this has had a catastrophic effect upon the liquid crystalline stability. A massive increase in melting point compared to compound **153**, is accompanied by a total loss of mesomorphism, despite the compound super cooling to a low temperature (40 °C). Compound **160** also has the bend towards the centre of the molecule, and again this causes a raised melting point, and renders the compound non-mesogenic, despite supercooling to 60 °C. Compound **188** completes the potential sites for position of bend within this series of compounds, with the bend towards the opposite end of the molecule to the chiral centre, ie. the opposite of compound **153**. This results in a molecular structure, that like compound **153** is largely linear, with a bend at one end and in this case causes the exhibition of what appears to be a Twisted Grain Boundary (TGB) phase (Figure 5-11), with a clearing point extremely close to the melting point, making distinction difficult[102].

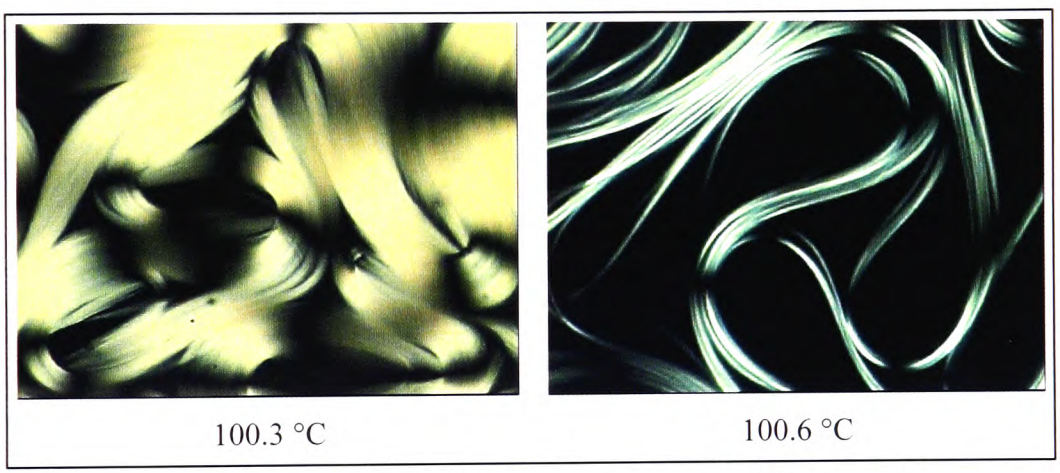
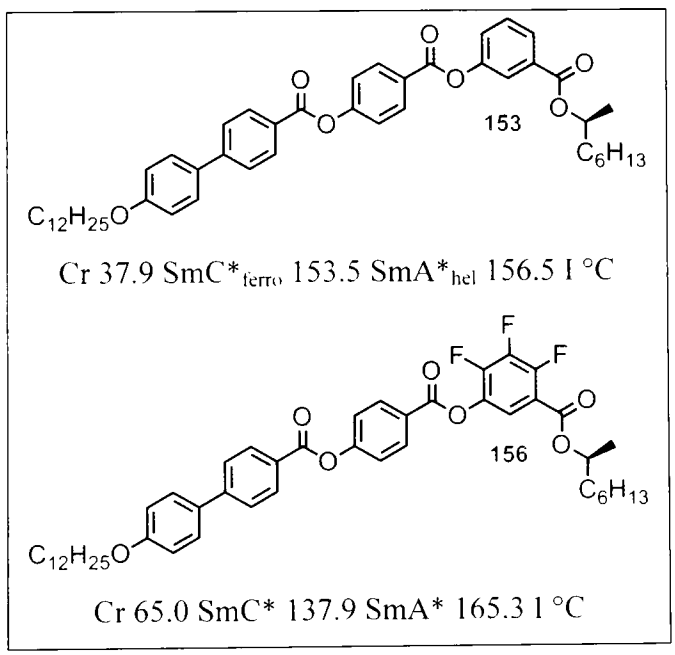


Figure 5-11. Photomicrographs of the TGB phase of compound **188**.

It should be noted that the clearing point (although not a precise value) is substantially reduced compared to compound **153**. In compound **188**, the position of the bend results in the dodecyloxy chain being angled such that it causes a large distortion in the breadth of the molecule, whereas with compound **153**, the position of bend results in only a heptyloxy chain increasing the breadth of the molecule. This difference in carbon chain length can contribute to the liquid crystalline stability being reduced in the compound with the longer chain near to the bend. Also, the heptyloxy chain of compound **153** is attached to an ester group, allowing for conformational flexibility which will further reduce the effect of the chain adding to the breadth of the molecule.

