THE UNIVERSITY OF HULL

The Synthesis and Properties of Liquid Crystals with Bulky Terminal Groups for Bookshelf Geometry Ferroelectric Mixtures

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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 a substantial research effort over the last century, particularly when the beneficial applications such as Liquid Crystal Displays (LCDs) were realised and developed. The changes to the molecular structure of liquid crystals can have a significant effect upon their mesomorphism and ferroelectric properties. Most of the research in liquid crystal for display applications concentrates on the design and synthesis of novel mesogenic cores to which straight terminal alkyl or alkoxy chains are attached. However, little is known about the effects upon the mesomorphism and ferroelectric properties of varying the terminal chains.

The synthesis and mesomorphic properties of a systematic range of *ortho* difluoroterphenyls with a bulky terminal chain are detailed. The bulky terminal chain consists of either a tertiarybutyl group or a trimethylsilyl unit, each separated from the core by a short (dimethylene) chain, with the other terminal chain being either octyloxy or heptyl. Unusually for liquid crystals with bulky terminal chains, the smectic phase stability (particularly smectic C) is upheld by more than the nematic phase stability, and in most cases the smectic C phase stability is actually higher than comparable analogues with conventional unbranched terminal chains. It is postulated that the surprisingly high smectic C phase stability results from a phase separation effect due to the incompatibility of the spherical bulky group and the conventional unbranched terminal chain, hence implying that the smectic 'layers' are well defined, and such definition of the layers bodes well for bookshelf geometry in ferroelectric mixtures.

Two mono- and four trifluoroterphenyls with a bulky terminal chain were prepared in this work to study the effect on the mesomorphic behaviour of varying the degree of fluoro substituents upon the multi-ring system. Two chiral *ortho* difluoro-substituted terphenyl compounds were prepared also in this work for future ferroelectric mixtures.

Publication and Presentations

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

- The synthesis and mesomorphic properties of liquid crystals with bulky terminal groups for bookshelf geometry ferroelectric mixtures, I.A. Radini, M. Hird, *Liquid Crystals*, 2009, **36**, 1417-1430.
- Synthesis and mesomorphic properties of liquid crystals with bulky terminal groups for bookshelf geometry ferroelectric mixtures, I.A. Radini, M. Hird, **poster presentation** at the 12th International Conference on Ferroelectric Liquid Crystals, Zaragoza, Spain, August 2009.
- Synthesis and mesomorphic properties of liquid crystals with bulky terminal groups for bookshelf geometry ferroelectric mixtures, I.A. Radini, M. Hird, **poster presentation** at the 23rd British Liquid Crystals Society Annual Conference, Bristol, April 2009.
- Synthesis and mesomorphic properties of liquid crystals with bulky terminal groups for bookshelf geometry ferroelectric mixtures, I.A. Radini, M. Hird, **poster presentation** at the 22nd International Liquid Crystals Conference, Jeju, Korea, June, 2008.
- Synthesis and mesomorphic properties of liquid crystals with bulky terminal groups for bookshelf geometry ferroelectric mixtures, I.A. Radini, M. Hird, **invited oral presentation** at the 11th International Conference on Ferroelectric Liquid Crystals, Sapporo, Japan, September 2007.

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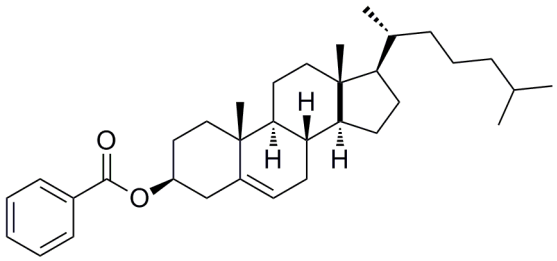
Finally, I would like to give my deep thanks to my wife Sara, my kids and my parents for their continuous support and encouragement without which this work could not have been under taken.

Contents

1 Introduction

Reinitzer and Lehmann[1-3] reported the first examples of unusual melting behaviour of an ester of cholesterol (compound **1.1**). They soon realised that they had discovered one of the most exciting properties arising from a wide family of synthetic and natural compounds. Liquid crystals have been for a long time the subject of scientific interest since the advent of this fourth state of matter in addition to the known states of solid, liquid, and gas.



1.1

A simple definition of mesogen or liquid crystal-forming material is that when a liquid crystal melts from a solid, it exhibits one or more thermodynamically stable intermediate states called mesophases, and it then finally becomes an isotropic liquid. The word 'mesophase' is derived from the Greek word 'mesos', meaning between, or intermediate[4]. In the overall change from solid to isotropic liquid, there is a stepwise breakdown of the molecular ordering, the molecules can rotate and oscillate rapidly about one or more axes[5]; and there is a stepwise collapse of their long range positional ordering, and finally disruption in the short-range order, but the orientational order remains[6]. A liquid crystal mesophase could be defined as an elastic fluid-like ordered state. There are only about 50 liquid crystal phases so far defined compared to the 230 crystalline space groups[7].

Molecules in a liquid-crystalline state are free to move around as in an isotropic liquid, however, they tend to orient in a preferred direction with one another, breaking the isotropy of the physical properties of the system. Liquid crystals are anisotropic meaning that their physical properties are not identical in all directions, and the

anisotropy of the optical, electric, elastic and magnetic properties has led to the use of liquid crystal materials in display devices and as sensors[8]. These liquid-crystalline phases are usually identified using an optical polarising microscope in conjunction with differential scanning calorimetry (DSC) and X-ray diffraction studies.

1.1 Types of Liquid Crystal Mesogens

There are two main families of liquid crystals: thermotropic and lyotropic liquid crystals[9] (figure 1.1). The thermotropic liquid crystals exhibit liquid-crystalline mesophases on melting from the crystal phase or cooling from the isotropic liquid, whereas the lyotropic materials exhibit liquid-crystalline mesophases when mixed with a particular solvent.

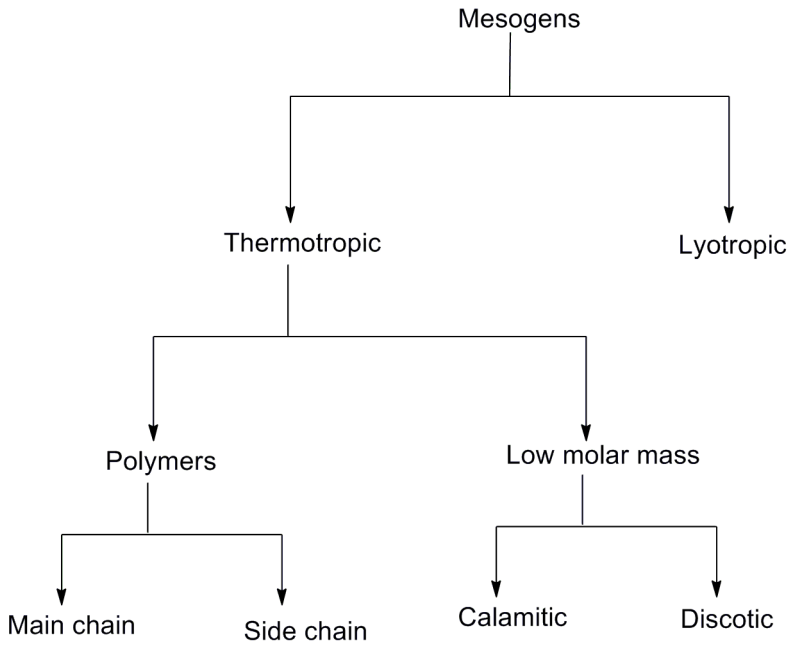
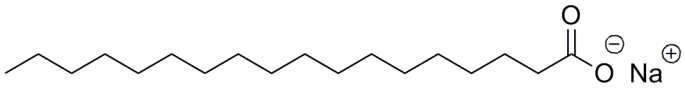


Figure 1.1. The different classes of Liquid Crystals.

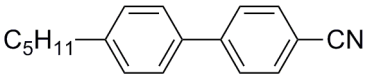
'Lyotropic' liquid crystals are comprised of amphiphilic molecules, where one end of the individual molecule is hydrophilic, and one end is hydrophobic, such as compound **1.2**[10]. Upon interaction between the compound and an appropriate solvent (usually water) at a certain concentration, the molecules arrange into spheres, rods or discs, called micelles[10, 11], and it is upon this basis that lyotropic liquid crystals are prevalent in everyday life. Examples include soap and detergents, whilst not so obvious examples include the structural conformation of biological phospholipid membranes[12]. Lyotropic

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



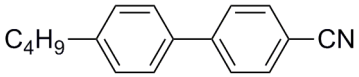
1.2

Thermotropic mesogens exhibit liquid crystal mesophases on heating or cooling, and the temperature range over which the mesophases are exhibited varies from material to material. When a material displays a mesophase both on cooling and heating the mesophase is called an enantiotropic mesophase (*e.g.*, compound **1.3**). However, when the mesophase is solely displayed on cooling from the isotropic liquid, and below the melting point of the material, the phase is called a monotropic phase (*e.g.*, compound **1.4**)[10].



C 24.0 N 35.0 I

1.3



C 48.0 (N 16.5) I

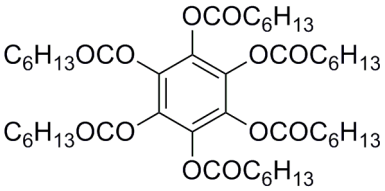
1.4

The term calamitic means that the molecules are rod-like with a high length to breadth ratio. Calamitic liquid crystals[13] are the most common type of thermotropic liquid crystals. The molecules are generally composed of a core unit with two terminal alkyl or alkoxy chains and, in some cases, lateral substituents are present (figure 1.2). The material incorporates a rigid central core system, which maintains the rod-like shape of the molecule and encourages the ordering of the molecules necessary to form mesophases. The type of rings, A and B, that can be incorporated into this core system are varied, from aromatic rings (usually 1,4-disubstituted-phenyl rings *e.g.*, compound **1.3**) with or without heteroatoms, to alicyclic rings, cyclohexyl rings, bicyclo[2.2.2]-octanes and cyclobutyl rings.

Figure 1.2. A general structural template for calamitic liquid crystals.

In the 1970s, working at the University of Hull, Gray and his team synthesised the 'cyanobiphenyls'[14] which have since become an integral feature of the liquid-crystalline nomenclature. The most familiar compound synthesised by Gray was 4-cyano-4'-pentylbiphenyl (**1.3**), or '5CB' as it has become known.

Discotic liquid crystal molecules are usually disc shaped[9, 15] molecules composed of a core based on benzene or triphenylene[13] to which several peripheral groups are attached. Discotic liquid crystals have two basic types of mesophase: columnar and nematic. Columnar mesophase are polymorphic (similar to smectic phases). Compounds such as **1.5** were established as thermotropic liquid crystals by the work of Chandrasekhar in 1977[16]. Other molecular shapes have also been shown to exhibit a variety of liquid-crystalline phases, such as 'wedge-shaped'[17], 'T-shaped'[4] and 'banana-shaped'[18].



C 68 Col_h 86 I

1.5

1.2 Liquid Crystal Phases

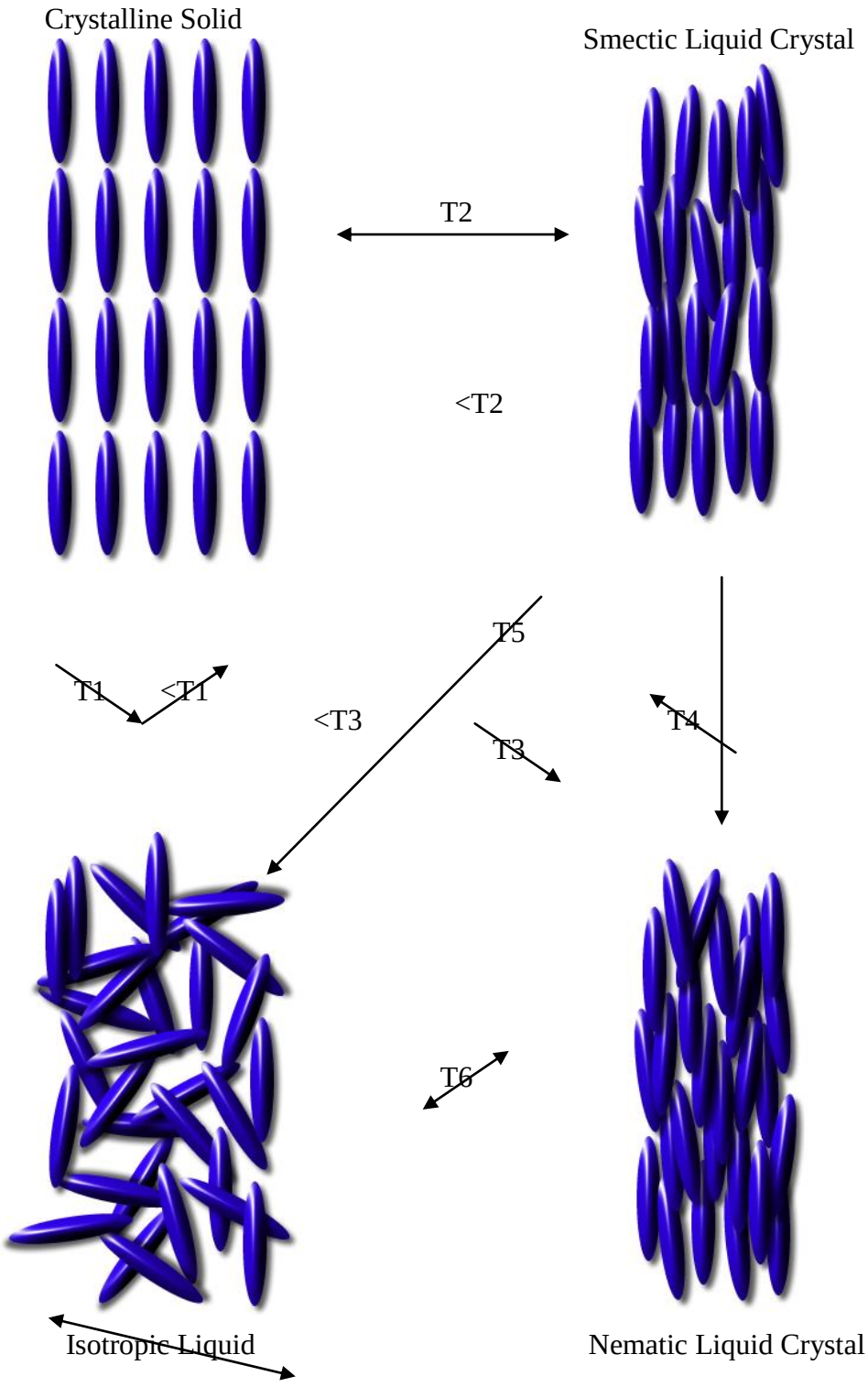


Figure 1.3. Possible melting sequences of thermotropic liquid crystals , adapted from reference[4].

The melting behaviour of Calamitic Thermotropic Liquid Crystals is illustrated in figure 1.3. When heating the crystal, the thermal motions of the component molecules will increase in intensity. At the melting point, the molecules have enough energy to overcome the lattice energy, and the lattice breaks apart. T_1 is the melting point of a non-mesogenic material, T_2, and T_3 are crystal-to-liquid crystal mesophase transition temperatures. T_4, T_5, and T_6 are transition temperatures between liquid crystal mesophases or between a liquid crystal mesophase and the isotropic liquid.

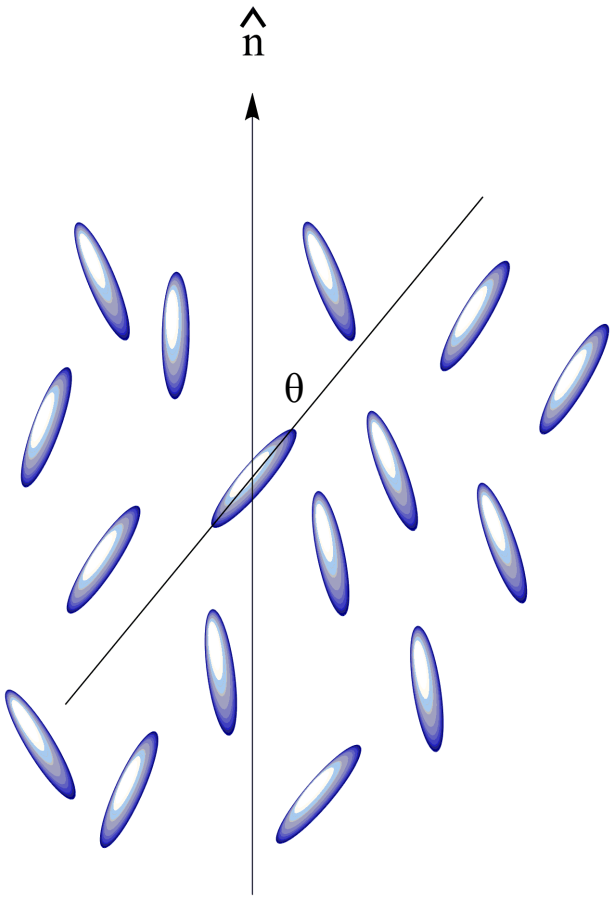


Figure 1.4. Molecular order in a nematic liquid crystal.

The nematic liquid crystal phase[10, 14, 19] is different from the isotropic liquid by the presence of long range orientational ordering of the long molecular axis (figure 1.4). However the nematic phase is the least ordered liquid crystal phase. The degree of alignment along the director is called the order parameter (S) which can be defined as in equation 1.1[3], where θ is the average angle between the molecular long axis and the director. The nematic phase also has a rotational symmetry with respect to the director. The value of order parameter S is equal to 1 if the molecules are perfectly oriented, that

is when θ = 0 for all molecules. When there is no orientational order that is when the molecular axes point in all directions with equal probability, thus, S is zero if there is no orientational order. In a typical liquid crystal, S decreases as the temperature is raised, taking on values between 0.3 and 0.8. As the molecules in the nematic phase are rotationally and orientationally disordered with respect to their short axes, the phase is uniaxial. If their breadth is increased, their rotation about their long molecular axis is restricted and therefore the phase is biaxial.

$$|S| = \langle \frac{1}{2} (3cos^2\theta - 1) \rangle \qquad 1.1$$

The cholesteric mesophase, which was first observed for chiral derivatives[2] of cholesterol, should in fact be called the chiral nematic mesophase, N^*. In this mesophase the molecules are still arranged in the same fashion as in the nematic phase, however the presence of chirality forces the local director to form a helix (figure 1.5). This helical structure is usually known as a single-twist structure[5]. The helical structure has a temperature dependent pitch which can be defined as the distance required on rotating the average direction of the molecules through 360°, which is the full turn of the helix.

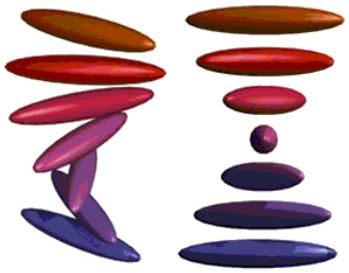


Figure 1.5. A representation of the cholesteric mesophase, adapted from reference [20].

The smectic state is another distinct mesophase of liquid crystal substances. The word "smectic" is derived from the Greek word for soap. This seemingly ambiguous origin is explained by the fact that the thick, slippery substance often found at the bottom of a soap dish is actually a liquid crystal phase and has all the properties of a smectic liquid crystal[3, 20]. The smectic mesophase is more ordered than the nematic phase and furthermore, whereas only at present only biaxial and uniaxial are known to exist, the

'smectic phase' exhibits polymorphism. Smectic phases have lamellar structures which enable various molecular configurations and orientations within and between the layers to occur, and so smectic phases exhibit polymorphism. The SmA, SmC, SmB, SmI, and SmF[19] are five different smectic liquid crystal mesophases (figure 1.6). The crystal B, J, G, E, K, and H, are six quasi-smectic disordered crystal phases, which are not liquid crystals since they possess long range positional order in three dimensions. The smectic phases could be identified by optical polarising microscopy. The smectic and crystal phases are classified on the basis of the degree of local positional order and upon whether the molecules are tilted with respect to the layer normal[19].

The smectic A phase[21] is the least ordered smectic phase. The molecules are arranged in diffuse layers so that their long molecular axes are on average perpendicular to the layer planes and give a one-dimensional density wave for the centre of molecular mass.