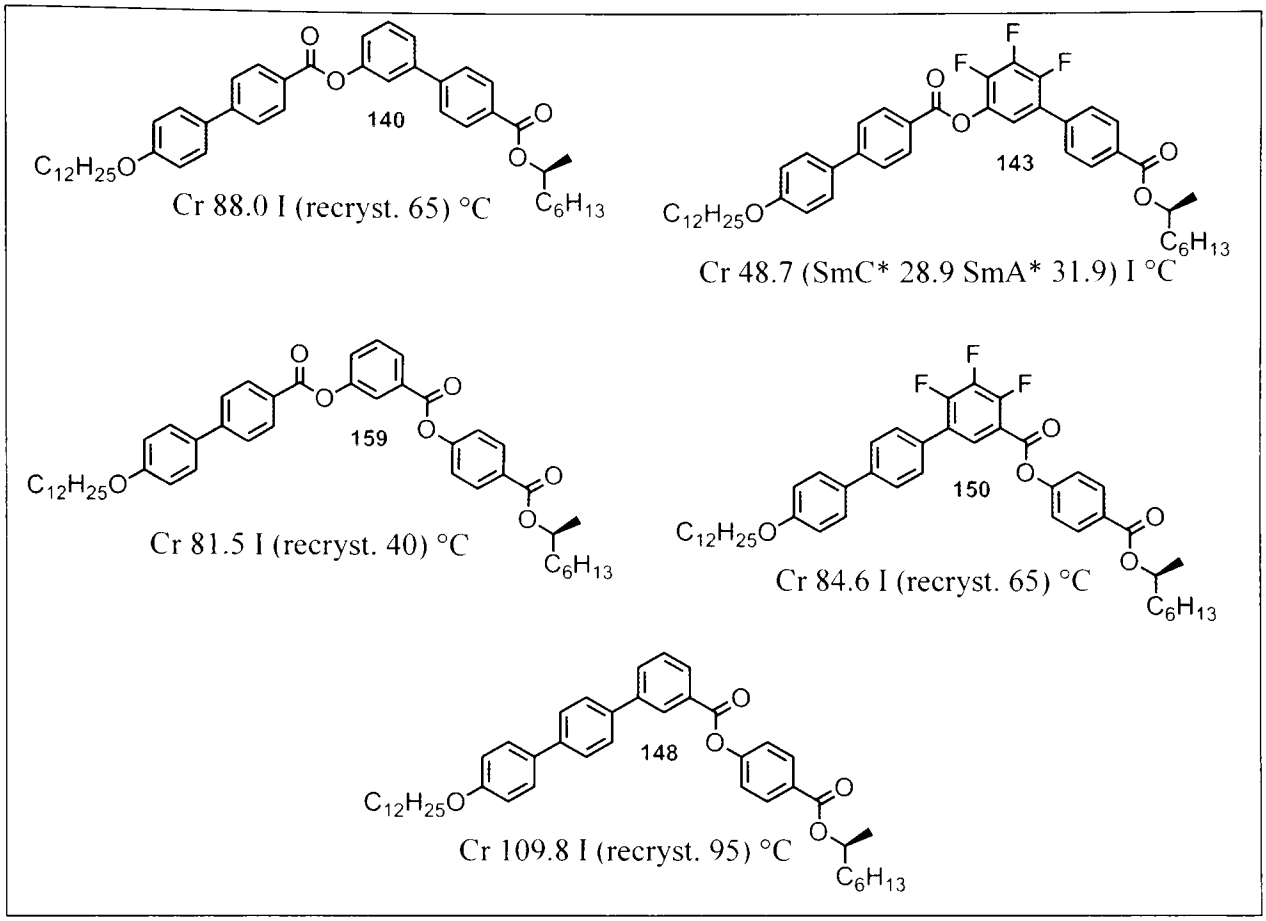
From these four compounds, it is obvious that the position of the bend is having an enormous effect upon the liquid crystalline properties. The two compounds which are largely of a linear conformation (153 and 188) provide interesting mesomorphism, whereas the compounds with the bend towards the middle of the molecule result in a complete loss of mesomorphism. This is an interesting contrast to what is observed in the achiral, 'banana-shaped' compounds, where a 'straighter' molecule resulted in a change of mesomorphism from banana (B) phases to a conventional calamitic nematic phase. However, direct comparisons between the two types of compound can not be made, as these bent-core chiral systems are not typical banana architectures (therefore providing further evidence for the straightening effect from the interaction of a fluoro-substituent with the adjacent ester group), but the overall range of the mesomorphism has been reduced due to the increased melting point. This is presumably attributable to the straightening effect of the substituents, which causes less disruption to the molecular packing, along with the increased polarity from the three fluoro units, therefore generating the higher melting point.



Compound 156 incorporates the trifluoro-substituents into the same structure as the interesting compound 153. Again, the same effect, as seen previously in the three-ring structures, is observed in terms of the relative stabilities of the SmA* and SmC* phases

Although there is an increase in the clearing point of compound 156 (compared to compound 153), the SmA* phase itself does not appear to show the same characteristics as the helical nature exhibited by compound 153. The homeotropic texture observed for compound 156 does exhibit a slight mottled appearance, but does not show any change in colouration upon rotation of the polariser, therefore leading to the conclusion that the phase is in fact a 'standard' SmA* phase. As the molecule is now of a more linear conformation, it does not impart a helical nature to the phase. Compound 153, however, with the greater bend results in a reduction of symmetry, in the same way that the bend within true banana-shaped molecules results in reduced symmetry mesophases. Therefore, a possible link between banana liquid crystals and bent-core systems has been established, and possibly a result which shows that 'bend' is required for reduced symmetry mesophases in achiral systems. It should also be noted that, compounds 153 and 156 follow the same trend observed for other non-fluoro versus fluoro homolgoues, where the stability of the SmA* phase of the fluorinated compound (156), is 9° higher than in compound 153, and the SmC* phase has been reduced by 15°. Again this confirms that the SmC* phase is favoured by bent molecular structures, whereas the more linear conformation of the trifluoro analogue (156) results in a promotion of the SmA* phase.

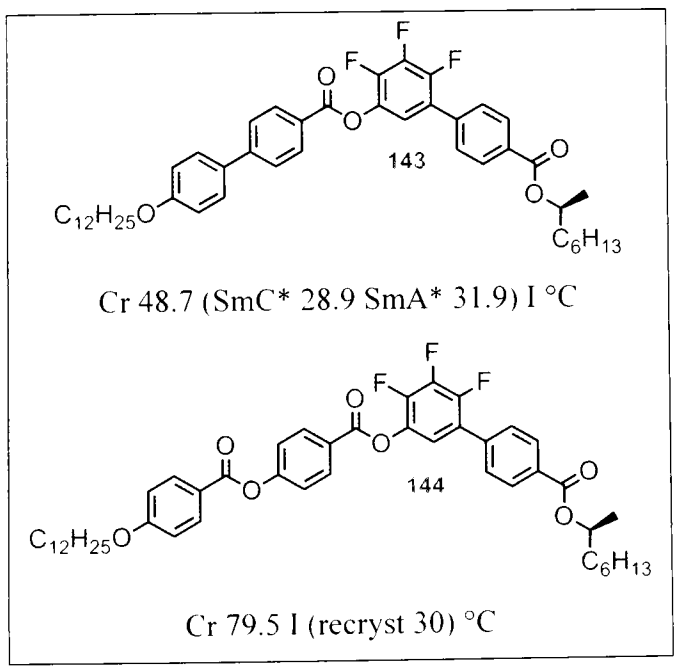
As has been seen in previous examples, the addition of the trifluoro-substituents to the bent-core of these chiral systems has resulted in a positive change in mesophase stability, in respect of the SmA* - I transition. Not only does this provide evidence for the effect that the fluoro-substituents are having, but it also imparts important considerations for future structures, ie. using the trifluoro-unit in order to generate liquid crystalline phases from a structure that otherwise would not be expected to exhibit mesomorphism, therefore providing compounds such as 143 and 150 with the potential to exhibit liquid crystalline phases. Compound 140 is of a similar composition to compound 159, with the bend towards the centre of the molecule, but also incorporating a second biphenyl moiety, through the loss of an ester linkage, which therefore increases the rigidity within the molecule, in this case at the bent-core. Compound 159 is non-mesogenic (as discussed earlier) and it is therefore to be expected that by increasing the rigidity within the molecule (compound 140), the molecule will once again be non-mesogenic, as is observed.