The smectic C phase[8] has molecules which are arranged in diffused layers as in the smectic A phase, but it is different from the smectic A in that in the smectic C, the long molecular axis is tilted from the layer normal through an average angle θ (figure 1.6). The tilt angle (θ) in the smectic C phase usually increases as the temperature decreases. To a first approximation, after a second-order transition to the smectic C phase from a smectic A phase, the tilt angle varies in the following manner with respect to temperature, T, as described by equation 1.2 where T_c is the transition temperature, T is the temperature, θ_0 is a constant, and α is an exponent (which has a theoretical value of 0.5).

$$\theta\,(T) \;=\; \theta_0 (T_c - T)^{\alpha} \qquad 1.2$$

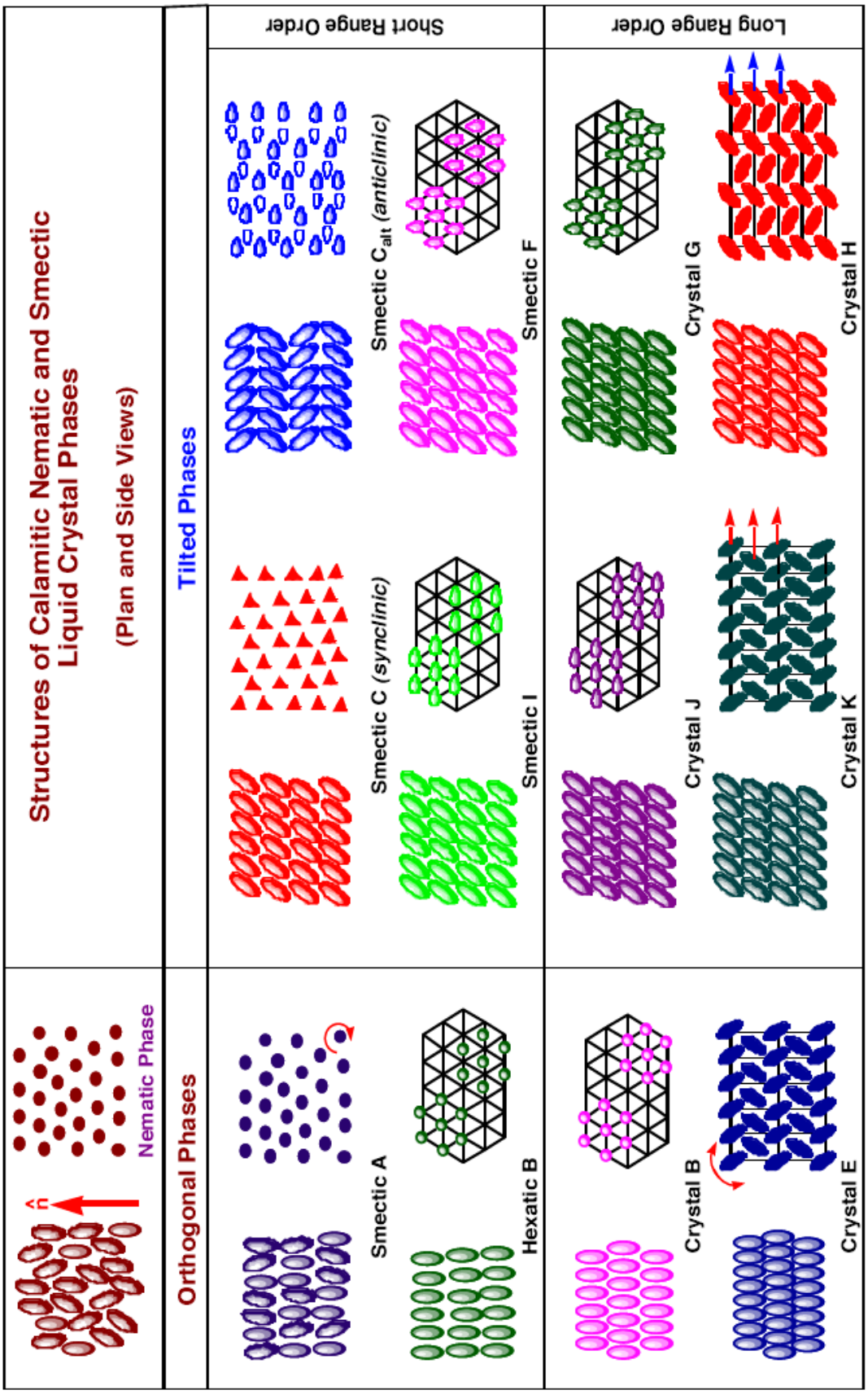


Figure 1.6. Structures of the nematic and smectic phases, adapted from references[4, 22].

1.3 Physical Properties of Liquid Crystals[3, 10, 14, 23]

The main interest in the physical properties of liquid crystals arises because of the anisotropic nature of the properties which are not identical in all directions. Each mesophase has specific properties. These properties are particularly important for using that mesophase in distinctive applications. The main physical properties relevant to the nematic and smectic mesophases will be discussed here.

1.3.1 Viscosity

Liquid crystals are fluids that show anisotropy in their flow behaviour. This can be understood by imagining measuring the viscosity of a liquid crystal by placing it between two flat plates and measuring the force necessary to slide one plate over the other. In figure 1.7, the plates lie in xy plane and are separated by a distance d. The bottom plate is fixed and force acting on the top plate is in the x-direction, f_x. The velocity of the top plate is also in the x-direction, v_x[10, 23].

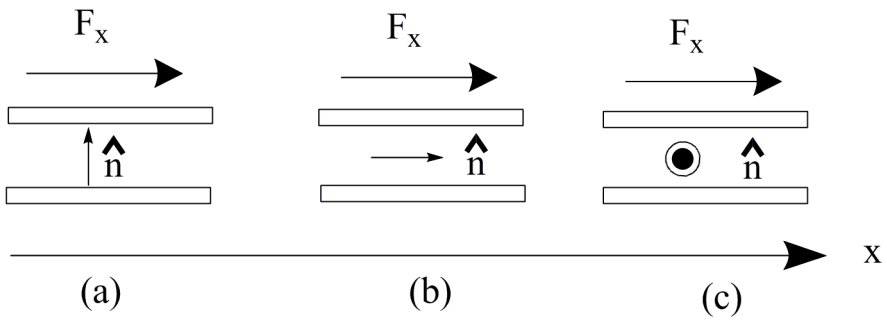


Figure 1.7. Measuring the three viscosities of nematic liquid crystals[10].

The force necessary to slide the plates over each other is different for each case, being nearly the same cases for (b) and (c) but much higher for case (a). No such effect exists for a liquid placed between the two plates. The resulting three viscosities, sometimes called the Miesowics coefficients[10], are η_1 where the director is perpendicular to the flow pattern and parallel to the velocity gradient, η_2 where the director is parallel to the flow pattern, η_3 where the director is perpendicular to both the flow pattern and the velocity gradient.

1.3.2 Optical Anisotropy (Birefringence)[24]

When an incident beam of light propagates through a solid, the electric field component of the light beam interacts with the atoms of the solid *via* their electron clouds. This is due to the fact that the wavelength of the incident light beam is greater than the interatomic separation of the solid, *i.e.*, the electric field minima and maxima are widely spaced in comparison to the atomic spacings. However, when light propagates through anisotropic media such as liquid crystals, the interaction between the electric field component of the light and the constituent atoms of the material will be affected by:

a) The direction of the propagation and,
b) The orientation of the electric field vector with respect to the crystal structure.

In an anisotropic medium, a ray of light entering with a propagation direction other than parallel to the optical axis is divided into two rays which travel through the material at different velocities, and therefore have different refractive indices. This phenomenon is called double refraction or birefringence. The two emerging rays are polarised in planes perpendicular to one another, and are called the ordinary ray (coupled to the molecular optic axis), and the extraordinary ray (which is perpendicular to the optic axis), and will have refractive indices n_o and n_e respectively. The relationship between the velocity of light, V, and the refractive index, n, can be found in equation 1.3, where C is the velocity of light in a vacuum.

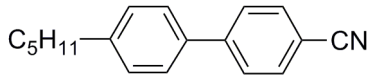
$$n = \frac{C}{V} \qquad 1.3$$

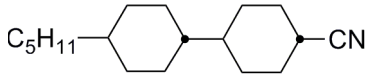
The difference of the velocities of both ordinary ray (*o*-ray) and extraordinary ray (*e*-ray) will be zero along the optic axis, since no double refraction can occur. The difference between the refractive indices, Δn, is given in equation 1.4, and may be positive or negative in its sign.

$$\Delta n = n_{\parallel} - n_{\perp} \qquad 1.4$$

The two refractive indices are temperature dependent and decrease when the nematic mesophase transforms to the isotropic liquid state. The birefringence is a very important

property for display applications and the appropriate value for Δn can be designed by molecular engineering. Materials containing electron-rich mesogenic cores and terminal chains give high Δn values *e.g.*, compound **1.3**, conversely, materials which consist of saturated alicyclic rings and terminal alkyl chains have low birefringence values, often close to zero *e.g.*, compound **1.6**.

1.3  Δn = 0.20

1.6  Δn = 0.05

1.3.3 Dielectric Anisotropy

A material that is polarisable, but non-conducting is referred to as dielectric. Non-polar molecules may acquire an induced dipole moment in an electric field as the field causes a distortion in their electronic distributions and nuclear positions. In a polar molecule a permanent dipole moment is present, this is due to the partial charges on the atoms in the molecule, which arises from differences in electronegativity. Any existing dipole moments are modified by an applied electric field.

Since uniaxial liquid crystals are anisotropic in nature, such a medium will have two dielectric permittivities. It is usual to discuss the dielectric anisotropy of a liquid-crystalline material as defined as shown in equation 1.5, here $\varepsilon_{||}$ is the permittivity along the long molecular axis, parallel to the director, and $\varepsilon_{\perp}$ is the permittivity perpendicular to the long molecular axis and to the director.

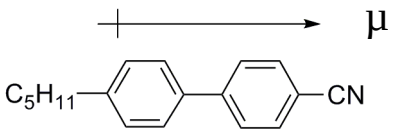
$$\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp} \quad 1 \qquad 1.5$$

The magnitudes of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ are dependent upon several factors, namely:

a) The spatial structure of the molecules,
b) The degree of order within the phase which is also dependent upon the temperature and most importantly,

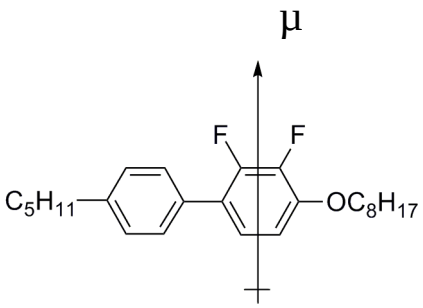
c) The presence of permanent or induced dipole moments within the structure acting along directions parallel and perpendicular to the long molecular axis. (compounds **1.3** and **1.7**)

1.3



$\Delta\varepsilon = +12$

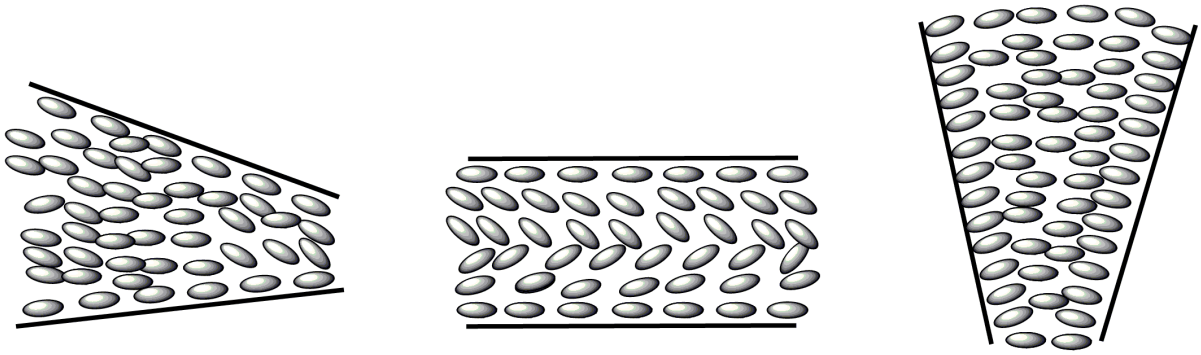
1.7



$\Delta\varepsilon = -5$

1.3.4 Elastic Constants

When a solid is torn or stressed in the limit of its elasticity, restoring forces act to retain the original shape of the solid. For the case of a liquid-crystalline mesophase and in particular for the nematic mesophase, there are three possible deformations. Though these elastic forces are not as great as for the case of a solid, they play a vital role for display applications. The elastic constants drive the relaxation *e.g.* the motion from the homeotropic alignment of the molecules back to their planar configuration in a twisted nematic display. There are three possible deformations: splay, twist and bend (figure 1.8) and more important than their individual values is the ratio of bend/splay (k_{33}/k_{11}), which needs to be low for optimum electro-optical characteristics with typical values in the range 0.6 to 0.8. The values and ratio of the elastic constants are more difficult to obtain through molecular engineering than are the viscosities, and the optical and dielectric anisotropies.



Splay K_{11} Twist K_{22} Bend K_{33}

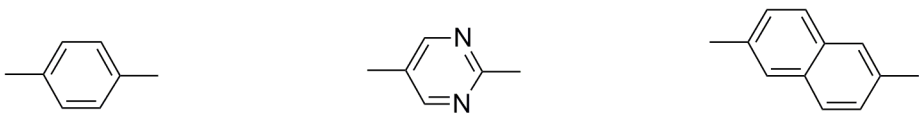
Figure 1.8. Representations of elastic deformation for a nematic material.

1.4 Basic Structural Features of Calamitic Thermotropic Liquid Crystals

Figure 1.2 shows a general template that can be used to describe the structure of a calamitic liquid crystal compound. One or more core units (A and B) can be linked directly together, but sometimes a linking group (Z) is used. Terminal chains (R and R') can be linked to the core with groups X and Z, but usually the terminal chains are directly linked to the core. Lateral substituents (M and N) are used to modify the mesophase morphology and the physical properties exhibited by a compound.

The primary requirement for mesogenic behaviour is structural rigidity, which is mostly provided by linked cyclic units, such as 1,4-phenyl, 2,5-pyrimidyl and trans-1,4-cyclohexyl. Typical linking groups used are carboxylate, dimethylene, and ethynyl. The rigid core alone is not usually sufficient to generate liquid crystal phases and certain flexibility is needed to have low melting points and to stabilise the molecular alignment within the mesophase structure[10]. The flexibility is provided by the terminal substituents R and R' which are usually a straight alkyl or alkoxy chain[10]. Small polar species have also been used, such as cyano or isothiocyanate. Modification of the core unit, thus tailoring the mesophase morphology and /or physical properties, is often achieved by inserting lateral substituents M and N. Many different types of lateral substituents have been used (*e.g.*, F, Cl, CN, CH_3). However, fluorine is most commonly used because of its subtle combination of small size and high electronegativity; the larger units are less successful in generating mesophases.

1.4.1 Core Units

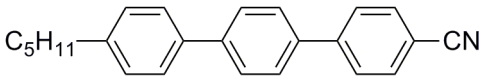


1,4-phenyl 2,5-pyrimidinyl 2,6-naphthyl

Figure 1.9. Selected aromatic core units.

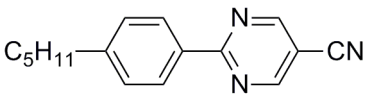
The standard building block used in the synthesis of liquid crystalls is the 1,4-disubstituted benzene ring (figure 1.9). It is highly polarisable and determines the basic rod-shaped structure, also 2,5-pyrimidine and 2,6-naphthalene are common.

After benzene, the next most frequent unit is biphenyl. The linearity of the biphenyl provides the necessary rod-like structure in the crystalline state[25]. Compound **1.3** or 5CB was the first commercially viable nematic liquid crystals for use in display devices. Three ring systems, such as *para*-terphenyl is similarly linear and thus is a very common unit in mesogenic materials. Terphenyl materials exhibit high liquid crystal phase stabilities and, since all three rings are structurally compatible, *i.e.*, the lateral forces of attraction are strong, they possess a high smectic phase stability. A small amount of 4-alkyl-4"-cyanoterphenyl **1.8** is used in commercial nematic mixtures of biphenyls to extend nematic phase stability[10].



C 130.0 N 239.0 I

1.8



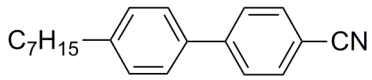
C 71.0 (N 52.0) I

1.9

Heteroaromatic rings have been investigated as possible core units *e.g.*, compound **1.9**[26, 27]. Comparisons have been made between the mesogenic properties of bi-, and ter-phenyls and their heterocyclic analogues[27]. If the heteroatom is nitrogen, as in the majority of cases investigated, a higher clearing point and melting point is often observed. The use of a heterocyclic pyrimidine ring *e.g*, compound **1.9** causes a moderate increase in T_{N-I} that is possible because the steric hindrance in the inter-ring, bay region from the protons of compound **1.3** has been removed and the two aromatic rings can now adopt a planar arrangement without interannular twisting of the parent system; this gives enhanced longitudinal polarisability and hence a higher T_{N-I} value[10]. However, the increased polarity conferred by nitrogens generates a disadvantageously high melting point[10].

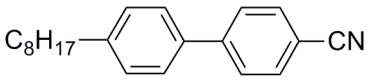
1.4.2 Terminal Groups[3, 10, 28]

Terminal groups (represented by letters R and R' in figure 1.2) are nearly always employed in liquid crystal systems. The physical properties and the type of liquid crystal phase are strongly dependent upon the choice of terminal units. The most successful terminal units are either a small polar substituent (*e.g.*, cyano group) or a fairly long, straight hydrocarbon chain which is mostly alkyl or alkoxy. The role of how the terminal units play when generating the liquid crystal phases is still not yet fully understood. However, the alkyl/alkoxy chains could be responsible for stabilising the molecular orientation necessary for liquid crystal phase generation. In addition to stabilising the molecular orientation, the long alkyl/alkoxy chains add flexibility to the rigid core structure that tend to reduce melting points and allow liquid crystal phases to be exhibited[10].



C 30.0 N 43.0 I

1.10



C 21.5 S_A 33.5 N 40.5 I

1.11

The melting points are considerably reduced by increasing the length of the chain because of increased flexibility, however, when very long, the excessive van der Waals intermolecular forces of attraction increase melting points. The change in the T_{N-I} (clearing points) values could be very similar to that described about melting points, the T_{N-I} drop with increasing chain length, and increase with very long chains. However, odd-membered chains generate higher T_{N-I} than the even-membered chains, this is called odd-even effect. This can be explained by comparing the structure of compound **1.10** and **1.11**, the extra carbon which makes the chain even in compound **1.11** generates a deviation from the linear structure of the more favourable all-*trans* conformation of the chain, which results in reducing T_{N-I} value. As the length of the terminal chain increase, the smectic tendency increases. The long chain facilitates the lamellar packing required for smectic phase generation[10].

Branching the alkyl chain causes a disruption in the molecular packing which often reduces melting points and invariably reduces the liquid crystal phase stability. Where the branch is close to the core the disruption is enhanced which results in a low melting point. However, extending the chain and moving the branch away from the core dilutes the effect of the branch.

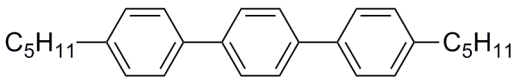
1.4.3 Lateral Substituents

Lateral substituents, *i.e.,* substituents that are attached off the linear axis of a molecule, have long been used to modify mesophase morphology and the physical properties of liquid-crystalline materials. A wide range of different lateral substituents have been incorporated into liquid crystal systems, these include F, Cl, CN, NO_2, CH_3, and CF_3.

Lateral substituents are unfavourable to the formation of liquid crystal phases since they disrupt molecular packing, particularly lamellar packing, thus reducing liquid crystal phase stabilities especially in the case of smectic phases. However, lateral substituents are necessary in order to reduce melting points and to enable the generation of the desired liquid crystal phases. For example, a fluoro substituent is widely used in some systems to eliminate all smectic phases in generating nematogens having a low melting point. Another important reason for using a lateral substituent is to tailor the physical properties, such as the dielectric anisotropy, elastic constant etc., of a liquid crystal to a particular device application. Relevant steric factors (such as molecular breadth), the resultant polarisability anisotropy and the effect on polarity are all important factors to consider when a lateral substituent is incorporated into a mesogenic system[29, 30].

Of the many types of lateral substituents that have been utilised, fluorine is the most significant and most widely used. Its high electronegativity (the highest of the elements, 4.0) in combination with its small size (the smallest van der Waals redius except for hydrogen, 1.47 Å) means that the fluoro substituent can exert a significant, but not too drastic effect on the molecular breadth to allow tailoring of the melting point and liquid crystal phase morphology. Additionally, the polarity of the fluoro substituent can aid the generation of the tilted smectic C phase. In terms of physical properties, the lateral fluoro substituent is useful because the small size minimises the viscosity whilst generating a zero or negative dielectric anisotropy value, hence enabling the subtle modification of the physical properties of a system, without too much disruption to liquid crystal phase stability.

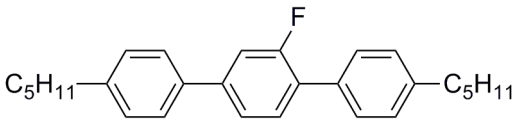
The terphenyl core is a good core for generation of liquid crystal phases (*e.g.*, compound **1.12**) because it has a very high length to breadth ratio and a very high polarizability anisotropy[31]. Hence, such a core unit would be expected to support a lateral fluoro substituent or two, and still be capable of generating high liquid crystal transition temperatures.



C 192.0 SmA 213.0 I

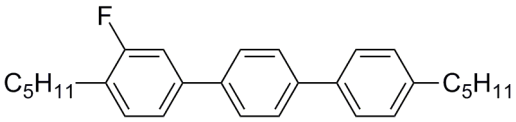
1.12

In a typical unsymmetrical 4,4"-disubstituted terphenyl, there are 6 different positions in a total of 12 that a fluoro substituent can be located, thus 6 monofluorosubstituted compounds are possible. In general there can be considered two types of location for a lateral fluoro substituent in such terphenyls, 'inner-core' and 'outer-edge'. At an 'inner-core' location (*e.g.*, compound **1.13**) a lateral fluoro substituent causes much disruption in the side-to-side intermolecular packing, and hence smectic phase stability is severely depressed, which allows the generation of a nematic phase. Also, at such an 'inner-core' location, the fluoro substituent causes an interannular twisting, which is greater than that caused by the hydrogen, at the appropriate join of the two benzene rings, which reduces the polarizability anisotropy, and hence further reduces the liquid crystal phase thermal stability[31]. On the other hand, the fluoro substituent at the 'outer-edge' position (*e.g.*, compound **1.14**) tends to fill space with a polar unit, facilitating the side-to-side intermolecular forces of attraction, and hence upholding the smectic phase stability, despite the steric effect, and the nematic phase is not exhibited. Also, there is no additional interannular twisting from a fluoro substituent, which means that the polarizability anisotropy will be relatively high, thus supporting high transition temperatures[31].



C 51.5 B 62.0 SmA 109.5 N 136.5 I

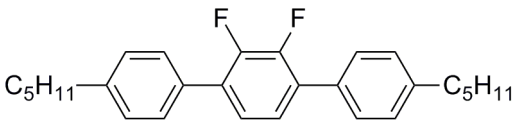
1.13



G 156.5 SmA 185.5 I

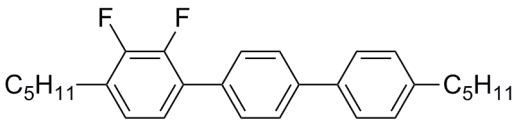
1.14

The most promising location for two fluoro substituents is next to each other, *i.e.*, ortho-difluoroterphenyls. The molecular breadth is minimized because both fluoro substituents are inherently fixed on one side of the molecule which results in liquid crystal phase transition temperatures being upheld. When the two fluoro substituents are at an 'inner-core' position in the centre ring (*e.g.*, compound **1.15**) and the terminal chains are relatively short, and both alkyl, then the materials are nematogens to a high temperature, although melting points are higher than ideal[28, 31]. When the two fluoro substituents are in an outer ring, (*e.g.*, compound **1.16**) smectic phases are prevalent because of the space-filling influence of the polar substituent.



C 60.0 N 120.0 I

1.15



C 81.0 SmC 115.5 SmA 131.0 N 142.0 I

1.16

1.5 Ferroelectricity

In 1975, Meyer *et al.*[32] using symmetry arguments demonstrated that chiral tilted smectic phases are ferroelectric *i.e.* display a spontaneous polarisation. When the molecules are achiral the environmental symmetry of the smectic C phase consists of a centre of symmetry, a two-fold axis and a mirror plane containing the molecular tilt and perpendicular to the layers. The group symmetry of the plan is C_{2h} (figure 1.10).

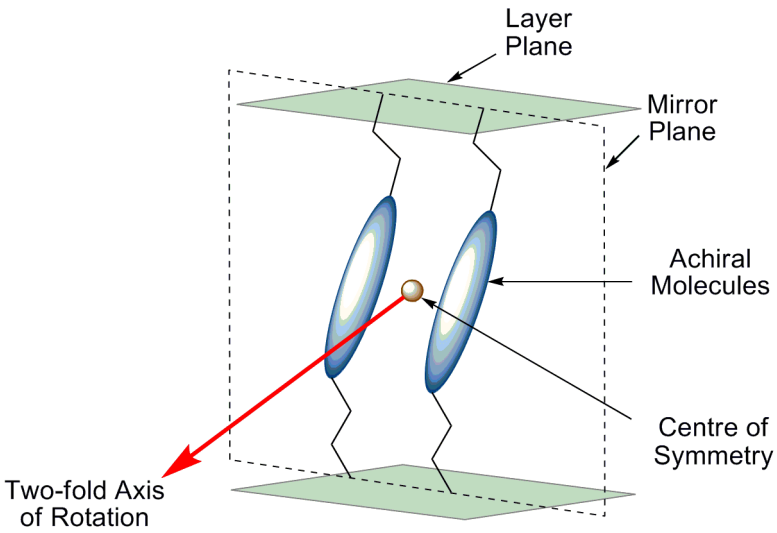


Figure 1.10. C_{2h} symmetry of the achiral SmC phase.

When the molecules of the smectic C phase are chiral, the symmetry is reduced to a two-fold axis[33] of rotation and the group symmetry is now C_2. The dipoles associated with the environment about the chiral centres align because of molecular interactions, and this results in a spontaneous polarisation, Ps, that develops along the C_2 axis of the phase (figure 1.11).

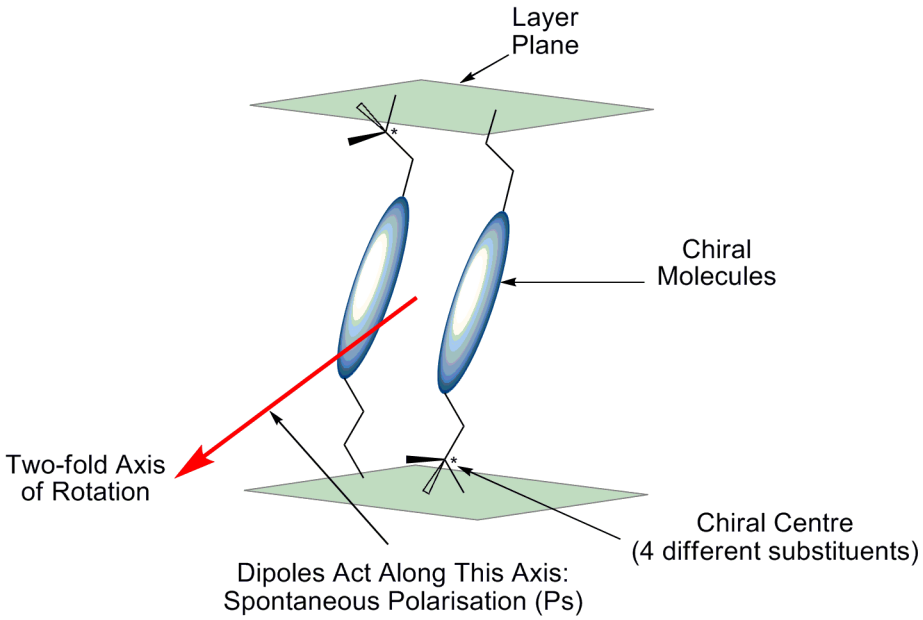


Figure 1.11. C_2 Symmetry of the chiral SmC* phase.

Figure 1.11 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. However, 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, the structure of the SmC* is inherently more complex[34]. As can be seen in figure 1.12, 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 1.12) 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 1.12 illustrates one complete rotation of the director, which corresponds to the pitch length of the material, and the overall polarisation is equal to zero, leading the phase to be classed as 'helielectric', rather than 'ferroelectric'[10]. The tilt angle of the SmC* phase is temperature dependent, and results in the largest tilt angle being generated at lower temperatures.

Therefore, the helical nature of the SmC* phase also exhibits optical properties similar to the chiral nematic phase , and in both cases the pitch length is affected by the temperature. 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[5, 10].

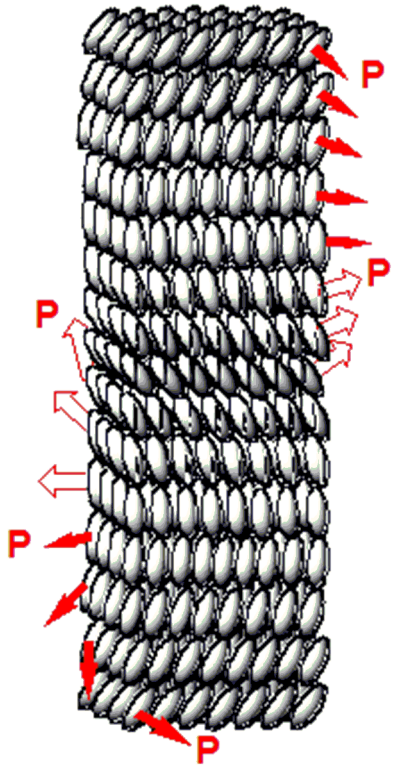


Figure 1.12. Structure of the chiral SmC* phase.

1.5.1 Surface Stabilised Ferroelectric Liquid Crystal Display

In 1980, Clark and Lagerwall invented a symmetrically bistable, fast-switching electro-optical device described as the 'surface-stabilized ferroelectric liquid crystal' (SSFLC) display device[35]. In the SSFLC geometry, the helix of the SmC* phase spontaneously unwinds due to elastic interactions with two polyimide-coated glass sides separated by a gap has been suggested that the pitch should be four times larger than the cell gap. By forcing the tilt plane of each SmC* layer to orient in the plane of the glass plates 'bookshelf geometry', two degenerate director orientations can exist (+θ, - θ), which correspond to two opposite orientations of P_S along the polar axis, as shown in figure 1.13.

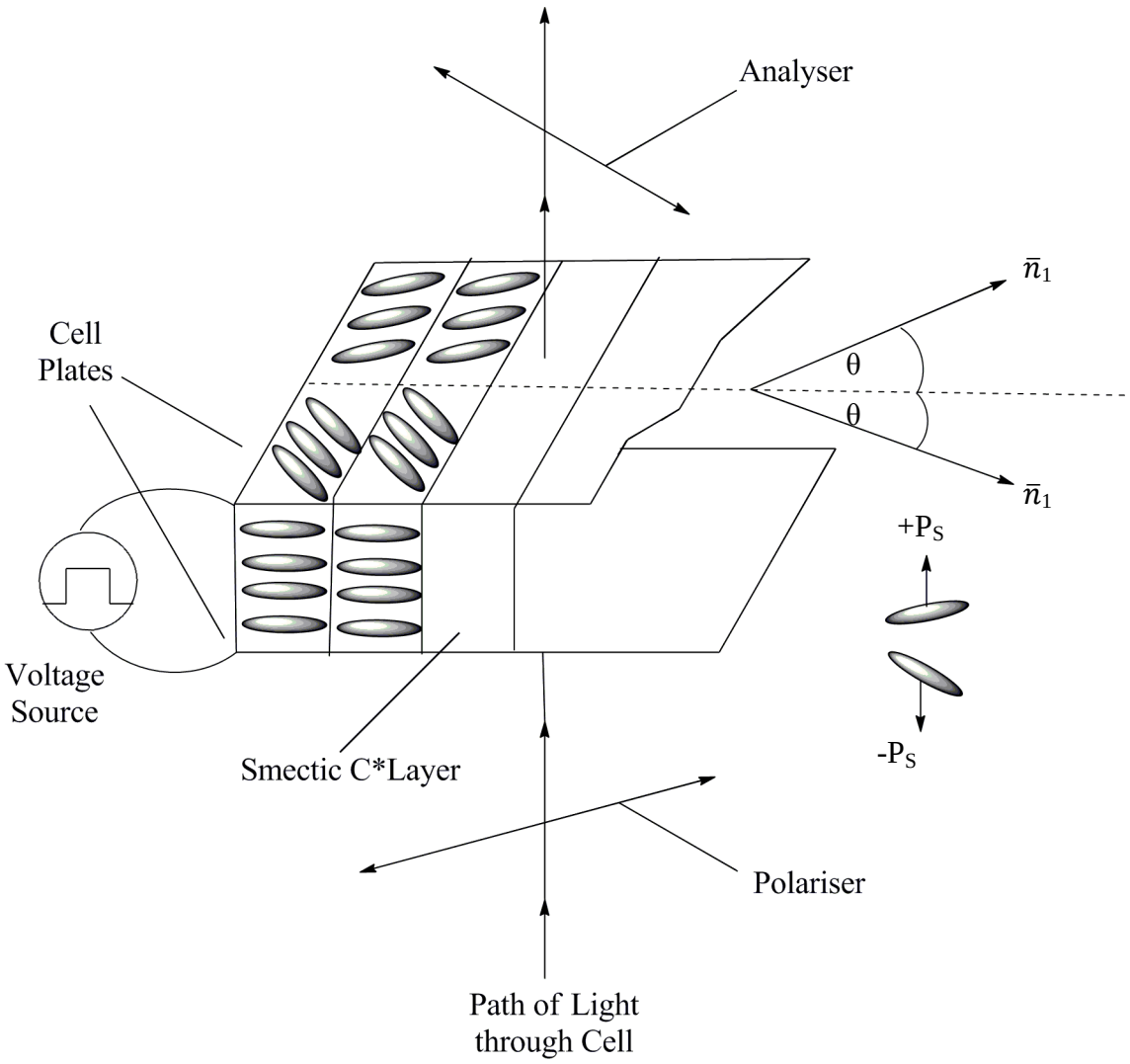


Figure 1.13. Structure of the SSFLC display device.

The cell consists of a liquid-crystalline material contained between parallel glass plates which have been coated with an electrode layer (ITO) and then an alignment material (*e.g.,* a polymer coating such as polyimide, nylon or PVA which has been rubbed in a single direction)[36] to ensure a planar and unidirectional oriented specimen of the liquid crystal molecules due to liquid crystal-surface interactions. On cooling from the isotropic to SmC* mesophase for a material with a SmA*-SmC* phase transition, the molecules in contact with the orientation layer are forced to lie in the plane of the glass plates where in the SmC* phase only two orientations are possible, *viz.,* the tilt directions corresponding to the cross-section between the plane of the glass plates and the switching cone (figure 1.14)[36, 37].

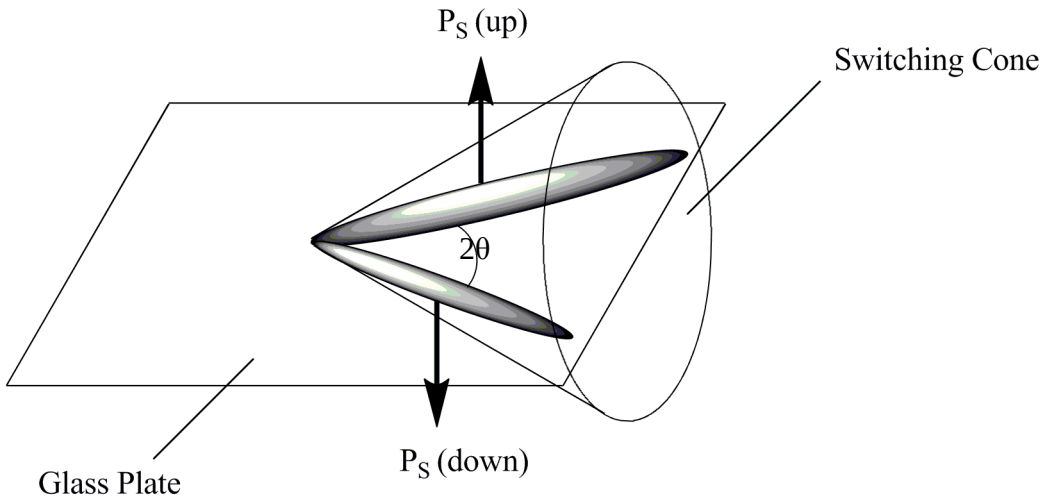


Figure 1.14. The two molecular orientations in the SSFLC device.

Ideally, the smectic C layers are perpendicular to the plane of the cell in the so called bookshelf configuration. The polarisers are crossed (90°) with one polariser parallel to the optic axis of one bistable state (figure 1.15). When the molecular optical axis is aligned parallel to the plane of polarisation, the light passes through the liquid crystal material and is absorbed by the analyser and so the cell appears dark. On the other hand, when an external DC field is applied, the inversion of the direction of spontaneous polarisation occurs and forces the long molecular axis to rotate around the smectic C cone (ideally 45°) with respect to the polarisers and in effect the material becomes a half wave plate which rotates the plane of incident light through 90° and therefore the cell appears bright. In this way, the light that passes through the SSFLC can be switched ON and OFF by reversing the polarity of the applied field.

The SSFLC display offers multiple advantages compared to the conventional twisted-nematic liquid crystal displays. The switching time τ_s is on the order of microseconds, as opposed to milliseconds for twisted nematic LC cells. In addition, the SSFLC cell affords higher viewing contrast, wider viewing angles, bistability (the two surface stabilized-states are maintained by surface interactions in the absence of an electric field), and low power consumption[36, 38-40].

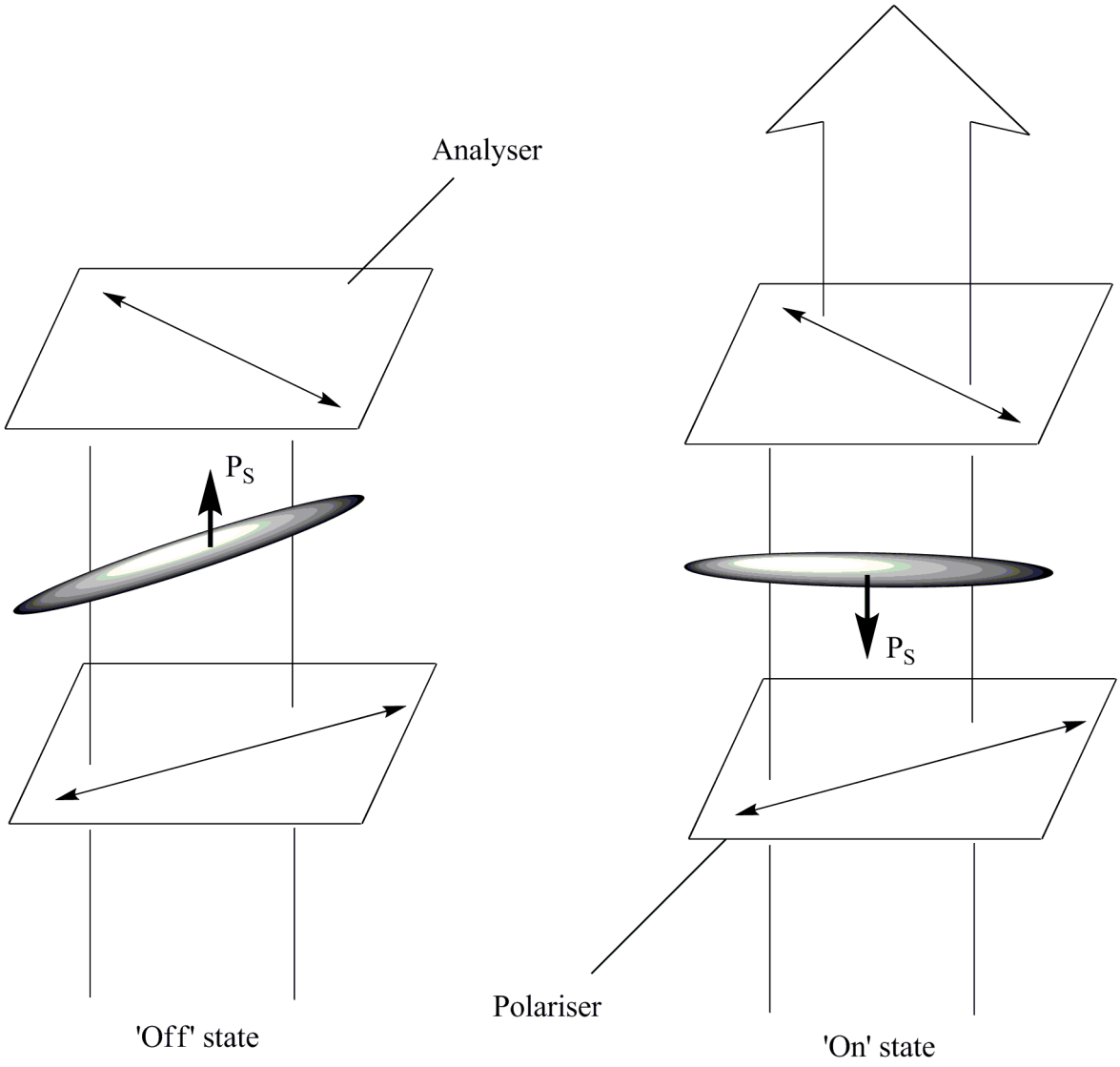


Figure 1.15. ‘Off’ and ‘On’ states in a SSFLC display device.