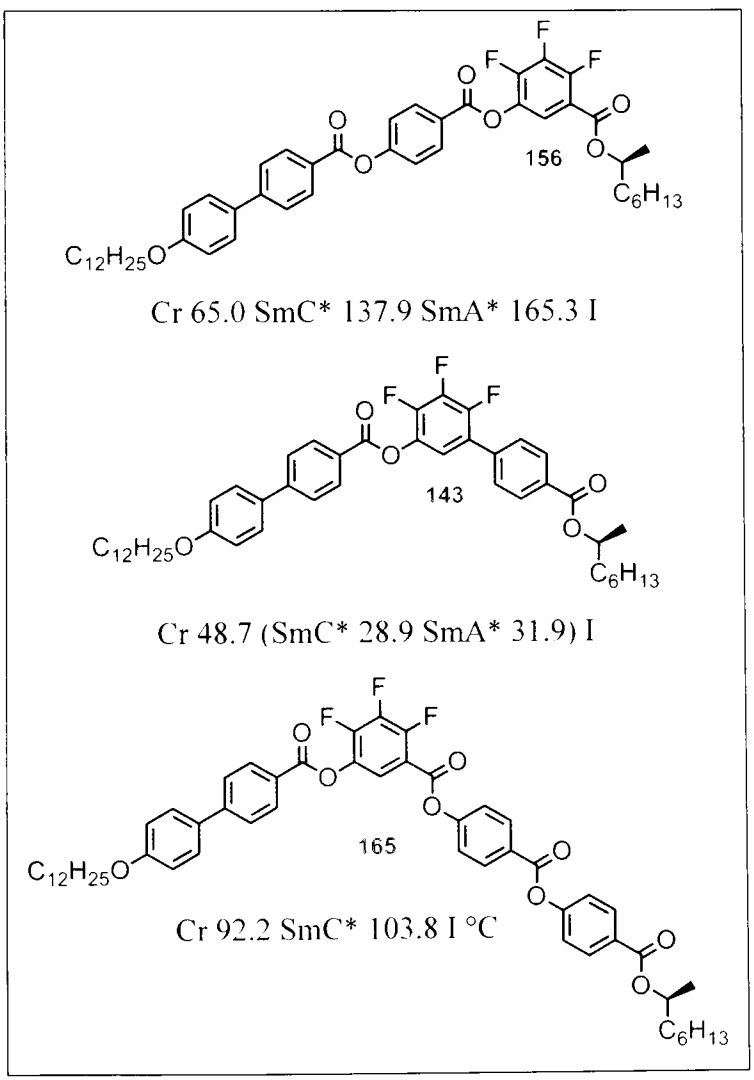
Incorporating the trifluoro- core (compound 143) provided one of the most surprising and interesting results of the research project. Despite the bend being towards the centre of the molecule, and one 'arm' being rigidly linked to the bent-core by a carbon-carbon bond, the effect of the fluoro-substituents upon the single remaining ester unit has resulted in the observation of both a SmA* and SmC* phase, albeit both monotropic. The fact that liquid crystal phases are exhibited at all is as a result of the relatively low melting point. It has been shown by other compounds previously that the fluorinated compounds enhance the SmA* - I transition compared to the unfluorinated compounds. Therefore, the potential clearing point of compound 140 would be expected to be below that of compound 143, around 30 °C or lower. The higher melting point of compound 140 combined with the insufficient super cooling therefore prevents any potential phases being exhibited.

Compound 148 is another variation upon the four-ring structure, incorporating a terphenyl moiety, which increases the rigidity within the molecule. With this increase in rigidity, and again the bend being towards the centre of the molecule, it is not a surprise that the compound is non-mesogenic, and indeed has a higher melting point than compound ,

which will further reduce the scope for liquid crystalline character. Compound **150** has a lower melting point compared to the unfluorinated compound **148**, but despite this, the compound is also mesogenic. Similarly to compound **140**, this lack of liquid crystalline phases is likely due to the relatively high melting point, combined with the insufficient super cooling. The negative result obtained for compound **150** is possibly of more interest than is obvious at first glance, when compared with the positive result for compound **143**. The ester group linkage at the bent-core of compound **143** is directed towards the bent-core, whereas the ester group of compound **150** is pointing away from the core. It can therefore be envisaged that the 'straightening' effect of the fluoro substituent (by halogen bonding) in compound **143** will result in a similar conformation to that depicted in figure 5-3c, for the achiral systems. Compound **150**, however, will be unable to adopt such a structure, as the direction of the carbonyl unit is inherently pointing away from the effect of the fluoro unit and therefore any potential weak halogen bond between the fluoro substituent and the neighbouring ester group will not result in the same 'straightening' effect as seen in other compounds, where mesophase generation has been promoted (as in the case of compound **143** compared to compound **140**). Any potential straightening of the arm of the molecule by the halogen bonding of the fluoro unit with the ester group is, however, irrelevant due to the high melting point of compound **150**, and insufficient supercooling.



The positive result observed for compound **143** prompted the synthesis of compound **144**, where one of the rigid biphenyl moieties has been broken up by the addition of an additional ester group, to generate greater conformational flexibility. As has been observed for many calamitic systems, the addition of an ester group usually increases / enhances liquid crystal phase stability and the potential for smectic phases[102] and therefore it was expected that the monotropic phases of compound **143** would be enhanced by a sufficient amount that may cause them to be enantiotropic. However, this is not the case, as compound **144** super cools to 30 °C, which is lower temperature than the SmA* - I transition of compound **143**, but does not exhibit any liquid crystalline phases.