The originally described bistable ‘bookshelf’ structure is only the simplest in the SSFLC geometry. Unfortunately, the bookshelf geometry is sensitive to external perturbations, *i.e.*, mechanical shock[36], thus resulting in the formation of defects within the cell. X-ray scattering studies performed by Rieker *et al.*,[41, 42] revealed that the layers are somewhat tilted and bent within the cell; this smectic layer bending results in a ‘chevron’ structure being present (figure 1.16).

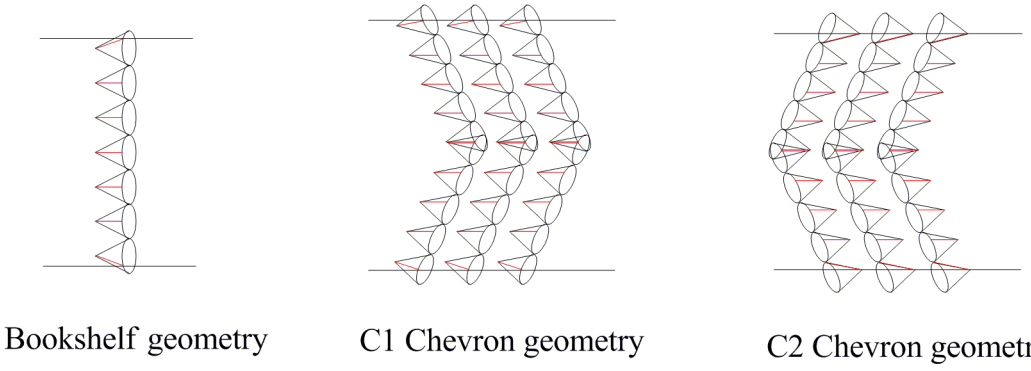


Figure 1.16. Examples of different layer geometries in a surface-stabilized ferroelectric liquid crystal (SSFLC).

It is generally accepted that the thermodynamically most stable configuration within an FLC cell is the chevron structure. The chevron is a planar defect in the local layer structure. Its existence has consequences for the electro-optical properties of SSFLC cells. One undesired manifestation of chevrons is called zig-zag disclination[36] which is formed when chevron structures (C1 and C2) co-exist, *i.e.*, regions within a cell where chevrons with opposite direction are in contact. The cone angle of switching near the middle is virtually zero meaning very poor contrast.

1.5.2 Physical Properties of Ferroelectric Liquid Crystal Materials[10, 19]

The physical properties of ferroelectric liquid crystals which directly influence the performance in a SSFLC cell are birefringence, tilt angle, spontaneous polarisation, and rotational viscosity.

The intensity of the light transmitted, I, through the cell is expressed by Equation 1.6.

$$I = I_o \, sin^2 4\theta \, sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) \qquad 1.6$$

Where I_o is intensity of incident light, Δn is the effective material birefringence, d is cell thickness, and λ is wavelength of incident light. The intensity of transmitted light is maximised when $I=I_o$, which is the case if twice the switching angle (4θ) is equal to 90° and the material birefringence, Δn, and cell thickness, are such that condition $\Delta nd = \lambda/2$ is fulfilled.

The spontaneous polarization P_s has been shown to be temperature dependent. An expression[5] has been derived to predict the behaviour of the polarization, as follows

$$P_s = P_o (T_c - T)^{\beta} \qquad 1.7$$

where P_s is the magnitude of the polarization at a given temperature T, P_o a constant dependent upon the nature of each dopant, Tc is the transition temperature for the second-order smectic A to smectic C* phase change, T is the actual temperature and β is an exponent which has a value theoretically equal to 0.5. As the temperature decreases, the value of the P_s increases to an almost constant value.

The switching time (the time required to produce a change in optical transmission from 10% to 90%) is approximated by Equation 1.8[36]:

$$\tau_s = \frac{\eta}{P_s.E} \qquad 1.8$$

In this expression η is the rotational viscosity of the liquid crystal, P_s is the spontaneous polarization, and E is the applied electric field. In order to obtain a fast switching time τ_s, the design of new FLC materials has focused on the development of compounds having a high P_s and a low viscosity η (Equation 1.8).

Therefore, short switching times can be obtained with a low rotational viscosity, applying a high electrical field and using a material with a high Ps. However, applying a high electrical field is not a suitable solution for several reasons, including the possibility of conductivity problems, shorting the cell and the disadvantage of using high power supplies. A high P_S can be undesirable due to the build up of charge in the cell. Hence, a low viscosity is a most desirable attribute.

1.6 Ferroelectric Liquid Crystal Materials[10, 34]

The performance and appearance of a surface-stabilised ferroelectric liquid crystal (SSFLC) display device is directly influenced by the material properties in addition to mesomorphic behaviour. The relationship between material parameters and device performance is complex and thus material optimisation according to the requirements of the device is essential. It is therefore necessary to have a fundamental understanding of how the physical properties of a liquid crystal are dependent upon the chemical composition of the material. However the physical criteria for a ferroelectric smectic C material to be suitable for display applications are harder to satisfy than for nematic materials used in twisted or supertwisted devices. All the physical requirements listed below have to be optimised[43] although inevitably a less ideal property has to be accepted.

- A cooling phase sequence N* → SmA* → SmC* is required to obtain optimum alignment.
- A wide SmC* temperature range with no underlying ordered smectic phases to allow use of the device over the normal ambient temperature range *i.e.* well below room temperature (– 20 °C) to over 60 °C.
- A high spontaneous polarisation. The response time is determined by the magnitude of the spontaneous polarisation (Ps) of the material.
- The pitch of the helix of the chiral nematic phase should be greater than four times the cell gap to prevent the tendency to form a helical chiral smectic C phase and to permit good alignment.
- The pitch of the helix of the chiral smectic C phase must be greater than the cell gap so that it can be suppressed in order to get a spontaneous polarisation (Ps).
- A suitable optical anisotropy (Δn) depending upon the cell thickness, the dispersion of which should be as small as possible.
- A low rotational viscosity to obtain fast switching times.
- A high dielectric positive biaxiality to retain good alignment as it couples to an AC external field in the direction of the Ps.
- A tilt angle of 22.5° to give optimum transmission.
- No absorption of visible light for optimum colour operation.
- The material must be chemically and photochemically stable.

1.6.1 The "All-Chiral" Approach

It is extremely unlikely that a single compound will possess the optimum combination of physical properties and mesomorphic behaviour as listed above. The use of many compounds in a mixture is therefore essential in order to achieve suitable materials for use in SSFLC display devices.

There are essentially two methods to realise broad temperature range FLC mixtures, these are as follows.

- The 'All Chiral' approach which uses only chiral smectic C compounds, hence, as all materials are intrinsically chiral they collectively contribute to the chirality of the mixture.
- The 'Host-Dopant' approach[44] where a chiral material (not necessarily mesogenic) is added to an achiral smectic C host material in order to induce a ferroelectric chiral smectic C phase.

The 'All Chiral' approach has several major drawbacks which makes its use in preparing mixtures for devices less attractive than the 'Host-Dopant' approach. The chiral compounds are more viscous due to the branched structure of the chiral chain hence, a mixture composed of several chiral smectic C compounds would consequently have higher viscosity. In addition to that, difficulties arise in adjusting pitch and Ps parameters. The synthesis of chiral materials is more complicated than the synthesis of achiral materials, however, the chiral functionality is usually provided by the starting material and chiral materials are often expensive or if they are synthesised, they are harder to purify.

The 'Host-Dopant' approach enables important fundamental physical properties (*e.g.*, mesomorphic behaviour, low rotational viscosity *etc.*) to be optimised in an achiral SmC host mixture. This is then doped with a relatively small quantity (*ca.* 10% or less) of a chiral material which has the effect of conferring chirality to the whole system without significantly affecting the optimised physical properties. Whilst the chiral dopant need not be mesogenic, it should be of similar structure to that of the host material in order to maintain the properties of the host mixture.

1.6.2 Host Materials

Many different physical properties need to be optimised in a host system, hence several components are mixed in order to develop a suitable achiral smectic C host mixture. Fine tuning of the physical properties, such as birefringence and dielectric anisotropy, according to device requirements, is possible by changing the mixture composition.

There has been extensive research into the design and synthesis of novel ferroelectric host materials[45-47] and the quality of the host will depend upon several criteria such as:

- A low melting point.
- A wide smectic C temperature range.
- A low viscosity.
- A high chemical and photochemical stability.

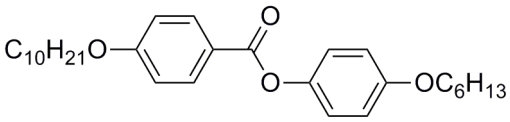
When designing ferroelectric host materials, careful consideration has to be given to the material, the most important being the generation of low viscosity, low melting (below room temperature) materials that exhibit a strong SmC tendency.

When designing a ferroelectric host material that exhibits a strong SmC tendency, particular attention has to be paid to the type of molecular structure that will generate a SmC phase. Firstly, molecules must have sufficient lateral attractions to adopt lamellar like ordering and secondly, the molecules must possess a lateral dipole to provide the necessary torque to enable tilting. The tilting mechanism requires the correct magnitude and relative positioning of lateral dipoles, and in some systems, the correct combination of terminal chain length.

A wide SmC temperature range is also required in a host system not only to ensure the minimisation of physical property fluctuation with changing temperature and hence support the performance of a display, but also because allowance has to be made for the possible depression of the SmC phase stability which can caused by the addition of the chiral dopant.

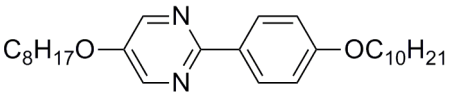
Most ferroelectric host materials contain at least two rings such as phenyl benzoates[48] phenylpyrimidines, difluorophenylpyrimidines and phenylpyridines[37], and three ring compounds such as phenyl biphenylcarboxylates, monofluorophenyl biphenylcarboxylates (MBF esters), cyclohexanecarbonitrile (NCB) derivatives[37], 2,5-

di-phenyl-1,3,4-thiadiazoles[49, 50], and mono- and di-fluoroterphenyls[28, 51], which are used to ensure broad temperature range SmC phases, a negative dielectric anisotropy and a suitable optical anisotropy.



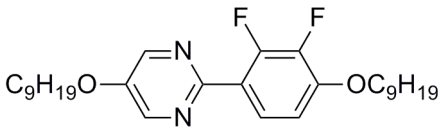
C 63.0 SmC 77.5 SmA 83.5 N 89.5 I

1.17



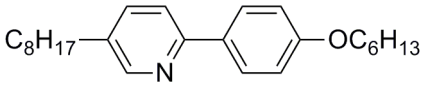
C 32.0 SmC 59.5 SmA 65.5 N 69.5 I

1.18



C 48.0 SmC 78.0 I

1.19



C 28.0 SmI 55.0 SmC 77.0 I

1.20

Figure 1.17. Different types of two-ring smectogens.

Compound **1.17** (figure 1.17) is an example of simple esters which were used as host materials for ferroelectric mixtures since they exhibit smectic phases. Generation of the smectic C phase is due to the presence of the ester linking group which confers a stepped structure to the core due to the sp^2- hybridisation of the carbonyl carbon which, when the terminal chains are both alkoxy and long, leads to a tilt of the molecules with respect to the layer normal. However, the need for long terminal alkoxy chains in order to generate a SmC phase in this class of compound, means that these simple esters exhibit a

fairly high viscosity and high melting points, both these properties being undesirable for compounds used in mixtures.

The phenylpyrimidines, such as compound **1.18** (figure 1.17), having long terminal chains make excellent host materials for ferroelectric mixtures as they show low viscosities and low melting points, but their smectic C temperature range is rather narrow. The smectic C range can be increased by using two alkoxy terminal chains, but this causes an increase in viscosity. It therefore appears that in order to generate a smectic C phase with acceptable properties, aromaticity is required in the central rigid core region with dipolar functionalities near one end and long terminal chains.

In contrast to the phenylpyrimidine, the difluorophenylpyrimidine (compound **1.19**, figure 1.17) exhibits only a smectic C phase. This is due to strong lateral dipole provided by the *ortho* fluoro substituents which enhances molecular tilting, and hence all the smectic character is seen as tilted SmC phase. However, as with the phenylpyrimidines, at least one alkoxy terminal chain is required in order to generate the SmC phase, preferably two.

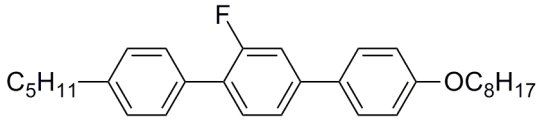
The phenylpyridine (compound **1.20**, figure 1.17) is particularly low melting (28 °C) and purely smectogenic in nature. The SmC phase stability is also improved in comparison to the phenylpyrimidine (compound **1.18**). However, the underlying more ordered smectic I phase can be disadvantageous when considering its use as a ferroelectric host material.

The three ring systems such as mono- and di-fluoroterphenyls have a higher length to breadth ratio and accordingly, have much higher liquid crystal phase stabilities than the two ring systems which might make them more sutable for use as ferroelectric host materials. However, the increased size of these molecules consequently leads to an increase in viscosity.

The best materials are those with no linking group within the core, so that the viscosity is not too great, and the SmC phase is exhibited to high temperature. Based on these ideas, Gray *et al*. [52, 53] developed achiral host materials for ferroelectric systems using a terphenyl core unit with one or more lateral fluoro substituents to modify the core. The fluoro substituent was used to modify the transition temperatures and mesophase behaviour because of its small size and its high electronegativity. Fluoro substitution

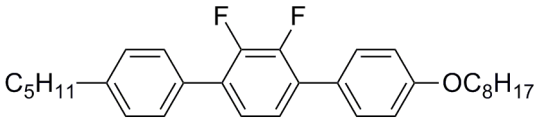
usually reduces the melting point, suppresses underlying smectic phases and introduces the tendency for the molecules to tilt.

Monofluoroterphenyls such as compound **1.21** (figure 1.18), have a high smectic tendency. The lateral dipole generated by the fluoro substituent causes a molecular tilting and hence the generation of tilted smectic phases, such as the smectic C phase[31]. Compound **1.21** (figure 1.20) generates a tilted smectic C phase, and indeed more ordered tilted smectic phases, this is because of the combination of the polarity of the lateral fluoro substituent and the ether oxygen in the terminal chain[31].



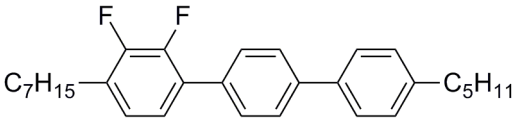
C 69.0 G 83.0 B 100.5 SmC 124.5 SmA 158.0 N 161.0 I

1.21



C 48.5 SmC 95.0 N 141.5 I

1.22



C 56.0 SmC 115.5 SmA 131.0 N 166.0 I

1.23

Figure 1.18. *O*-fluoro-substituted terphenyls.

Ortho dfluoroterphenyls **1.22** and **1.23** (figure 1.18) make excellent ferroelectric host materials. Both fluoro substituents are held inherently fixed on one side of the molecule which enhances the lateral dipole because both fluoro substituents reinforce each other. As a consequence of this, the difluoroterphenyl materials have a high negative dielectric anisotropy and fairly high SmC phase stability. The 2,3- or 2',3'-diflouroterphenyls (figure 1.18) are no broader than the mono-fluoro substituted terphenyls, the ordered

smectic phases are eliminated, the dielectric anisotropy becomes negative and neither the melting point nor the viscosity is affected. A major advantage of the *ortho*-difluoroterphenyls is that a relatively a high SmC phase stability can be generated from dialkyl analogues, so only C, H, and F are present, so despite the three rings, the viscosity is quite low.

The position of the *ortho*-difluoro substituents has an effect on the mesomorphism as well as on the melting and clearing points. The 2',3'-difluoroterphenyls[28, 54, 55] (*e.g.*, compound **1.22** figure 1.18) have a lower melting point and lower smectic C mesophase stability as well as a greater nematic tendency than 2,3-difluoroterphenyls (*e.g.*, compound **1.23** figure 1.18). The smectic C phase is enhanced when the two fluoro substituents are on an outer ring and gives the lateral dipole near one end of the molecule. Both cores show a smectic C phase when fairly long terminal chain are attached; the compounds have high negative dielectric anisotropies, high clearing points and usually have the desired cooling phases sequence of N→ SmA→ SmC.

A simplistic view of how mesogenicity arises in molecules is that the core provides the anisotropy necessary to give mesomorphic behaviour and the terminal chains serve to reduce the melting point so that mesophases can be observed. Most liquid crystal research has been concentrated on the design and synthesis of novel cores, and the flexible part of the calamitic liquid crystal has been alkoxy or alkyl terminal chains.

The effect of changing the nature of the terminal chains on the mesomorphism and transition temperatures has only been studied in detail with respect to their length. Only recently have researchers started to study the influence of the chain structure on the mesophase morphology and transition temperature[56]. Kelly has studied the effect of the position of a double bond along a chain[57] and Goulding and co-workers[58] have studied the effect of an oxygen atom at varying positions along a chain. Each of these investigations has shown that the length and the nature of the terminal chain can influence the mesomorphic properties of the material. Coates[59, 60] studied the effect of a methyl-branching at various positions along the chain and showed that the closer the branching point was to the core the more severely the mesophase stability is depressed. The melting points of the materials were also significantly reduced. When the branching point was further away from the core, its effect on the mesophase stability was less, but the melting points were still reduced.

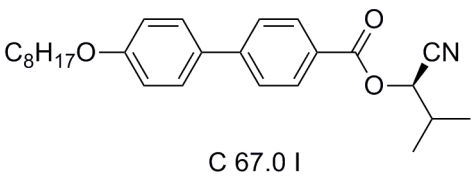
1.6.3 Chiral Dopants

Chiral dopants are required to be integrated into the structure of the achiral assembly in order to confer chirality to the whole system by generating a chiral environment. Only a small amount of chiral dopant needs to be added to confer chirality, however, the chiral properties will be strongly dependent upon both the nature and the amount of dopant that has been added. Ideally, chiral dopants for practically applicable FLC mixtures should be chemically stable and easily accessible chiral groups with a reproducible enantiomeric purity.

Although the chiral dopant only accounts for less than 10% of the total ferroelectric mixture, it is a most fundamental component. Whilst the chiral dopant need not be mesogenic in order to be useful in imparting ferroelectric properties to the smectic C host mixture, it should have a mesogenic-like structure, preferably similar to that of the host materials in order to help maintain the properties of the host mixture. Care should be taken when considering the structural nature of the chiral dopant to ensure it does not depress the SmC phase stability of the host mixture to uselessly low levels. For example, when the SmC phase stability of the host mixture is low, it is important that the chiral dopant exhibits a chiral smectic C phase in order to maintain the the chiral Smectic C phase (SmC*) stability in the ferroelectric mixture. However, in host mixtures where the SmC phase stability is high, the mesogenic nature of the dopant is less important and more attention can be paid to other essential features of the dopant, *e.g.*, a high Ps, good solubility and long chiral nematic pitch length.

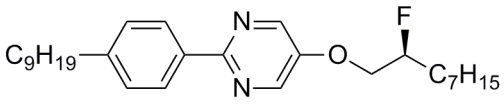
The majority of chiral dopants for use in ferroelectric mixtures have a polar group at the chiral centre (*e.g.*, Cl, F, or CN) which provides the necessary high Ps. Figure 1.19 illustrates the chemical structure of two chiral dopants. The cyanohydrin ester, compound **1.24**[10], has a polar cyano substituent at the chiral centre. The large dipole associated with the cyano unit ensures the generation of high Ps magnitude. However, although compound **1.24** is non-mesogenic, it has a mesogenic-like architecture and accordingly, should be useful as a chiral dopant for ferroelectric mixtures.

It should be noted that problems arise in using a cyano group at the chiral centre in that whilst the cyano group generates the desired high Ps, the high polarity and size of the cyano substituent can lead to viscosity and solubility problems in addition to significant depressions in the SmC phase stability of the host mixture.



C 67.0 I

1.24



C 53.0 SmC* 67.0 SmA* 82.0 I

1.25

Figure 1.19. The chemical structure of two chiral dopants

The use of a fluoro at the chiral centre offers many advantages when designing chiral dopant materials. Its small size and high electronegativity ensure the generation of high Ps without enhancing viscosity or adversely affecting solubility. Additionally, the small size of the fluoro substituent upholds, or even enhances, the SmC phase stability of the original host mixture. This is particulary important for ferroelectric host mixtures based on phenylpryimidines which have particularly low SmC phase stabilities.