Compound 165 was synthesised in order to further extend the work to incorporate five phenyl rings, and to extend the promising results of compound 143 and 156, where liquid crystallinity was observed despite the bent and semi-rigid core. Compound 165 incorporates an additional phenyl ring, combined with two additional ester groups, therefore generating greater conformational flexibility, which will be of significant benefit due to the bend being towards the centre of the molecule, which previously has not been conducive to the generation of liquid crystalline phases (compounds 159 and 160, although these were unfluorinated, and therefore do not permit a direct comparison). The molecular structure also results in a molecular shape which is similar to that of a true banana-shape, although the direction of the ester linking groups remain in one direction and therefore a symmetrical shape, as usually associated with a banana molecule, is not achieved. However, with the overall molecular shape being similar, it was considered a possibility that a banana phase may be generated through the employment of a bent 'calamitic-type' molecule, particularly as SmC* phases (closely related to the B_2 banana phase) have been observed for previous compounds within this discussion. Of particular note is the fact that the SmA* phase seen in previous compounds is not exhibited in compound 165 and that only a SmC* phase is observed. This indicates that the structure is now too bent in conformation to be able to be accommodated within the layers of a SmA* phase, despite the straightening effect being imparted on the conformation of the molecule by the fluoro-substituents on the bent-core. Compared to compound 143, there has been a substantial increase in the stability of the SmC* phase in compound 165, which could be expected for the addition of the extra phenyl and ester moieties. The phase is also enantiotropic, despite the accompanying rise in melting point. Initial investigation by POM revealed what appeared to be a SmA* phase, upon cooling from the isotropic liquid (figure 5-12a). Batonet formed, which coalesced to form a focal conic texture. As the sample was cooled further, the focal conic fans developed dechiralisation lines (figure 5-12b) and the homeotropic areas showed differing colours dependent upon rotation of the polariser (figure 5-12c and figure 5-12d), therefore suggesting a transition into a SmC* phase. However, it was not possible to 'pinpoint' an exact temperature at which the transition occurred, and subsequent DSC analysis indicated the presence of only one phase. A second analysis by POM resulted in confirmation that there was just one phase being observed, a SmC* phase. If a sample undergoes a transition from the isotropic liquid directly to the SmC* phase, then the focal conic fans formed often resemble that of a SmA* phase, as the transition from SmA* - SmC* has not occurred which usually results in the observation of 'broken fans'. This would explain the confusion

regarding the initial thought that a SmA* phase was being observed. In addition to this, the effect on the pseudo-homeotropic texture of rotating the polariser was observed throughout the phase range, right up until the clearing point was reached. The dechiralisation lines observed on initial analysis were once again observed and it was discovered that they appeared at approximately 90 °C on cooling, remaining until approximately 73 °C where they disappeared again. This can be attributable to the fact that the pitch length of the helix will change as a function of temperature. In this case, above 90 °C results in a pitch length that is longer than the thickness of the sample being observed, and that below 73 °C, the pitch length becomes too short to be observed by visible light.

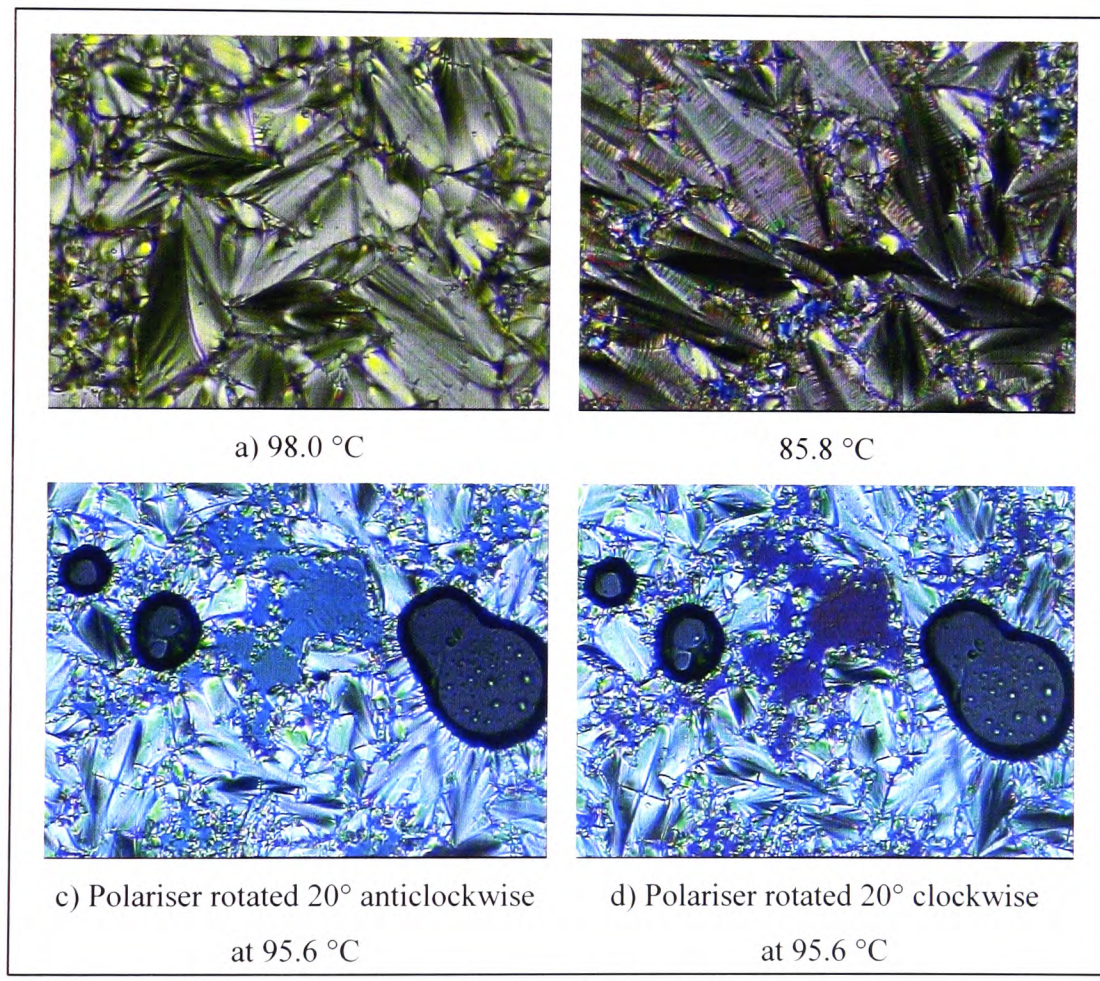
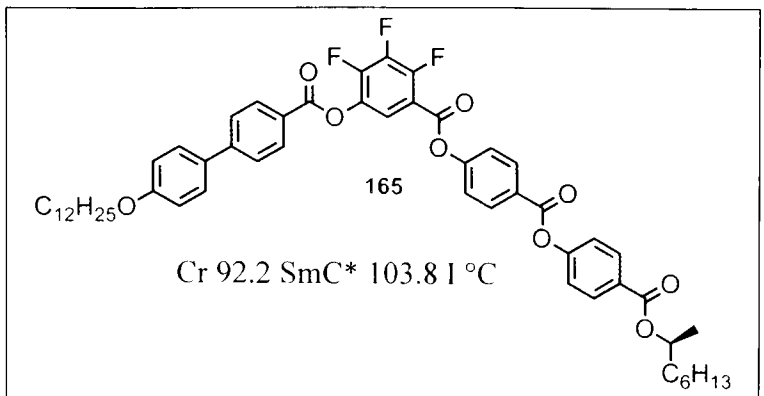


Figure 5-12. Photomicrographs of the textures observed for compound **165**.

These results are certainly interesting, and allowed for a degree of comparison with the achiral banana-shaped syetms previsouly synthesised and analysed. It is interesting to note

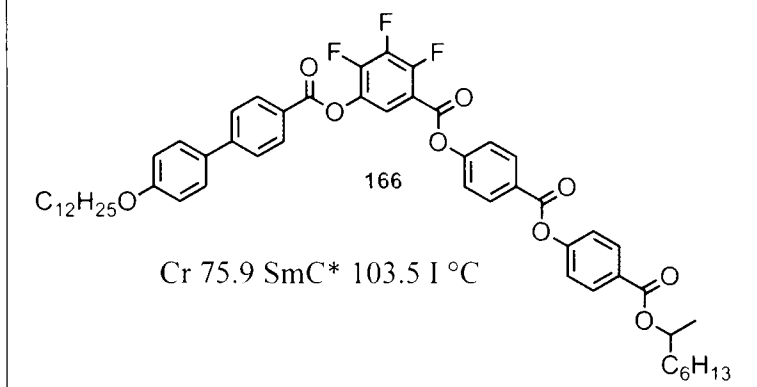
that in going towards a more 'banana-shaped' molecule (although not a true banana as described previously), the result has been the generation of just a single phase (SmC*), which is very similar in phase strucutre to the B_2 banana phase exhibited by many true banana-shaped compounds (eg. Compound 84). This prompted the synthesis of compounds 166, 126, and 127, in order to investigate the effect of removing the chirality associated with the molecular structure of compound 165.

Compound 166 is the racemic version of the enantiopure compound 165. As can be expected with the comparison between a racemic and an entantiopure compound, there is a reduction in melting point, and a very slight reduction in the clearing point, as a result of the compound effectively being a 'mixture', even though it is a mixture of the stereoisomers (*R* and *S*). The formation of the phase upon cooling the isotropic liquid was very similar to that observed for the enantiopure compound 165, where batonet grew and then coalesced to give a focal conic texture. In the case of compound 166, the texture was very much dominated by the focal conic texture (figure 5-13a), although there were some areas where a Schlieren texture was observed (figure 5-13b), and therefore the phase was designated as SmC*, as was compound 165. The most interesting aspect of the texture was the focal conic fans, which exhibited what appear to be dechiralisation lines (figure 5-13a), which would not be expected for a SmC phase generated from a racemic system, as the helix generated by one enatiomer should be cancelled out by the other enantiomer. The observation of the dechiralisation lines lead to the classification of the phase as SmC*, rather than SmC which would usually used to denote a racemic smectic C phase.