Compound **1.25** [10]has a fluoro substituent at the chiral centre, however compound **1.25** shows a high smectic C phase stability, which is useful for ferroelectric applications[31]. The pyrimidine-based compound **1.25** finds use in ferroelectric mixtures based on phenylpyrimidine host materials, usually high percentages (20%) are used in order to confer a reasonably high spontaneous polarization, but the overall smectic C phase stability does not suffer because it exhibits the chiral smectic C phase to high temperature[31]

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2 Aims and Objectives[1]

It was way back in 1975 that the chiral smectic C (SmC*) phase was shown to be ferroelectric when confined in a thin cell[2], and in 1980 that the concept of a surface-stabilized ferroelectric display was reported[3]. Display devices based on ferroelectric technology offer huge advantages over the conventional nematic displays in terms of very fast (microsecond) switching times, bistability, high resolution and wide angles of view, and hence prompted intense research into the synthesis and properties of new materials and into device engineering[4-7].

One important issue is the control of alignment of ferroelectric liquid crystal materials. Usually, the material possesses a cooling phase sequence of nematic, smectic A, smectic C, with the theory that the fluid nematic phase aligns molecules homogeneously, the molecules then order in the usual smectic layers of the smectic A phase, and on further cooling the molecules tilt within the layers to generate the necessary smectic C phase[4, 7-9]. Unfortunately, the process of tilting causes a layer shrinkage, which tends to cause the layers to buckle in order to fill free space created, such a buckling causes chevrons[7, 10-14] rather than a perfect 'bookshelf geometry. Such chevrons are detrimental to the appearance of the display by introducing a visible defect (zigzag defect) at the point of layer kinking which reduces contrast. The generation of suitable chiral smectic C mixtures which do not give a layer shrinkage on cooling would eliminate the chevron formation and generate the desired bookshelf geometry. Thus enhancing the scope and value of ferroelectric liquid crystals technology in commercial device applications, particularly for microdisplays for projection displays where defects in alignment are more detrimental.

2.1 Host Materials

It is now well-established that the only viable way of generating appropriate ferroelectric liquid crystal mixtures is to use achiral host materials to fine tune the essential properties such as mesomorphism, birefringence, and viscosity. An optimized achiral host mixture is then doped with a suitable chiral material to introduce the essential reduced symmetry properties to the mixture[4, 7, 8, 14]. The *ortho*-difluoroterphenyl materials are well-established as excellent host materials for ferroelectric mixtures. Both dialkyl and alkyl-

alkoxy analogues tend to give low melting points, generate the SmC phase over a wide temperature range, confer a low viscosity (particularly the dialkyl analogues), show the birefringence required for small cell spacings, and they are of high resistivity[8, 14]. This research is aimed at maintaining the desirable properties of the difluoroterphenyl compounds, and hence the core unit has been retained, but one of the terminal chains has been replaced with a short, bulky unit.

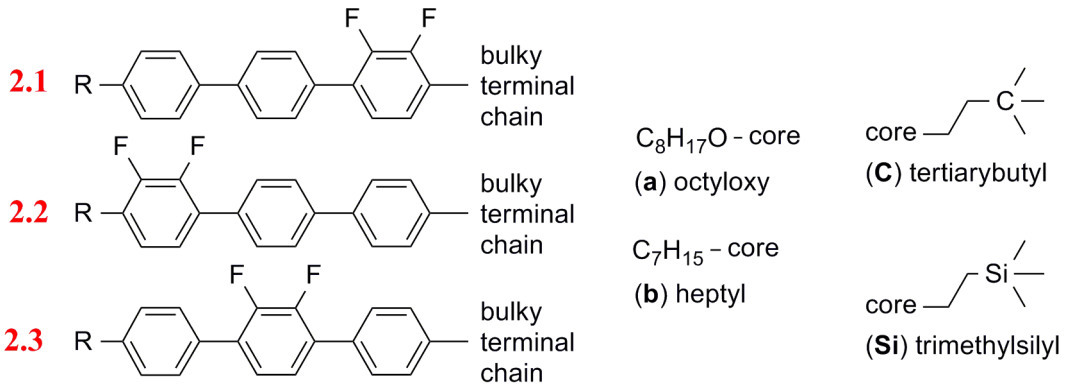

Figure 2.1. The general molecular architectures of the targeted novel materials

Two bulky units were chosen, a tertiarybutyl group and the slightly larger trimethylsilyl group, which are located very close to the core in order to effect the maximum influence on the molecular properties. It is expected that the bulky terminal chain will be incompatible with the conventional unbranched terminal chain causing phase separation, thus making the smectic layers more distinct, less inter-dependent and be conducive towards a bookshelf phase structure. As shown in figure 2.1, all three possible *ortho*-difluoroterphenyl cores (**2.1**, **2.2** and **2.3**) have been investigated, in combination with the two conventional terminal chains, octyloxy (**a**) and heptyl (**b**), and the two bulky terminal units of tertiarybutyl (**C**) and trimethylsilyl (**Si**). Such systematic combinations provide for a total of 12 novel liquid crystals, and enable a comprehensive investigation of initially melting point, mesophase morphology and transition temperatures in comparison with the known analogues with conventional terminal chains.

The effect on the mesomorphic behaviour of varying the degree of fluoro substituents upon the multi-ring system is also planned to be investigated, some mono- and tri-fluoro systems were targeted. Monofluoroterphenyls[15, 16] give access to higher liquid crystal phase thermal stability, and is view of the use of sterically challenging terminal units,

there were thought worth of investigations. Trifluoroterphenyls[17, 18] are known to generate low melting points, which is an aim for the novel materials with bulky terminal units, and since such short units might be expected to give relatively high melting points, then these systems were essential to investigate.

2.2 Chiral Dopants

As already detailed, a chiral dopant is essential to generate ferroelectric mixtures. Although, 'only' chiral dopant may confer such ferroelectricity, it was thought useful to develop novel chiral dopants of compatible structure to the host materials. Hence, two chiral compounds were targeted, one containing the bulky terminal units of tertiarybutyl (C), and the other containing trimethylsilyl (Si) to be used as chiral matched dopants are needed for addition to a host mixture for the formulation of FLC mixtures.

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18. M. E. Glendenning, J. W. Goodby, M. Hird and K. J. Toyne, *Journal of the Chemical Society-Perkin Transactions 2*, 1999, 481.

3 Experimental

3.1 Techniques and Methods of Analyses

A number of techniques[1-3] have been used for the synthesis and characterization of the materials discussed in this report and descriptions of these procedures and specification are given here.

3.1.1 Purification of Materials

Since impurities in liquid crystal materials can greatly influence their mesomorphic properties and other physical properties, great care was taken to ensure the total purity of all final products. The compounds were synthesized from commercially-available starting materials, which were used without further purification, and 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[4]. Reactions were frequently monitored by thin layer chromatography (TLC) and/or gas liquid chromatography (GC). Compounds were purified by distillation, recrystallisation, and column chromatography on silica gel or by a combination of these techniques.

Gravity column chromatography was carried out using BDH silica gel, 33-70 μm, and eluted using the solvents stated in the appropriate preparation. Final products were additionally filtered through Schleicher & Schuell filter papers to remove particulates.

Many distillations were carried out using a standard distillation process and the temperature and pressure are as quoted in the text. Fractional distillations were carried out using a Vigreux column which allows reasonable separation of compounds with a boiling point difference of 10-30 °C. Distillation under reduced pressure was used for the compounds which have high boiling points.

3.1.2 Structural Analysis and Purity

Confirmation of the structures and purity of the intermediate products was obtained by the ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) for all intermediate

products and Mass Spectrometry (MS) for most cases. In addition to ^{1}H NMR and MS, final compounds were subjected to additional ^{13}C NMR, High Performance Liquid Chromatography (HPLC), Elemental Analysis (EA) and Optical Rotation (OR), as appropriate. The liquid crystalline properties of all final products were assessed using Polarising Optical Microscopy (POM), and confirmed by Differential Scanning Calorimetry (DSC).

3.1.2.1 ^{1}H and ^{13}C Nuclear Magnetic Resonance Spectroscopy (NMR)

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[5, 6].

3.1.2.2 Mass Spectrometry (MS)

Mass Spectra were recorded using one of two instruments[7]:

- Solid Probe EI MS spectra were recorded using a Shimadzu QP5050A quadropole GC/MS instrument at 70 eV, 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.

3.1.2.3 High Performance Liquid Chromatography (HPLC)

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[5] utilising (typically) dichloromethane 30% and acetonitrile 70% as eluent.

3.1.2.4 Elemental Analysis (EA)

Elemental analysis was carried out using a Fissons EA1108 CHN Elemental Analyser[5]. Some compounds don't show elemental analysis because incomplete composition caused by presence of silicon.

3.1.2.5 Polarising Optical Microscopy (POM)

Transition temperatures for the final compounds 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[5].

3.1.2.6 Differential Scanning Calorimetry (DSC)[5]

Transition temperatures for the final compounds were measured and observed using POM and then 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 Nomenclature and Abbreviations

Throughout this report the IUPAC system of nomenclature has been used as a guide. The meanings of the abbreviations used are listed below:

mp	-	Melting Point	bp	-	Boiling Point
Cr	-	Crystal	I	-	Isotropic Liquid
N	-	Nematic	SmA	-	Smectic A
SmC	-	Smectic C	SmCalt	-	Smectic C alt
N*	-	Chiral Nematic	SmA*	-	Chiral Smectic A
SmC*		Chiral Smectic C			

^{1}H NMR nomenclature

s	-	singlet	d	-	doublet
t	-	triplet	q	-	quartet
m	-	multiplet	b	-	broad
dd	-	double doublet	ddd	-	double, double doublet
dddd	-	double, double, double doublet	dt	-	double triple

Solvent and and Reagents

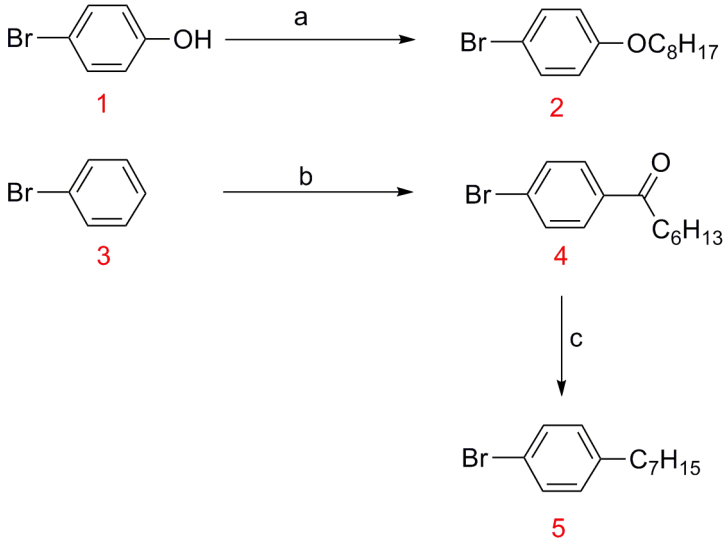
$CDCl_3$	-	deuterated chloroform	DEAD	-	diethyl azodicarboxylate
DCM	-	dichloromethane	DME	-	1,2-dimethoxyethane
DMSO	-	dimethylsulphoxide	THF	-	tetrahydrofuran
DMF	-	dimethylformamide	*n*-BuLi	-	*n*-butyllithium
sec-BuLi	-	*sec*-butyllithium	EtOH	-	ethanol
EtOAc	-	ethyl acetate	Et_2O	-	diethyl ether

Terphenyl: for ease terphenyl stands for [1,1':4',1"] terphenyl unless stated otherwise.

3.2 Synthetic Schemes

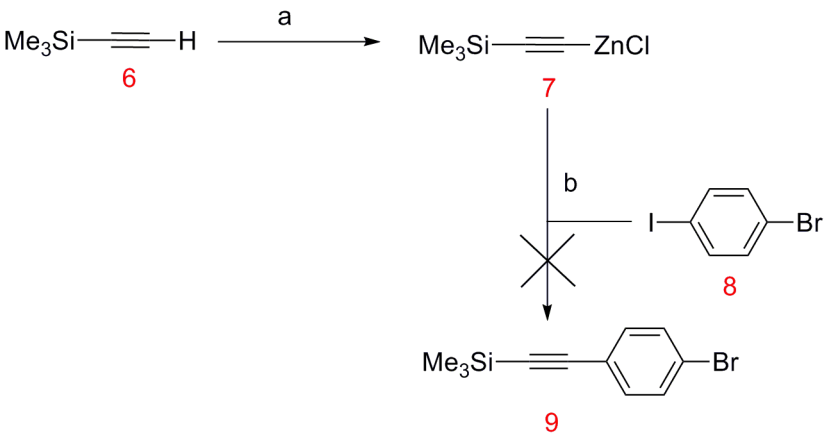
3.2.1 Required Intermediate Compounds

Scheme 1



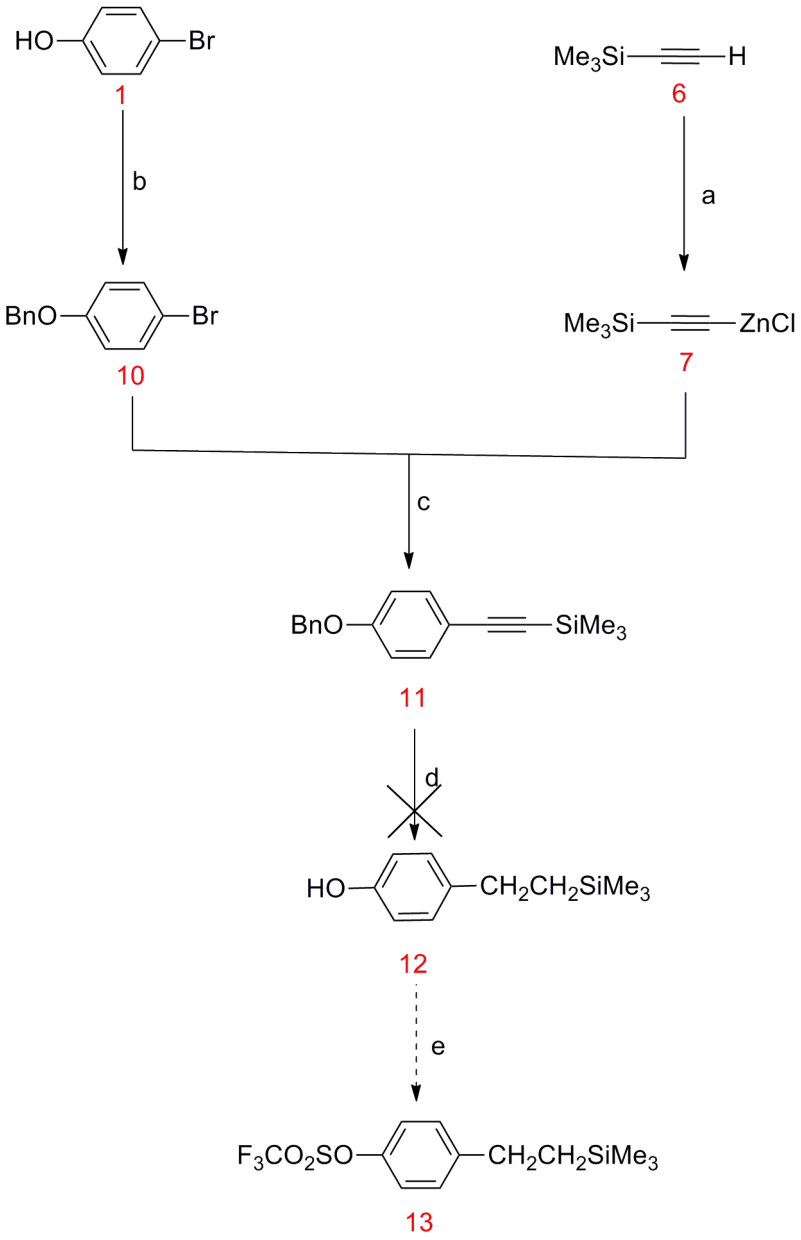
a...$C_8H_{17}Br$, K_2CO_3, Butanone
b...$C_6H_{13}COCl$, $AlCl_3$
c...$NH_2NH_2{\cdot}H_2O$, Diethyleneglycol, KOH

Scheme 2



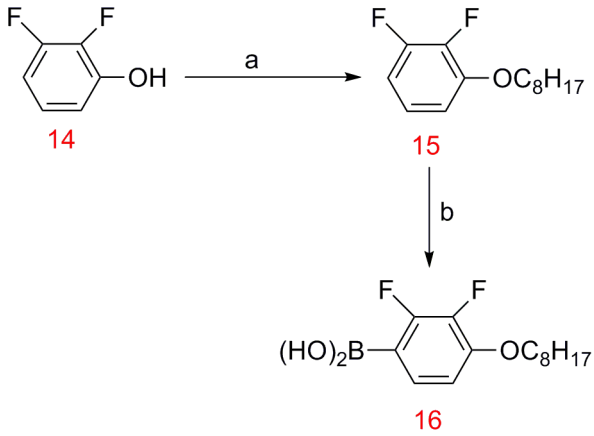
a...(i) *n*-BuLi; (ii) $ZnCl_2$,THF
b...$Pd(PPh_3)_4$, THF

Scheme 3



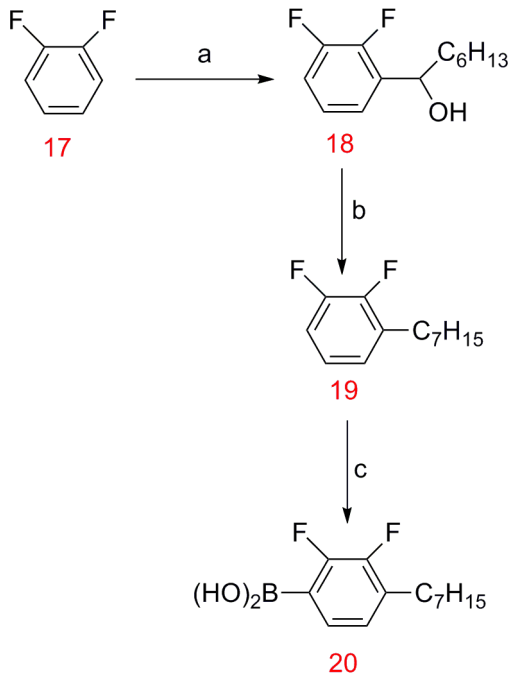
a...(i) *n*-BuLi; (ii) $ZnCl_2$
b...BnCl, K_2CO_3, Butanone
c...$Pd(PPh_3)_4$, THF
d...10% Pd/C, H_2, EtOAc
e...$(CF_3SO_2)_2O$, Pyridine

Scheme 4



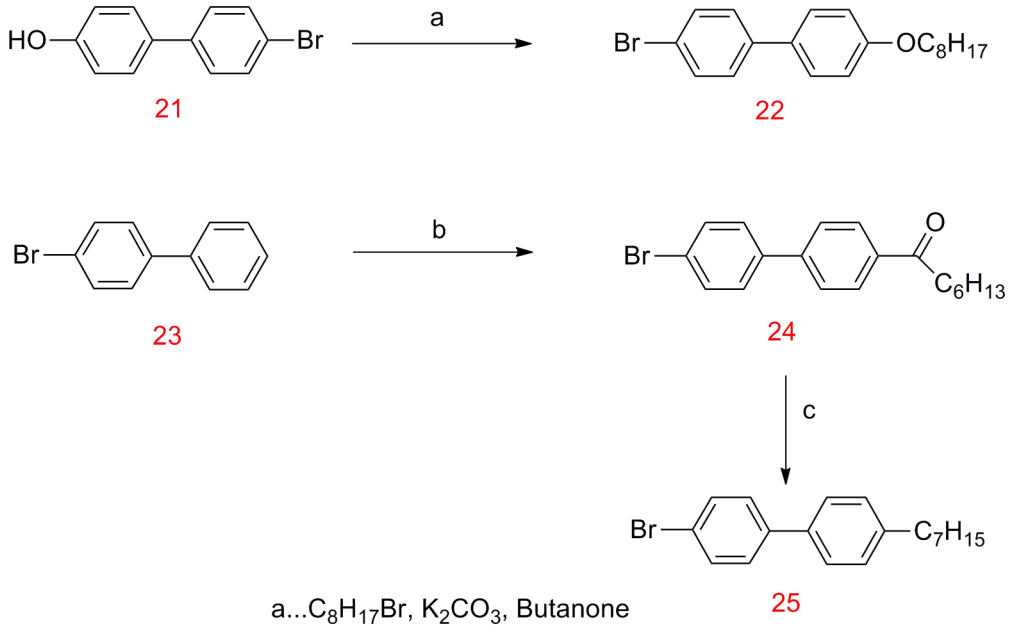
a...$C_8H_{17}Br$, K_2CO_3, Butanone
b...(i) *n*-BuLi, –78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl

Scheme 5



a...(i) *n*-BuLi, –78 °C; (ii) $C_6H_{13}CHO$; (iii) NH_4Cl (aq)
b...(i) PTSA, Toluene; (ii) 10% Pd/C, H_2
c...(i) *n*-BuLi, –78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl