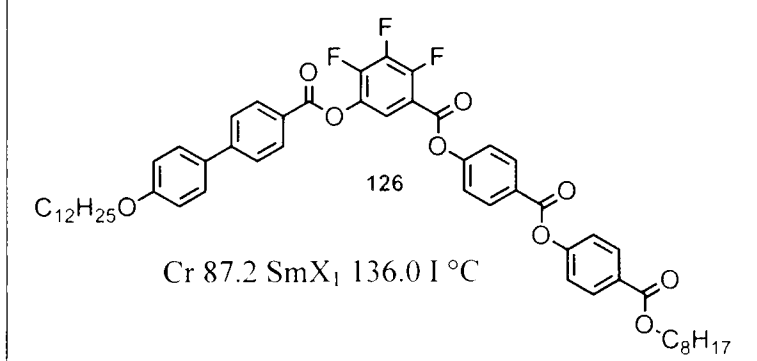
165

Cr 92.2 SmC* 103.8 I °C



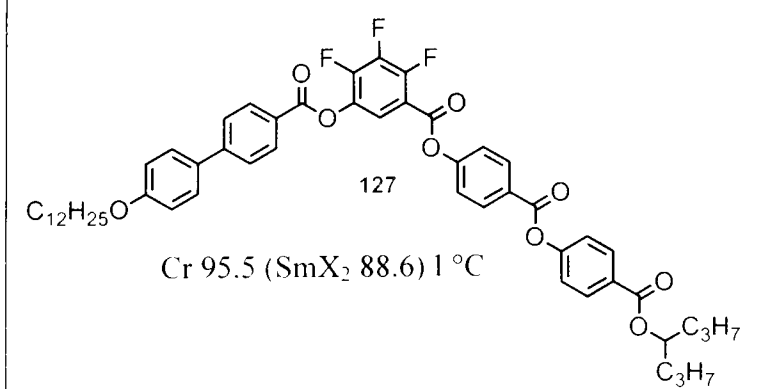
166

Cr 75.9 SmC* 103.5 I °C



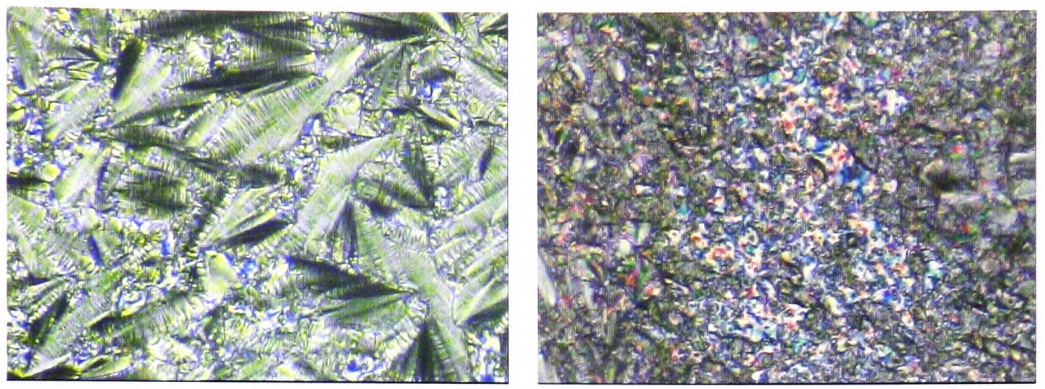
126

Cr 87.2 SmX_1 136.0 I °C



127

Cr 95.5 (SmX_2 88.6) I °C



a) 99.0 °C b) 85.9 °C

Figure 5-13. Photomicrographs of the SmC* phase of compound **166**.

As a result of the observation of the dechiralisation lines in compound **166**, it was considered whether the phase could indeed be a banana phase, as numerous banana compounds have been found to exhibit chiral domains within mesophases, even though the molecules themselves are achiral. In order to further explore these interesting compounds and to further examine the possibility of the generation of a banana phase from such a molecular structure, compounds **126** and **127** were synthesised, both being achiral.

Compound **126** was chosen as an ideal starting point as it is the closest in chemical composition to that of the 'parent' systems (**165** and **166**), where the chiral moiety has been replaced by the achiral, non-branched, octyl chain. The first thing to note is the enhanced phase stability and range in compound **126**. As a result of the alkyl chain no longer being branched (as it is in the chiral compounds **165** and **166**), the clearing point has risen by over 30 °C and a moderate melting point provides a range of nearly 50 °C, a very positive result. As has been seen previously, the optical textures observed for this compound are very interesting. Figure 5-14a shows the phase (designated as SmX_1) growing from the isotropic liquid as jagged batonet, which coalesce to form a focal conic texture. There are a number of regions where the texture is extremely brightly colooured, resembling the mosaic-like B_1 phase (figure 5-14b), but this has been ruled out as the edges seem very straight rather than the 'soft edges' observed for known B_1 phases (for example figure 5-2, compound **114**).

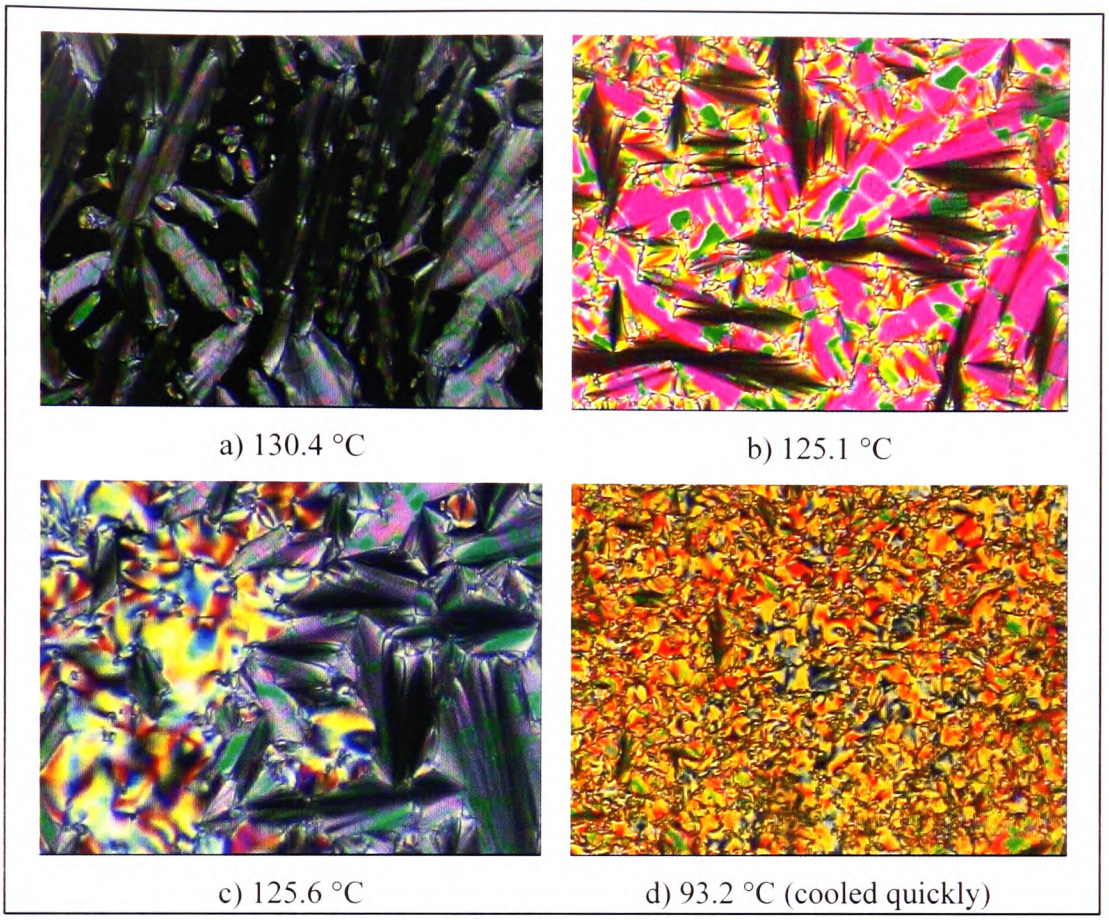
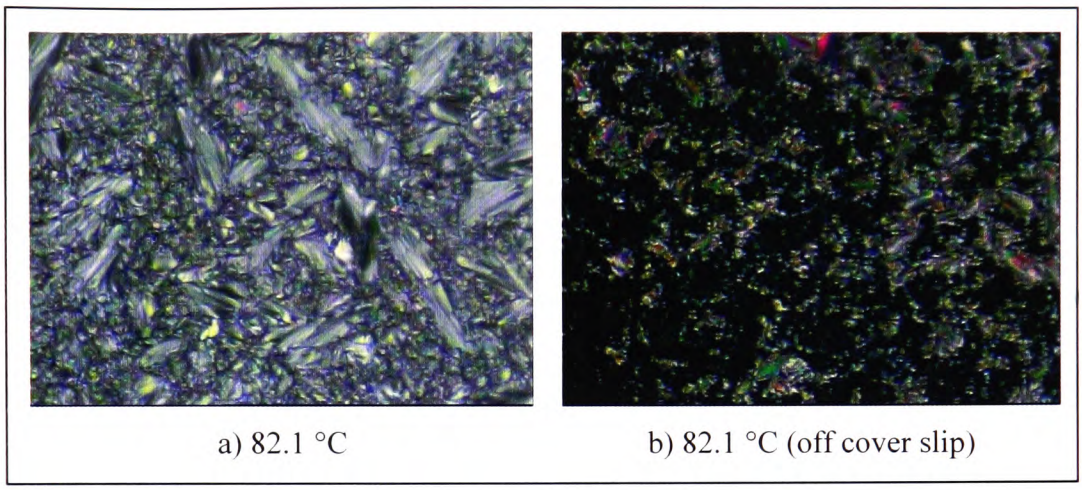