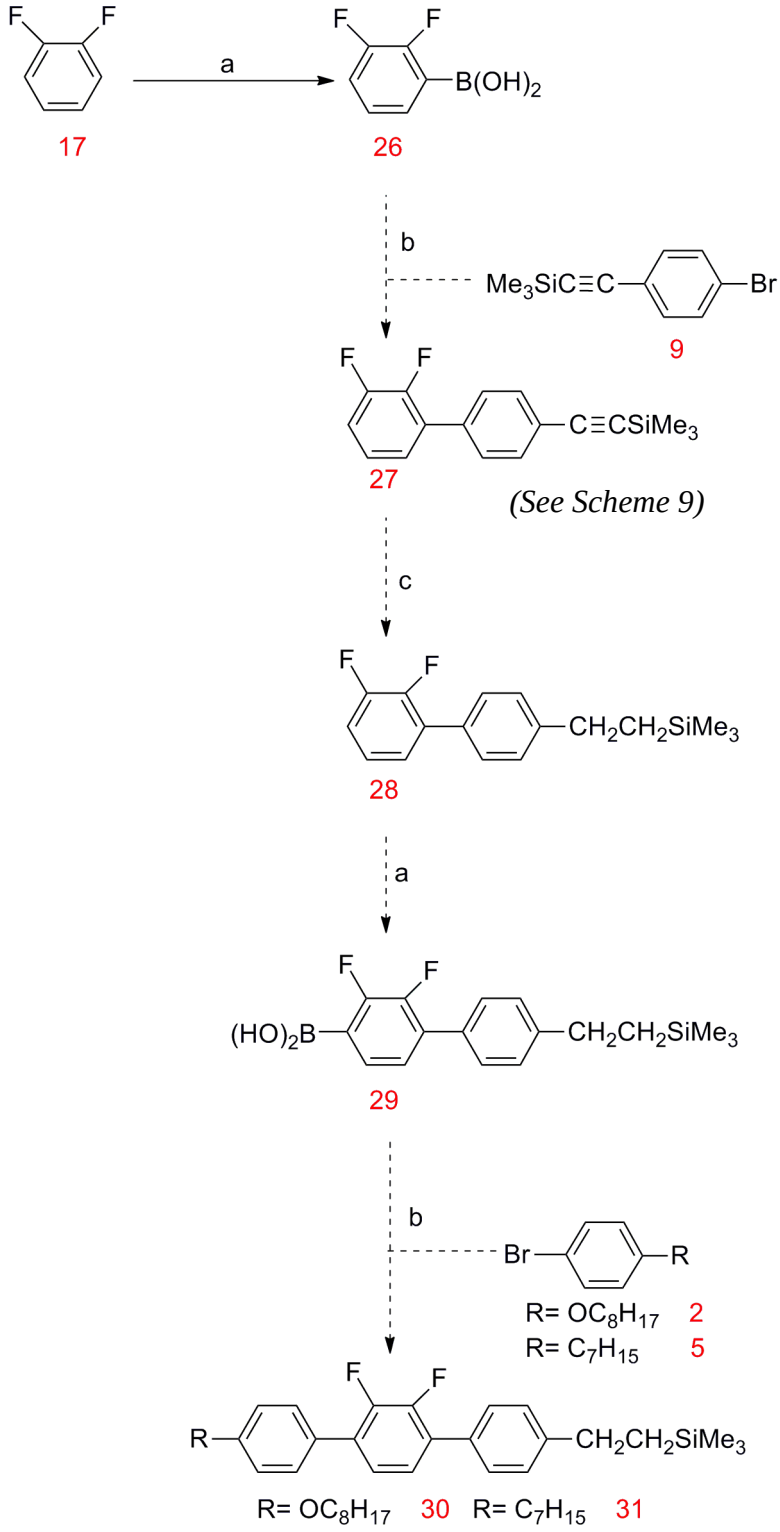
Scheme 6



a...$C_8H_{17}Br$, K_2CO_3, Butanone
b...$C_6H_{13}COCl$, $AlCl_3$, DCM
c...$NH_2NH_2{\cdot}H_2O$, Diethyleneglycol, KOH

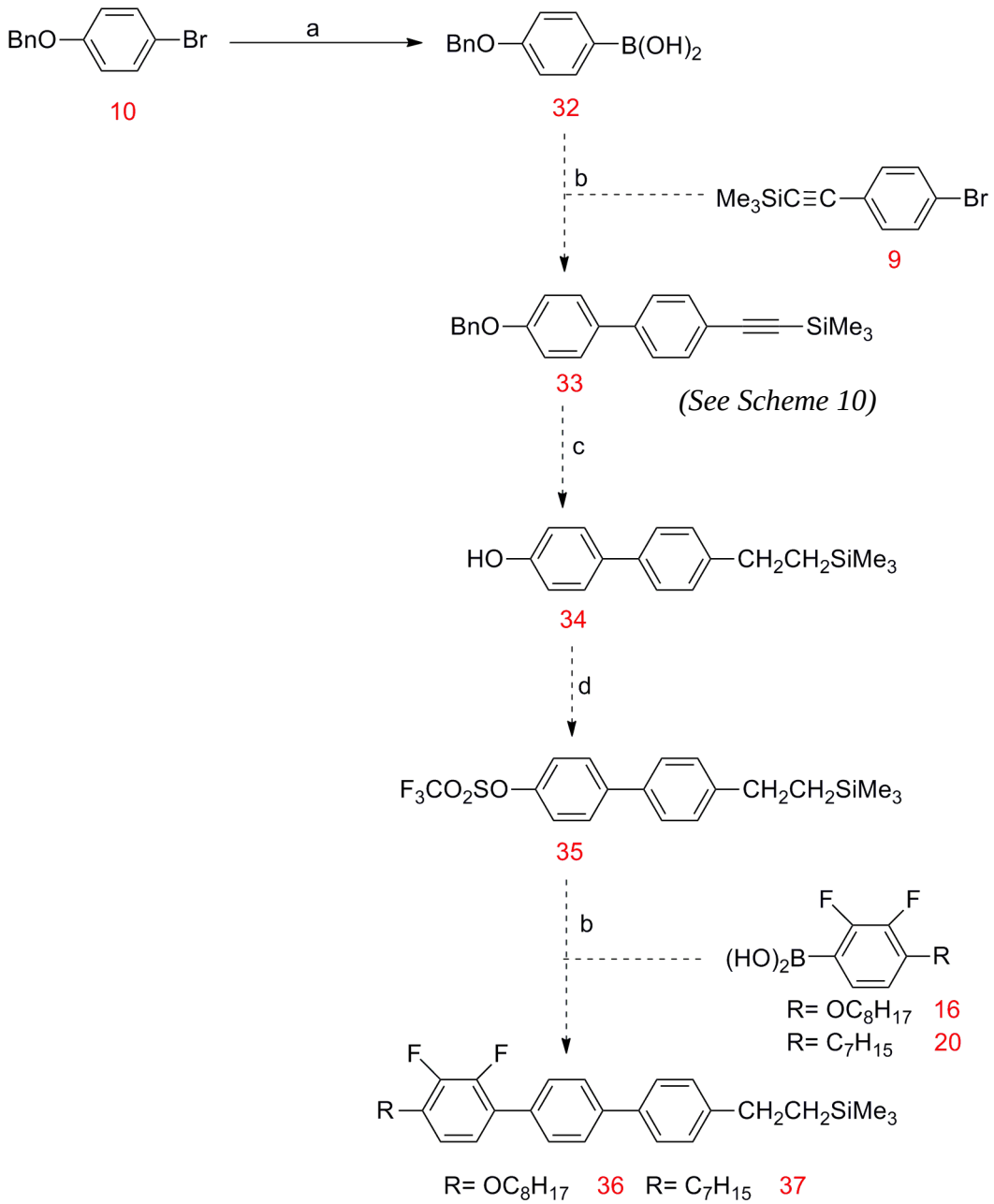
3.2.2 Difluoroterphenyl Compounds

Scheme 7



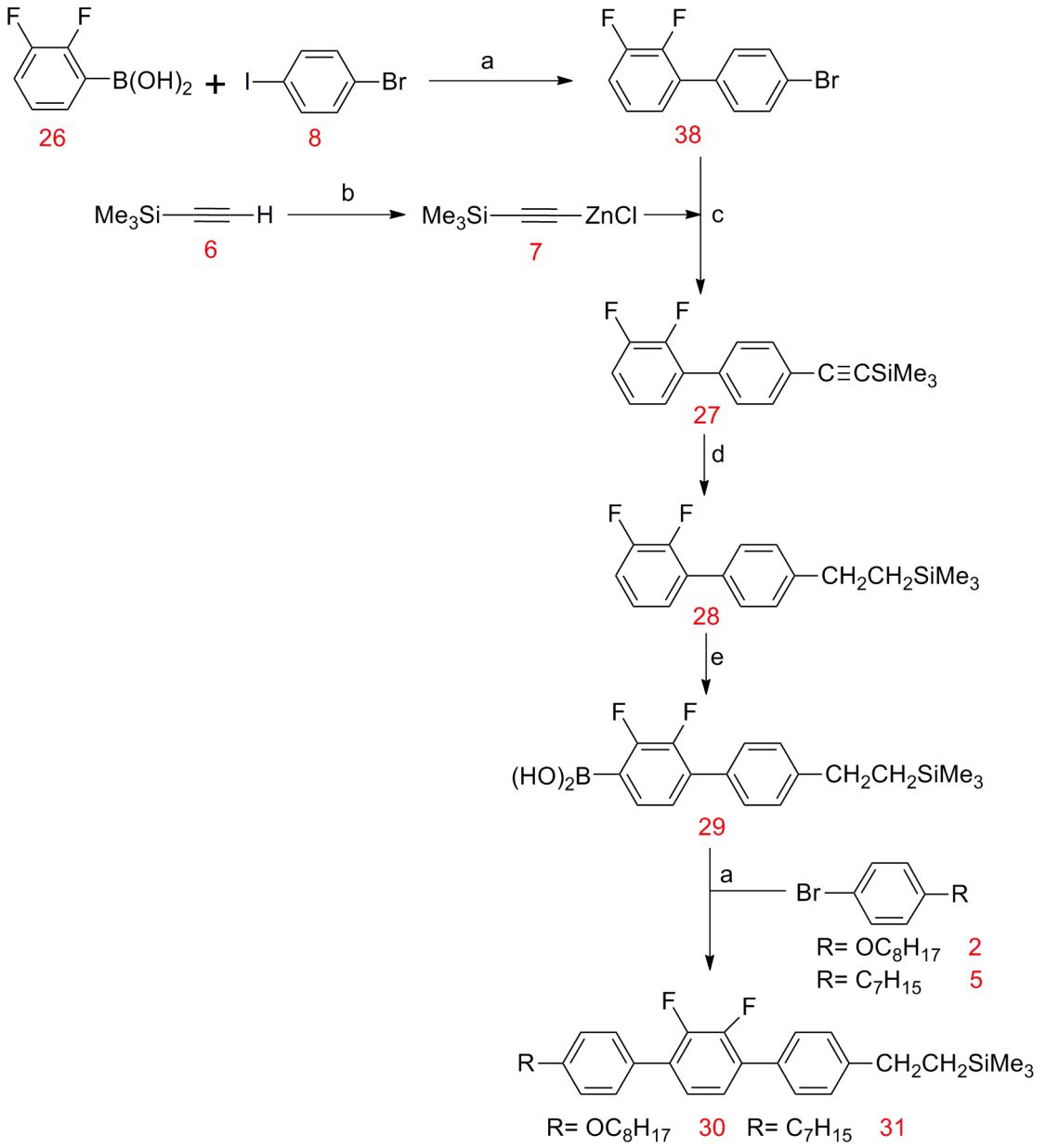
a...(i) *n*-BuLi, –78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl
b...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water
c...10% Pd/C, H_2, EtOAe

Scheme 8



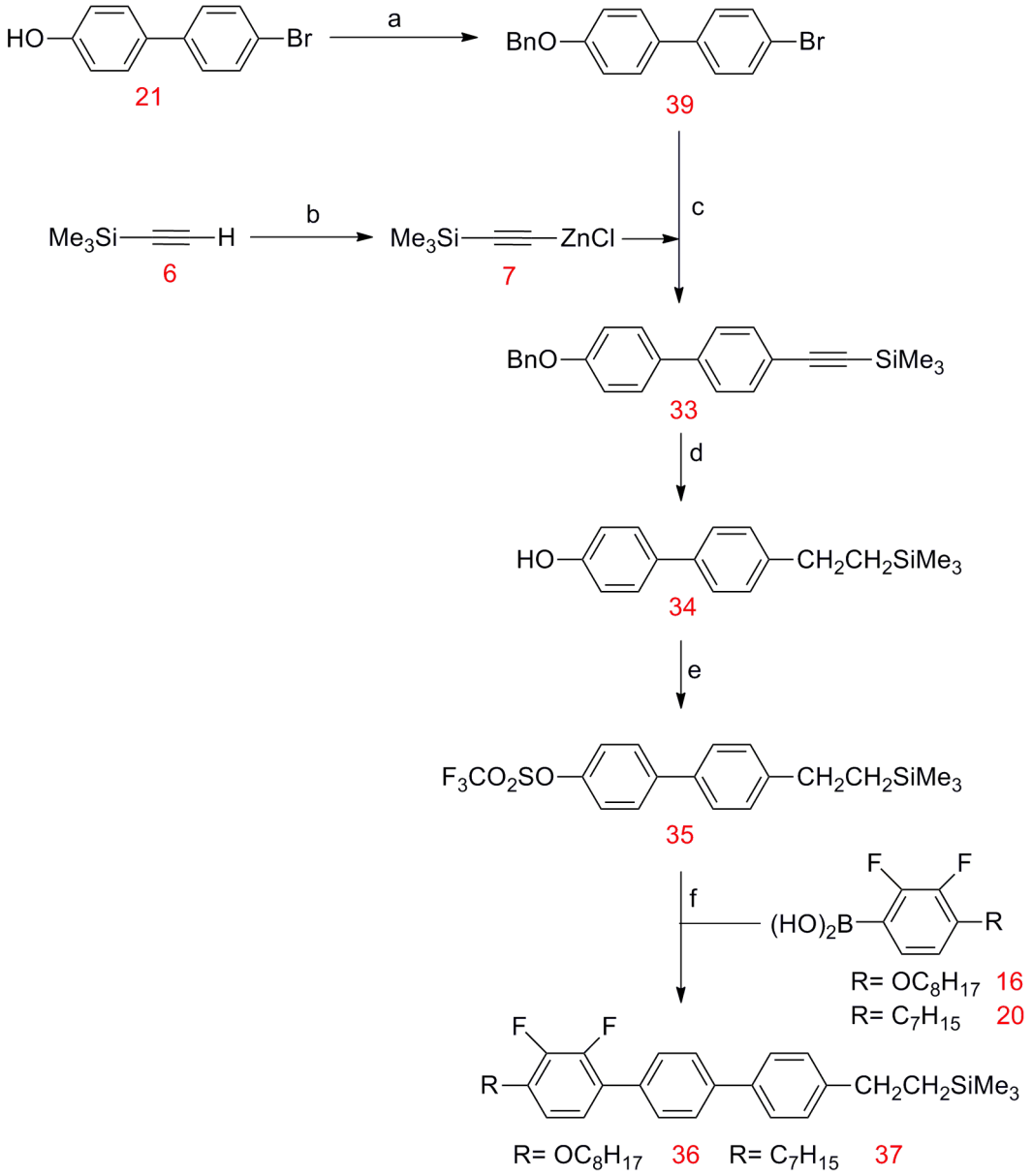
a...(i) Mg; (ii) $(MeO)_3B$; (iii) 10% HCl
b...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water
c...10% Pd/C, H_2, EtOAc
d...$(CF_3SO_2)_2O$, Pyridine

Scheme 9



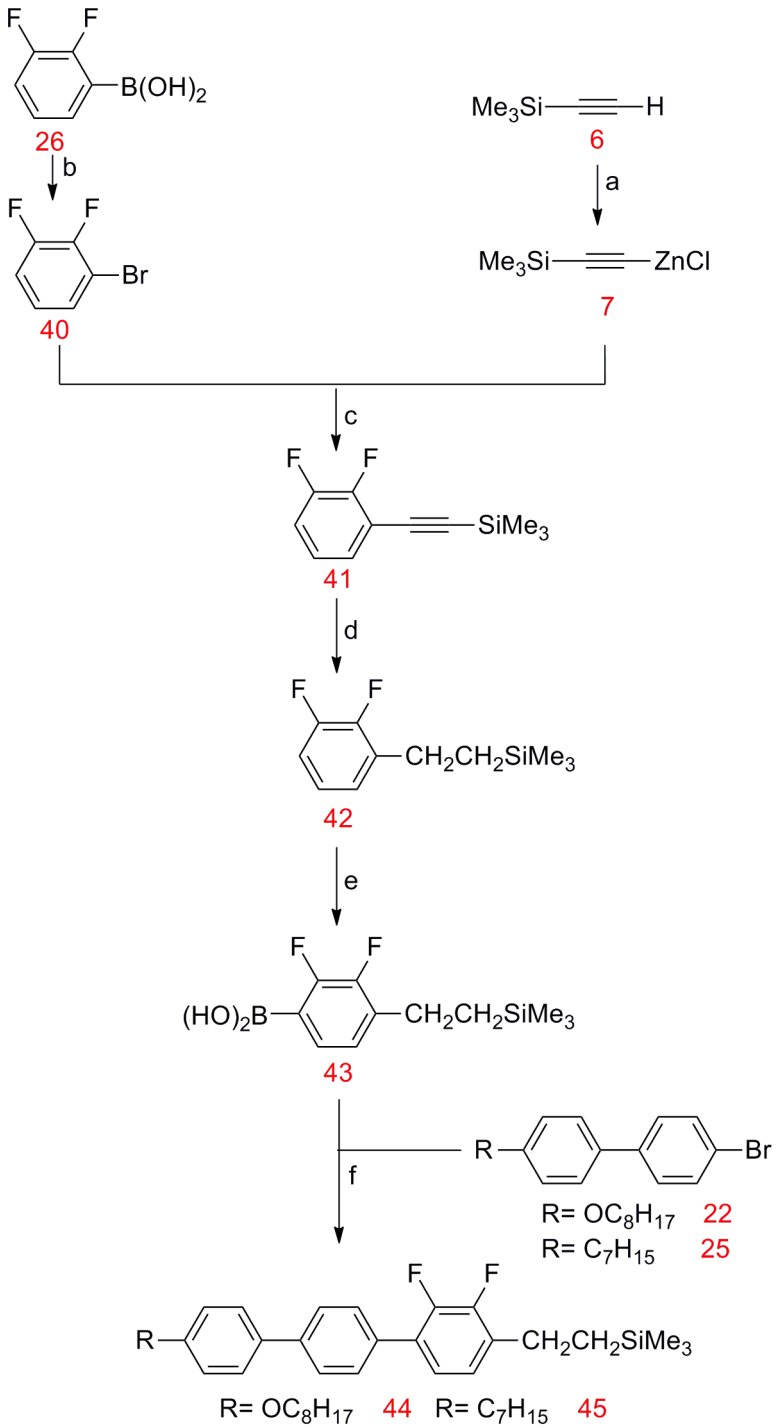
a...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water
b...(i) *n*-BuLi; (ii) $ZnCl_2$, THF
c...$Pd(PPh_3)_4$, THF
d...10% Pd/C, H_2, EtOH
e...(i) *n*-BuLi, –78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl

Scheme 10



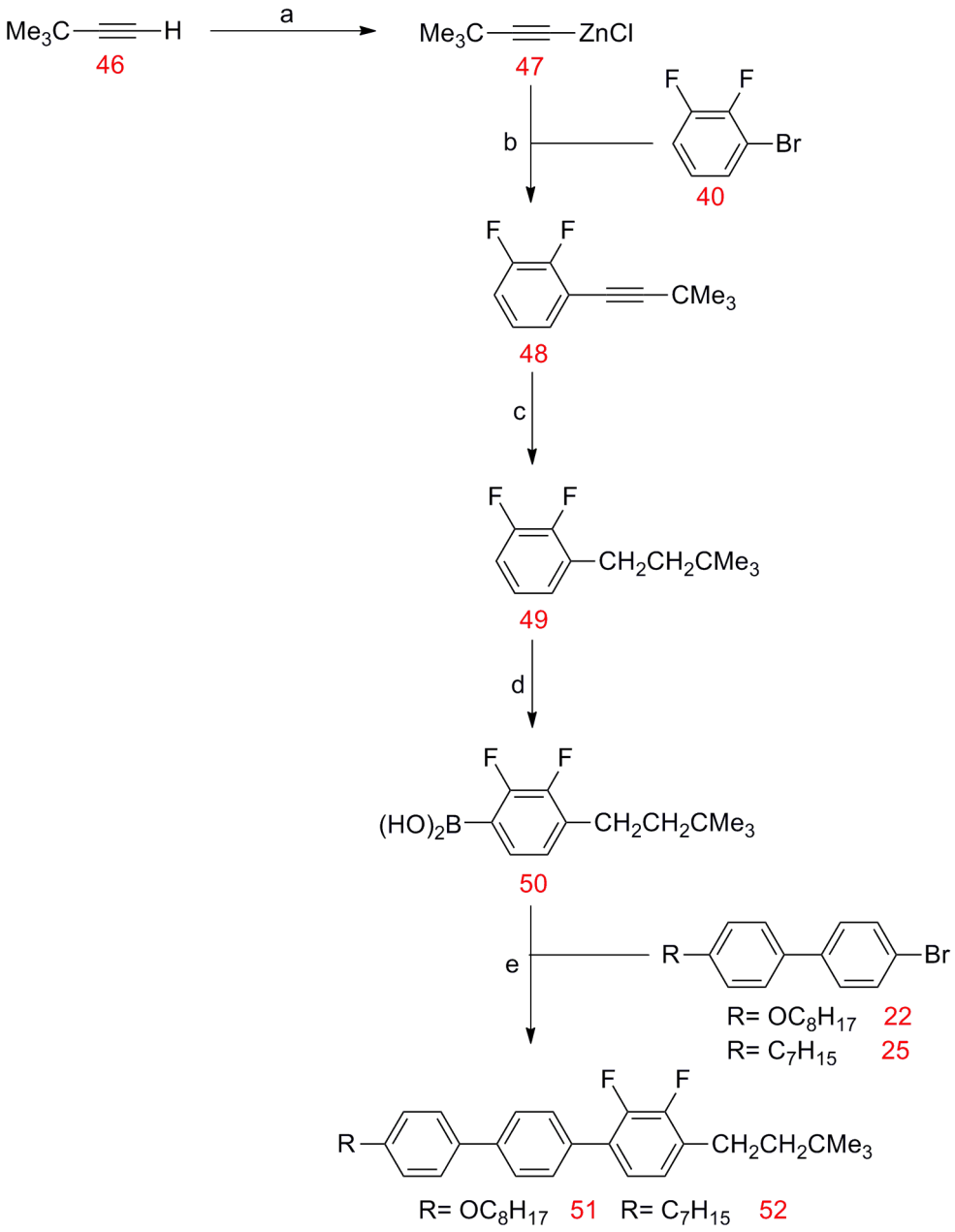
a...BnCl, K_2CO_3, Butanone
b...(i) *n*-BuLi; (ii) $ZnCl_2$, THF
c...$Pd(PPh_3)_4$, THF
d...10% Pd/C, H_2, EtOH
e...$(CF_3SO_2)_2O$, Pyridine
f...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water

Scheme 11



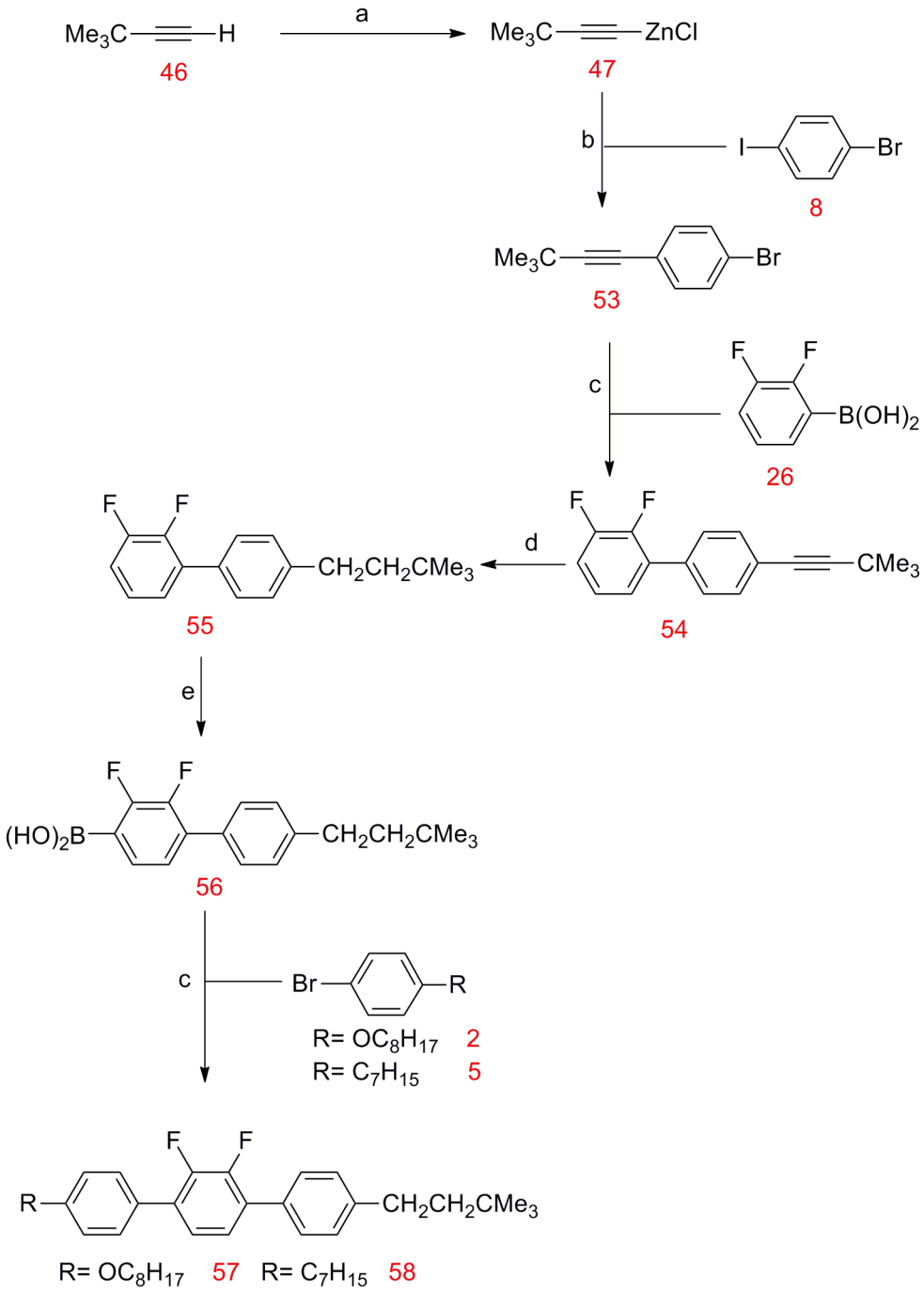
a...(i) *n*-BuLi; (ii) $ZnCl_2$, THF
b...NBS, CH_3CN
c...$Pd(PPh_3)_4$, THF
d...10% Pd/C, H_2, EtOH
e...(i) *n*-BuLi, –78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl
f...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water

Scheme 12



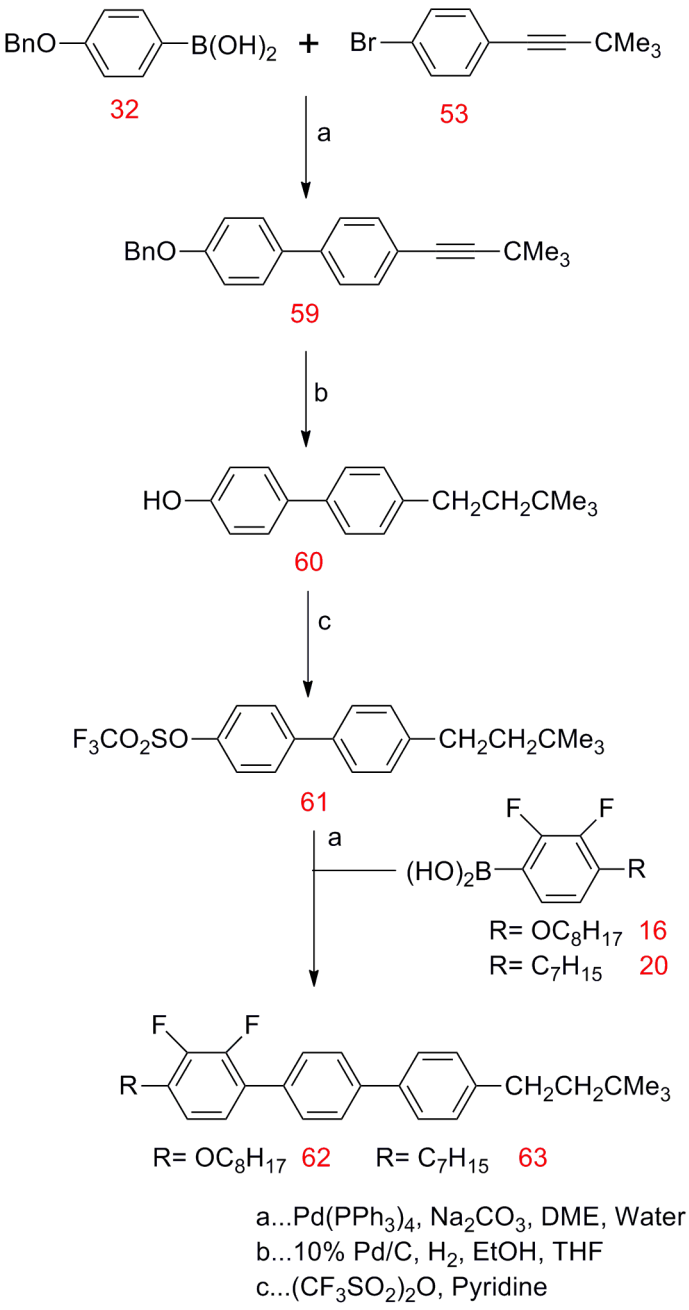
a...(i) *n*-BuLi; (ii) $ZnCl_2$, THF
b...$Pd(PPh_3)_4$, THF
c...10% Pd/C, H_2, EtOH
d...(i) *n*-BuLi, –78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl
e...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water

Scheme 13



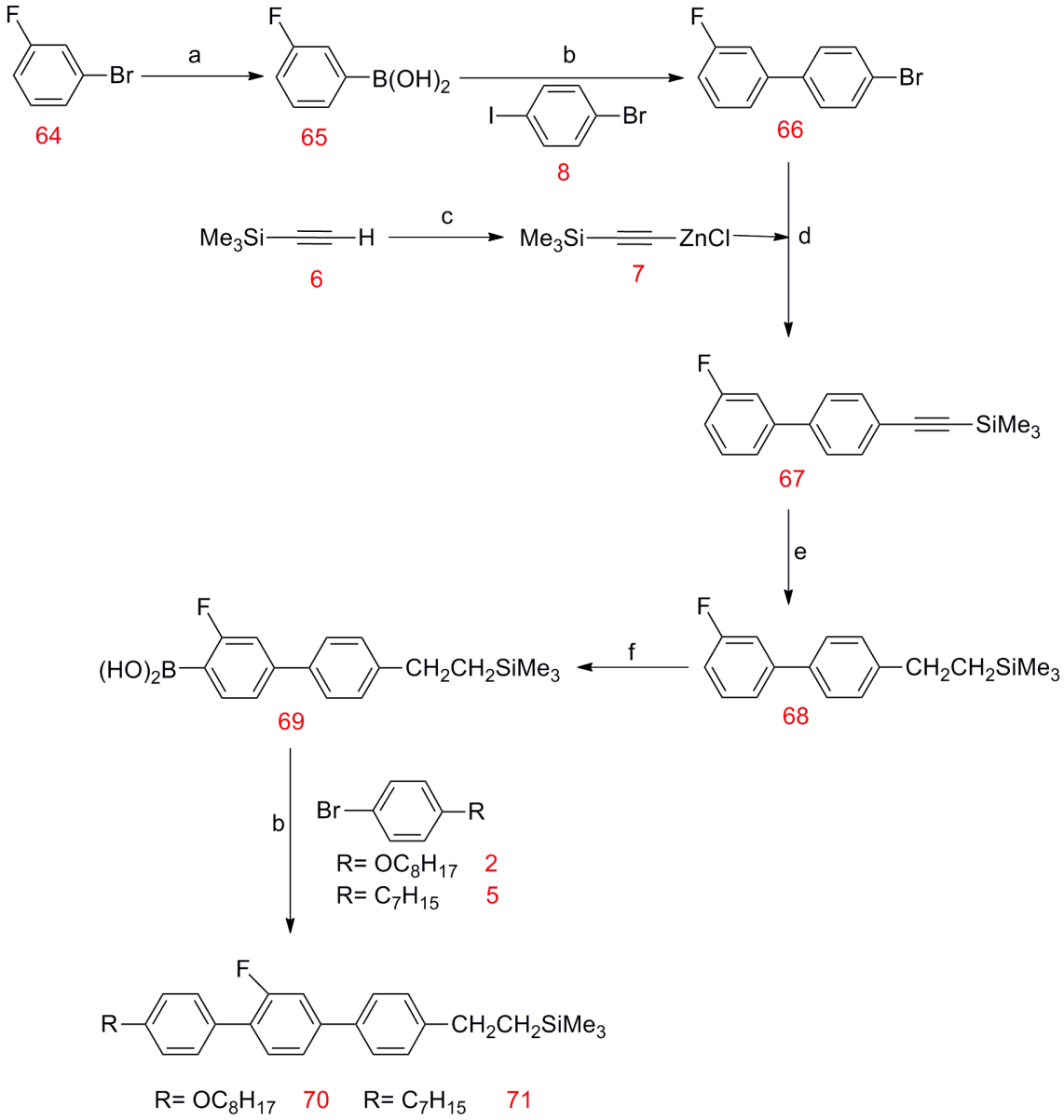
a...(i) *n*-BuLi; (ii) $ZnCl_2$, THF
b...$Pd(PPh_3)_4$, THF
c...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water
d...10% Pd/C, H_2, EtOH
e...(i) *n*-BuLi, –78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl

Scheme 14


BnO
B(OH)2
+
Br
CMe3
32
53
a
BnO
CMe3
59
b
HO
CH2CH2CMe3
60
c
F3CO2SO
CH2CH2CMe3
61
a
F
F
(HO)2B
R
R= OC8H17 16
R= C7H15 20
F
F
R
CH2CH2CMe3
R= OC8H17 62
R= C7H15 63
a...Pd(PPh3)4, Na2CO3, DME, Water
b...10% Pd/C, H2, EtOH, THF
c...(CF3SO2)2O, Pyridine

3.2.3 Monofluoroterphenyl Compounds

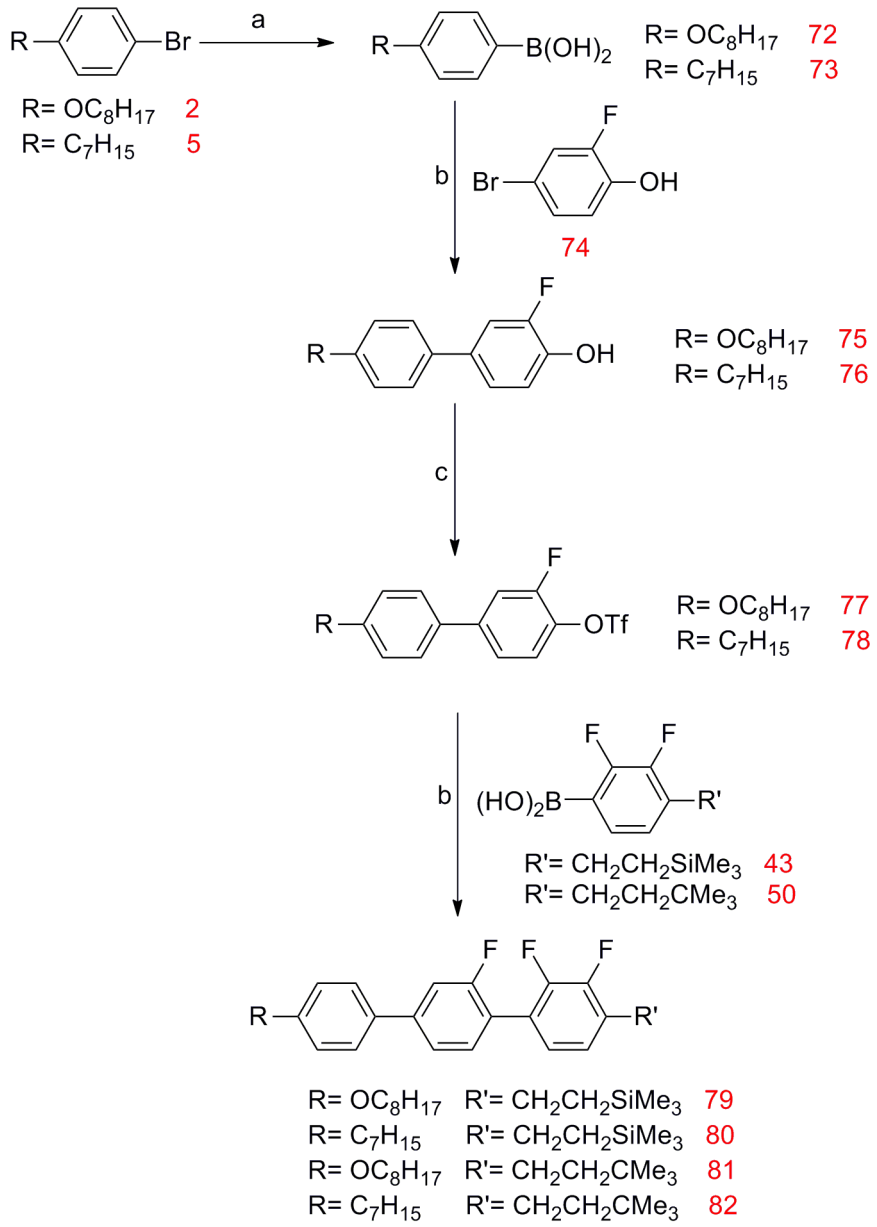
Scheme 15



a...(i) Mg; (ii) $(MeO)_3B$; (iii) 10% HCl
b...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water
c...(i) *n*-BuLi; (ii) $ZnCl_2$, THF
d...$Pd(PPh_3)_4$, THF
e...10% Pd/C, H_2, EtOH
f...(i) *sec*-BuLi, –78 °C; (ii) $(MeO)_3B$; (iii) 10% HCl

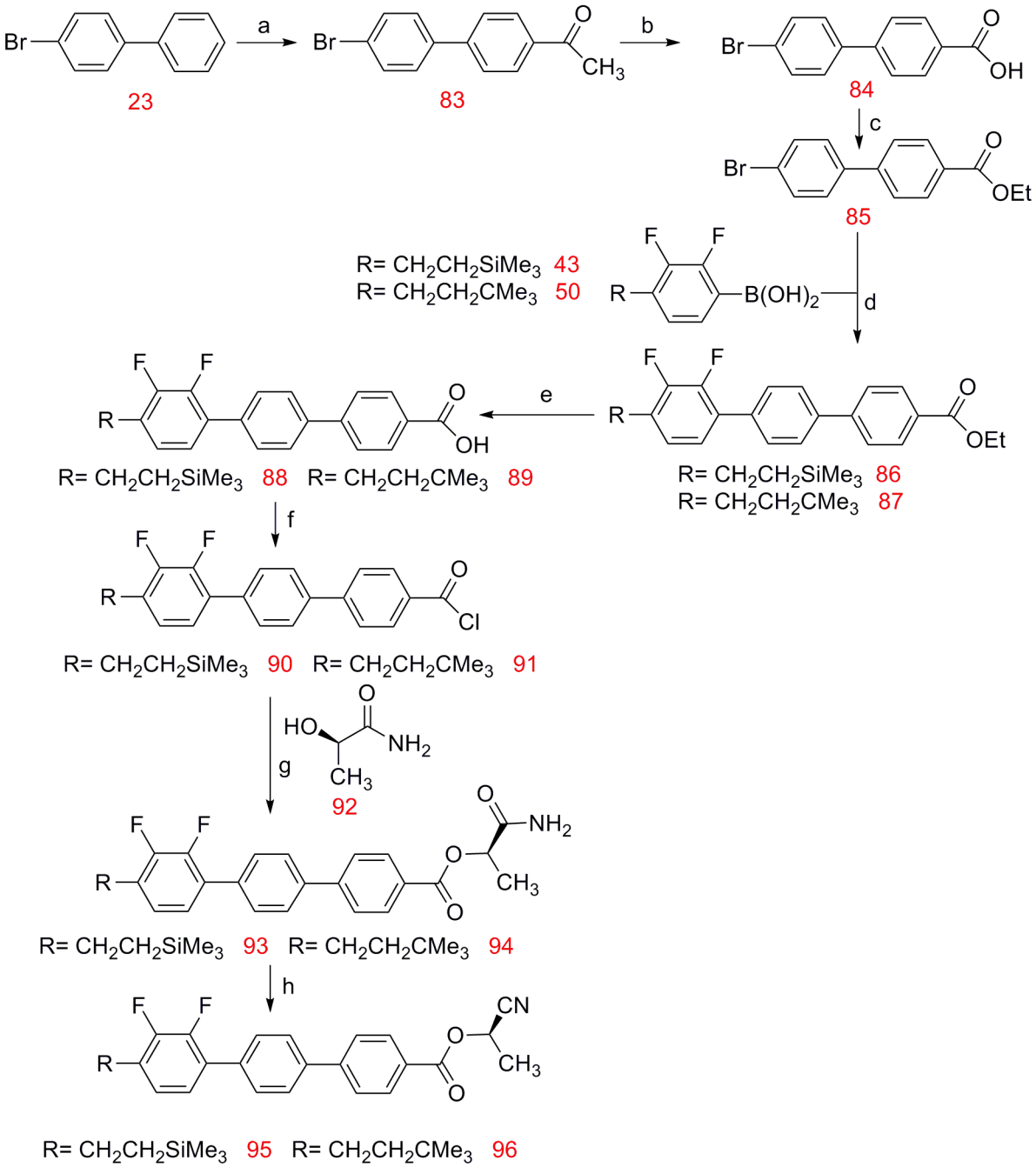
3.2.4 Trifluoroterphenyl Compounds

Scheme 16



3.2.5 Chiral Difluoroterphenyl Compounds

Scheme 17



a...CH_3COOCl, $AlCl_3$, DCM, 0 °C
b...Br_2,NaOH, HCl
c...Ethanol, H_2SO_4
d...$Pd(PPh_3)_4$, Na_2CO_3, DME, Water
e...(i) NaOH, Ethanol; (ii) HCl aq
f...Oxalyl chloride, DCM, DMF
g...Pyridine, THF
h...$POCl_3$, DMF

3.3 Experimental Procedures

3.3.1 Required Intermediate Compounds

Scheme 1

1-Bromo-4-octyloxybenzene (2)

A stirred mixture of 4-bromophenol (71.0 g, 0.41 mol), 1-bromooctane (96.57 g, 0.50 mol), and potassium carbonate (120 g, 0.87 mol) in butanone (300 ml) was heated under reflux for 24 h. The mixture was cooled, the potassium carbonate was filtered off, and the butanone was removed *in vacuo*. The residue was distilled to yield a colourless oil.