Figure 5-14. Photomicrographs of the SmX_1 phase of compound **126**.

The focal conic texture formed tended to dominate the texture, but there are areas of what appears to be a Schlieren texture (figure 5-14c), particularly if cooled quickly (figure 5-14d). Although these observations would seem to suggest a SmC phase, the unusual textures observed have at present prevented an accurate characterisation of the phase, hence it has been designated as SmX_1.

Compound **127** is also constructed of an achiral molecular architecture, but this time incorporating a symmetrical branched system, with two C_3 chains. As would be expected for comparing a branched system with a non-branched system, the increased breadth to the molecule has caused a substantial reduction in the stability of the liquid crystalline phase[9, 66], which coupled with the increase in melting point (compared to compound **165**, **166** and **126**), has rendered the phase monotropic. Similar to compound **126**, the SmX_2 phase of compound **127** grew in from the isotropic liquid as jagged batonet, which coalesced to a dominating

focal conic texture. However, when looked at closely do not appear as 'sharp', instead looking almost out of focus, as can be seen in figure 5-15a and figure 5-15b (off coverslip).



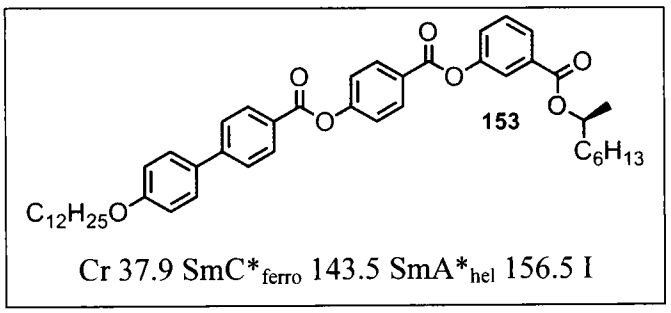
a) 82.1 °C b) 82.1 °C (off cover slip)

Figure 5-15. Photomicrographs of the SmX_2 phase of compound **127**.

It is unfortunate that, to date, it has not been possible to fully characterise and assign a classification to the SmX_1 and SmX_2 phases of compounds **126** and **127**, respectively. However, the four compounds (**165**, **166**, **126** and **127**) have all exhibited interesting optical textures and therefore their full classification will be a target for future work within the research group. In particular, it would be beneficial to investigate the electooptical properties of the materials, which could possibly aid the classification.

5.2.2 Evaluation by Electrooptic Methods

As has been previously mentioned, compound **153** was subjected to electrooptical measurements, in order to aid with the characterisation of the mesophases generated. Initial attempts at alignment of the sample (10 V / μm, 50 Hz, square wave) resulted in the sample adopting a homeotropic orientation. Therefore the sample was cooled from the isotropic liquid under a DC field (10 V / μm). However the alignment obtained was poor, dominated by a focal conic texture. Measurements were carried out applying an electric field of 10 V / μm, and a frequency of 30 Hz.



Cr 37.9 SmC^*_{ferro} 143.5 SmA^*_{hel} 156.5 I

The initial reasoning for conducting electrooptical measurements on compound **153** was to assess the higher temperature phase (subsequently termed SmA^*_{hel}), however, the phase showed behaviour consistent with that of a classical SmA* phase (no noticeable electrooptical switching or spontaneous polarisation). Measurements on the lower temperature phase of compound **153** identified the phase as being ferroelectric, exhibiting a single peak in the current response. However, the measurements also revealed some rather interesting and unusual results regarding the tilt angle and spontaneous polarisation. The transition from a SmA* to SmC^*_{ferro} normally shows a gradual, second order manifestation of the tilt angle, reaching a maximum of approximately 25°[132-134]. As can be seen in figure 5-16, a first order transition is observed for the development of the tilt angle (transition in the DSC thermogram is also observed to be first order), with a 20° tilt obtained when only 1 °C into the SmC^*_{ferro} phase, and then continuing to a maximum of 39° upon further cooling. The spontaneous polarisation of a compound usually parallels that of the tilt angle, but in compound **153**, this is not the case. As can be seen in figure 5-16, the spontaneous polarisation is manifested in a second order manner, obtaining a maximum of 50 nC cm^{-2}.

This value is very low, especially when combined with the high tilt angle (39°) obtained. To put these values into context, the classical compound MHPOBC (which has a comparable structure, incorporating the same chiral moiety as compound **153**), has a maximum spontaneous polarisation of 130 nC cm^{-2}, and a maximum tilt angle of 23°[132-134].

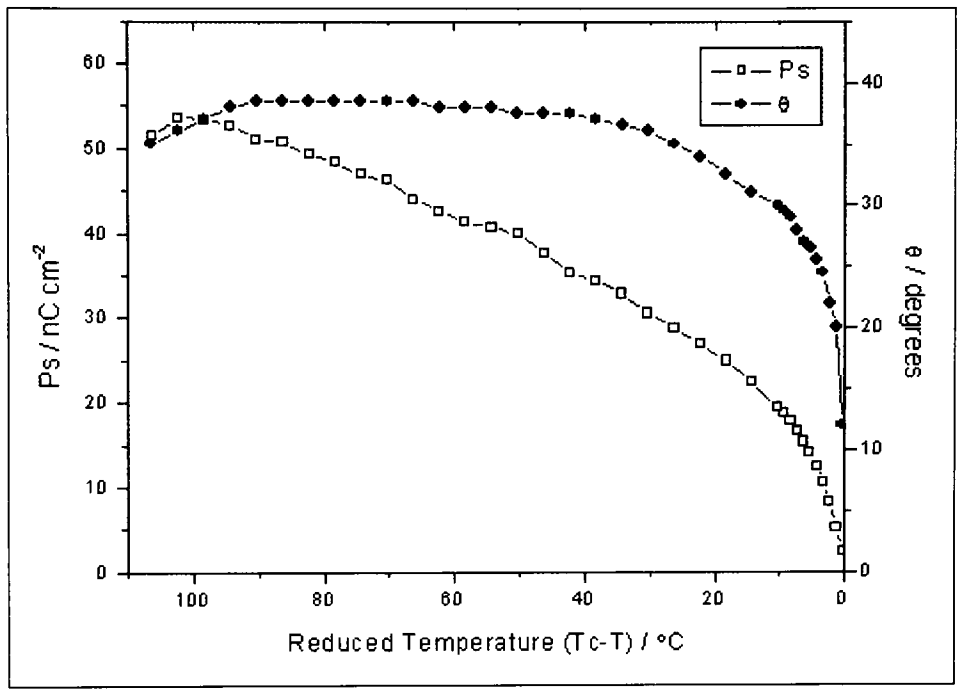


Figure 5-16. Graph showing tilt angle and spontaneous polarisation measurements as a function of temperature for compound **153**.

These interesting results, along with the unusual nature of the SmA^*_{hel} phase discussed in section 5.2.1 are published[131].

6. Conclusions and Summary

6.1 Achiral Compounds

A number of achiral, bent-core (banana-shaped) compounds have been synthesised, and their mesomorphic properties assessed. The introduction of asymmetry within the molecular architecture, and its resultant effect upon banana-phase generation, has been achieved by altering the chain length of the terminal alkoxy chains, along with reducing the number of phenyl rings from five to four (thereby moving away from a perfect, symmetrical 'banana-shape', eg. Compound 87). For the unfluorinated achiral systems, introducing asymmetry results in a reduction in the clearing points, and dependent upon alkoxy chain length, also a change in the nature of the banana phase exhibited, for example compound 84 generates a B_2 phase, whereas the unsymmetrical compound 88 generates a B_1 phase.

Of particular interest within the work of this thesis concerns the straightening effect upon the molecule, as a result of the interaction between the fluoro-substituent(s) and the adjacent ester linking group(s). Reduction of the degree of bend within the molecule, which confers a more-linear conformation to the molecular shape, facilitates the generation of conventional mesomorphism in the form of a nematic phase. Whilst this could be expected, in comparison to compounds such as 179 and 180, a possible reasoning for the observation of a nematic phase from such a bent-core structure has been discussed in section 5.1. In agreement with the literature[74, 77], chiral domains were also observed within the optical textures of the nematic phases generated.

The effect of varying the position, and degree, of fluoro-substitution on the bent-core was also investigated. In the case of the di-fluoro compounds (94, 95, 96 and 97), this resulted in a complete loss of liquid crystallinity, possibly as a result of the relatively high melting points. However, the mono-fluoro compounds, with the substituent between the two 'arms' of the molecule (compounds 102, 103 and 104) generated some interesting observations with regard to the optical textures exhibited (as described in section 5.1). It is unfortunate that to date it has not been possible to characterise the phases exhibited by compounds 102 and 104, and this will therefore be a subject for further work.

It is also interesting to note the electrooptical switching properties of compound [illegible], as demonstrated by Hirst[118].

6.2 Chiral Compounds

In addition to the achiral systems synthesised in order to assess the effect of asymmetry and degree of bend within a 'banana-shaped' system, the effect of introducing a bent-core to a linear, calamitic-like system was also investigated, whilst also combining the effect of the addition of trifluoro-substituents to the same bent-core. It is interesting to note the drastic effect of moving the position of the bend within the molecular structure (compounds **153**, **159**, **160** and **168**), which resulted in mesomorphism only being generated when the bend was towards one end of the molecule, thus minimising the deviation from linearity. The most significant results obtained have been for compound **153**, where the very low melting point allowed for a large range of mesomorphism, in the form of both a SmA*, and SmC* phase. In addition to this, it was found that both of the two phases exhibited interesting properties. It was found that the SmA* phase did not exhibit typical SmA* character, and was therefore subsequently termed SmA^*_{hel}[131]. It was also found that the SmC* phase was ferroelectric, possessing a very low value for Ps, despite a high tilt angle.

The effect of the addition of fluoro-substituents to the bent-core of the chiral structures results in the same change in structural conformation as described for the achiral systems, and results in an opposing effect upon the SmA* and SmC* phases. The straightening of the molecular conformation, as a result of the interaction between the fluoro-substituent and the neighbouring ester group, promotes the SmA* phase, where the more linear structure can be accommodated more efficiently within the layers of molecules lying orthogonal to the layer normal. However, the tilted SmC* phase is favoured by the molecules with a greater degree of bend within the molecular structure, ie. the unfluorinated systems. This trend is observed for comparable systems throughout the results of the chiral compounds synthesised.

7. References

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