Yield: 112.7 g (96%)

Boiling Point (°C): 138 at 0.2 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (3H, t), 1.31 (8H, m), 1.44 (2H, quintet),1.79 (2H, quintet), 3.88 (2H, t), 6.76 (2H, d), 7.35 (2H, d)

MS *m/z* 286 (M^+), 284 (M^+)

1-Bromo-4-heptanoylbenzene (4)

Heptanoyl chloride (50.49 g, 0.34 mol) was added dropwise to a mixture of bromobenzene (150 ml) and aluminium chloride (50 g, 0.38 mol). The mixture was stirred at 0 °C for 1 h, then heated at 80 °C for 2 h, cooled and poured into 10% hydrochloric acid. The product was extracted into dichloromethane twice, and the combined organic extracts were washed with water and dried ($MgSO_4$). The dichloromethane was then removed. The excess of bromobenzene was removed *in vacuo* and the residue was distilled to yield a colourless solid.

Yield: 75.50 g (82%)

Boiling Point (°C): 133-135 at 0.2 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.35 (6H, m), 1.72 (2H, quintet), 2.93 (2H, t), 7.61 (2H, d) 7.82 (2H, d)

MS *m/z* 270 (M^+), 268 (M^+)

1-Bromo-4-heptylbenzene (5)

Compound **4** (74.00 g, 0.281 mol), hydrazine hydrate (41.32 g, 0.819 mol), potassium hydroxide (46.33 g, 0.843 mol) were added to diethylene glycol (250 ml) and heated at 130 °C for 2 h. The excess of hydrazine hydrate was distilled off and the temperature was raised to 200 °C for 2 h. After cooling, the mixture was poured into 18% hydrochloric acid and the product was extracted into ether (twice). The combined extracts were washed with water and dried ($MgSO_4$). The solvent was removed and the residue was distilled to yield a colourless liquid.

Yield: 60 g (84%)

Boiling Point (°C): 100-104 at 0.2 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.30 (8H, m), 1.58 (2H, quintet), 2.55 (2H, t), 7.05 (2H, d), and 7.39 (2H, d)

MS *m/z* 256 (M^+), 254 (M^+)

Scheme 2

1-Bromo-4-(trimethylsilylethynyl)benzene (9)

Several methods were used in an attempt to synthesis this compound.

Method 1

n-Butyllithium (2.5M in hexanes, 60 ml, 0.15 mol) was added dropwise to a stirred, cooled (-5 to 0 °C) solution of (trimethylsilyl)acetylene (15 g, 0.15 mol), in dry THF (150 ml) under dry nitrogen. This mixture was stirred for 10 min and zinc chloride (25 g, 0.18 mol) was added. The mixture was then stirred at room temperature for 15 min and $Pd(PPh_3)_4$ (8 g, 0.0069 mol) was added. A solution of 1-bromo-4-iodobenzene (36 g, 0.127 mol) in of dry THF (80 ml) was added dropwise. The mixture was stirred at room temperature overnight, (GLC analysis revealed a complete reaction) and poured into 10% hydrochloric acid. The product was extracted into ether (twice). The combined extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed and the residue was distilled to yield a colourless solid. NMR showed the structure of the starting compound and the structure of some of compound **9**.

Method 2

This procedure as described in method 1 was repeated with the exception of the mixture was stirred overnight at gentle heating (30 °C). NMR showed a mixture of the starting compound, some of compound **9**, and some double coupled compound.

Scheme 3

1-Bromo-4-benzyloxybenzene (10)

A stirred mixture of 4-bromophenol (80.0 g, 0.46 mol), benzyl chloride (69.85 g, 0.55 mol), and potassium carbonate (135 g, 0.98 mol) in butanone (300 ml) was heated under reflux for 24 h. The mixture was cooled, the potassium carbonate was filtered off, and the butanone was removed *in vacuo*. The residue was recrystallised from ethanol to yield colourless crystals.

Yield: 89.6 g (74%)

Melting Point (°C): 63.7

^{1}H NMR (400 MHz, $CDCl_3$) 5.07 (2H, s), 6.89 (1H, d), 7.35- 7.46 (7H, m)

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

1-Benzyloxy-4-(trimethylsilylethynyl)benzene (11)

n-Butyllithium (2.5M in hexanes, 138 ml, 0.35 mol) was added dropwise to a stirred, cooled (-5 to 0 °C) solution of (trimethylsilyl)acetylene (33.8 g, 0.35 mol), in dry THF (200 ml) under dry nitrogen. This mixture was stirred for 10 min and zinc chloride (46.9 g, 0.35 mol) was added. The mixture was then stirred at room temperature for 15 min and $Pd(PPh_3)_4$ (8 g, 0.0069 mol) was added. A solution of compound **10** (60 g, 0.23 mol) in dry THF (80 ml) was added dropwise. The mixture was stirred at reflux overnight, (GLC analysis revealed a complete reaction) and poured into 10% hydrochloric acid. The product was extracted into ether (twice). The combined extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed and the crude product was purified by column chromatography [silica gel/ hexane] to give a colourless solid.

Yield: 56 g (88%)

Melting Point (°C): 57.1

^{1}H NMR (400 MHz, $(CD_3)_2SO$) 0.27 (9H, s), 5.08 (2 H, s), 6.92 (2 H, d), 7.35- 7.46 (7 H, m)

MS *m/z* 280 (M^+)

4-(Trimethylsilylethyl)phenol (12)

Several methods were used in an attempt to synthesis this compound

Method 1

10% Palladium-on-charcoal (5 g) was added to a solution of compound **11** (56 g, 0.20 mol) in ethyl acetate. The mixture was placed in a hydrogenation apparatus overnight, but did not take up any H_2. The palladium-on-charcoal was filtered off; the ethyl acetate was removed *in vacuo* and recrystallized from ethanol to yield a colourless solid. NMR showed the structure of the starting compound.

Method 2

10% Palladium-on-charcoal (6 g) was added to a solution of compound **11** (56 g, 0.20 mol) in ethyl acetate and some ethanol. The mixture was placed in a hydrogenation apparatus overnight, but did not take up any H_2. The palladium-on-charcoal was filtered off; the ethyl acetate was removed *in vacuo* and recrystallized from ethanol to yield a colourless solid. NMR showed the structure of the starting compound.

Scheme 4

1,2-Difluoro-3-octyloxybenzene (15)

A stirred mixture of 2,3-difluorophenol (25.0 g, 0.192 mol), 1-bromooctane (44.39 g, 0.23 mol), and potassium carbonate (63.69 g, 0.46 mol) in butanone (300 ml) was heated under reflux for 24 h. The mixture was cooled, the potassium carbonate was filtered off, and the butanone was removed *in vacuo*. The residue was distilled to yield a colourless oil.

Yield: 41 g (88%)

Boiling Point (°C): 94-99 at 0.2 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 0.87 (3H, t), 1.31 (8H, m), 1.45 (2H, quintet), 1.8 (2H, quintet), 4.00 (2H, t), 6.69 (1H, dd), 6.72 (1H, ddd), 6.94 (1H, dddd)

MS *m/z* 242 (M^+)

1,2-Difluoro-3-octyloxyphenylboronic acid (16)

n-Butyllithium (2.5M in hexanes, 64.5 ml, 0.16 mol) was added dropwise to a stirred, cooled (-78 °C) solution of compound **15** (39 g, 0.16 mol), in dry THF (300 ml) under dry nitrogen. This mixture was stirred -78 °C for 45 min, and a solution of trimethyl borate (33.49 g, 0.32 mol) in THF (30 ml) was added dropwise at -78 °C. The stirred mixture was allowed to warm up to room temperature overnight and 10% hydrochloric acid was added and the mixture was stirred at room temperature for 1 h. Water was added and the product was extracted into ether (twice). The combined extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed *in vacuo*, the residue was stirred in hexane overnight to remove the last traces of the THF, and the product was filtered off to yield colourless crystals.

Yield: 30 g (65%)

^{1}H NMR (400 MHz, DMSO-D_6): 0.85 (3H, t), 1.27 (8H, m), 1.45 (2H, quintet), 1.71 (2H, quintet), 4.06 (2H, t), 6.97 (1H, ddd), 7.29 (1H, ddd), 8.15 (2H, s)

Scheme 5

(2,3-Difluorophenyl)heptan-1-ol (18)

n-Butyllithium (2.5M in hexanes, 48 ml, 0.12 mol) was added dropwise to a stirred, cooled (-78 °C) solution of 1.2-difluorobenzene (15.16 g, 0.133 mol), in dry THF (400 ml) under dry nitrogen. This mixture was stirred -78 °C for 45 min, and heptanal (12.13 g, 0.1064 mol) was added dropwise at -78 °C. The stirred mixture was allowed to warm up to room temperature overnight. Aqueous ammonium chloride was added and the product was extracted into ether (twice). The combined extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed *in vacuo*; the residue was distilled to yield a colourless oil.

Yield: 19.8g (66%)

Boiling Point (°C): 80-86 at 0.1 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 0.86 (3H, t), 1.26 (8H, m), 1.69 (2H, quintet), 3.27 (1H, s), 4.94 (1H, t), 7.02 (2H, m), 7.15 (1H, dddd)

MS *m/z* 228 (M^+)

1,2-Difluoro-3-heptylbenzene (19)

Phosphorus(V) oxide (34.1g, 0.24 mol) was added to a stirred solution of compound **18** (19 g, 0.0837 mol) in hexane (100ml). The mixture was stirred at room temperature overnight (GLC analysis revealed a complete reaction) and the mixture was filtered. 10% Palladium-on-charcoal (1.85 g) was added to the filtrate and the stirred mixture was hydrogenated for 4 h at room temperature and atmospheric pressure (GLC analysis revealed a complete reaction). The palladium-on-charcoal was filtered off, the hexane was removed *in vacuo* and the product was distilled to yield a colourless oil.

Yield: 12.g (67%)

Boiling Point (°C): 84-85 at 0.1 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 0.91 (3H, t), 1.33 (8H, m), 1.63 (2H, quintet), 2.67 (2H, dt), 6.92- 7.00 (3H, m)

MS *m/z* 212 (M^+)

2,3-Difluoro-4-heptylphenylboronic acid (20)

Quantities: *n*-butyllithium (2.5M in hexanes, 22.6 ml, 0.057 mol), compound **19** (12 g, 0.0567 mol), trimethyl borate (11.73 g, 0.113 mol). The experimental procedure was as described for the preparation of compound **16,** to yield colourless crystals.

Yield: 7.5 g (52%)

^{1}H NMR (400 MHz, DMSO-D_6) 0.81 (3H, t), 1.23 (8H, m), 1.51 (2H, m), 2.46 (2H, t), 7.00 (1H, t), 7.20 (1H, ddd), 8.26 (2H, s)

Scheme 6

4-Bromo-4'-octyloxybiphenyl (22)

Quantities: 4-bromo-4'-hydroxybiphenyl (80.0 g, 0.32 mol), 1-bromooctane (74.2 g, 0.384 mol), and potassium carbonate (88.3 g, 0.64 mol). The experimental procedure was as described for the preparation of compound **2**, except that the product was recrystallised from ethanol to yield colourless crystals.

Yield: 100 g (90%)

Melting Point (°C): 128.3

^{1}H NMR (400 MHz, $CDCl_3$) 0.92 (3H, t), 1.35 (8H, m), 1.50 (2H, quintet), 1.82 (2H, quintet), 4.00 (2H, t), 6.98 (2H, d), 7.43 (2H, d), 7.50 (2H, d), 7.55 (2H, d)

MS *m/z* 362 (M^+), 360 (M^+)

4-Bromo-4'-heptanoylbiphphenyl (24)

Heptanoyl chloride (17 g, 0.118 mol) was added dropwise to a mixture of aluminium chloride (17.12 g, 0.128 mol) in dichloromethane (300 ml) at -5 to 0 °C. 4-Bromobiphenyl (25 g, 0.107 mol) was added slowly over 30 min to the mixture at -5 to 0 °C. The mixture was stirred at room temperature overnight, (GLC analysis revealed a complete reaction) and poured into iced 10% hydrochloric acid. The product was extracted into dichloromethane twice, and the combined organic extracts were washed with water, KOH, and dried ($MgSO_4$). The combined extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed to yield a colourless solid. The residue was recrystallised from ethanol to yield colourless crystals which were dried *in vacuo* over phosphorus pentoxide.

Yield: 35 g (94%)

Melting Point (°C): 99.6

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.35 (6H, m), 1.74 (2H, quintet), 2.97 (2H, t), 7.47 (2H, d), 7.57 (2H, d), 7.62 (2H, d), 8.01 (2H, d)

MS *m/z* 346 (M^+), 344 (M^+)

4-Bromo-4'-heptylbiphenyl (25)

Hydrazine hydrate (14.35 g, 0.286 mol) was added carefully to a mixture of compound **24** (30 g, 0.96 mol) in diethylene glycol (250 ml) at 80 °C. The mixture was heated at 130 °C -140 °C for 2 h, the excess of hydrazine hydrate was distilled off and then cooled to 100 °C. KOH (16.07 g, 0.27 mol) was then added carefully in portions to the mixture, which was heated at 180 °C for 2-3 h and then cooled down to about 80 °C and poured into ice/36% HCl and left overnight. The product was extracted into dichloromethane twice, and the combined organic extracts were washed with water dried ($MgSO_4$). The solvent was removed to yield a colourless solid. The residue was recrystallised from ethanol to yield colourless crystals which were dried *in vacuo* over phosphorus pentoxide.

Yield: 19 g (60%)

Melting Point (°C): 94.6

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.88 (8H, m), 1.62 (2H, quintet), 2.63 (2H, t), 7.25 (2H, d), 7.43 (2H, d), 7.47 (2H, d), 7.54 (2H, d)

MS *m/z* 332 (M^+), 330 (M^+)

3.3.2 Difluoroterphenyl Compounds

Scheme 7

2,3-Difluorophenylboronic acid (26)

Quantities: *n*-butyllithium (2.5M in hexanes, 176 ml, 0.44 mol), 2,3-difluorobenzene (50 g, 0.44 mol), trimethyl borate (91 g, 0.88 mol). The experimental procedure was as described for the preparation of compound **16**, to yield colourless crystals.

Yield: 28 g (40%)

^{1}H NMR (400 MHz, DMSO-D_6) 7.13 (1H, dddd), 7.29 (1H, dddd), and 7.38 (1H, dddd), 8.38 (2H, s)

Scheme 8

4-Benzyloxyphenylboronic acid (32)

Magnesium (8.8 g, 0.36mol) was added to an empty dry flask under nitrogen. A small portion (50 ml) of compound **10** (88 g, 0.33mol) in dry THF (220 ml) was added, followed by 1,2-dibromoethane (5 drops). The mixture was heated (heat gun) to reflux to initiate reaction. The remaining solution was added quickly dropwise to the stirred, refluxing solution, and the mixture was heated under reflux for 1 h and cooled (-78 °C). A solution of trimethyl borate (68.6 g, 0.36 mol) in dry THF (40 ml) was added at (-78 °C) under dry nitrogen. The stirred mixture was allowed to warm up to room temperature overnight and stirred with 10% hydrochloric acid (320 ml) at room temperature for 1h. The product was extracted into ether (twice), and the combined extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo*, the residue was stirred in hexane overnight to remove the last traces of the THF, and the product was filtered off.

Yield: 56.7 g (76%)

^{1}H NMR (400 MHz, DMSO-D_6) 5.03 (2H, s), 6.89 (2H, d), 7.22- 7.39 (5H, m), 7.65 (2H, d), 7.78 (2H, s)

Scheme 9

4'-Bromo-2,3-difluorobiphenyl (38)

A mixture of compound 1-bromo-4-iodobenzene (35 g, 0.124 mol) in 2M Na_2CO_3 (150 ml) and DME (150 ml) was flushed with N_2 for 30 min. $Pd(PPh_3)_4$ (5.35 g, 4.6 mmol) and compound **26** (23.44 g, 0.148 mol) were added to the mixture, which was heated under reflux for 16 h (until GLC / TLC analysis revealed a complete reaction). The product was extracted into ether (twice). The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed and the residue was distilled to yield colourless oil.

Yield: 19 g (57%)

Boiling Point (°C): 110-115 at 0.2 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 7.15 (3H, m), 7.41 (2H, dd), 7.59 (2H, d)

MS *m/z* 270 (M^+) 268 (M^+)

2,3-Difluoro-4'-(trimethylsilylethynyl)biphenyl (27)

n-Butyllithium (2.5M in hexanes, 28.55 ml, 0.0714 mol) was added dropwise to a stirred, cooled (-5 to 0 °C) solution of (trimethylsilyl)acetylene (6.9 g, 0.0714 mol),in dry THF (150 ml) under dry nitrogen. This mixture was stirred for 10 min and zinc chloride (12.04 g, 0.088 mol) was added. The mixture was then stirred at room temperature for 15 min and $Pd(PPh_3)_4$ (3.7 g, 0.003127 mol) was added. A solution of compound **38** (16.0 g, 0.059 mol) in dry THF (80 ml) was added dropwise. The mixture was stirred at reflux overnight, and poured into 10% hydrochloric acid. The product was extracted into ether (twice). The combined extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed and the residue was purified by column chromatography (silica gel / hexane) to give a colourless liquid.

Yield: 12 g (71%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.20 (9H, s), 7.04 (3H, m), 7.39 (2H, dd), 7.46 (2H, d)

MS *m/z* 286 (M^+)

2,3-Difluoro-4'-(trimethylsilylethyl)biphenyl (28)

10% Palladium in charcoal (3 g) was added to a solution of compound **27** (12 g, 0.042 mol) in ethanol (500 ml). The mixture was hydrogenated overnight. (GC analysis indicated absence of starting material). The catalyst was filtered off and the solvent was removed *in vacuo*. The residue was distilled to yield a colourless liquid.

Yield: 7 g (58%)

Boiling Point (°C): 115-122 at 0.2 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 0.04 (9H, s), 0.90 (2H, m), 2.67 (2H, m), 7.10 (2H, m), 7.18 (1H, m), 7.29 (2H, d), 7.46 (2H, dd)

MS *m/z* 290 (M^+)

2,3-Difluoro-4'-(trimethylsilylethyl)biphenyl-4-ylboronic acid (29)

Quantities: *n*-butyllithium (2.5M in hexanes, 9.7 ml, 0.024 mol), compound **28** (7 g, 0.024 mol), trimethyl borate (5.01 g, 0.048 mol). The experimental procedure was as described for the preparation of compound **16**, to yield colourless crystals.

Yield: 5.5 g (68%)

^{1}H NMR (400 MHz, DMSO-D_6) 0.03 (9H, s), 0.89 (2H, m), 2.66 (2H, m), 7.29 (1H, ddd), 7.33 (2H, d), 7.41 (1H, ddd), 7.49 (2H, d), 8.44 (2H, s)

2',3'-Difluoro-4-(trimethylsilylethyl)-4''-octyloxyterphenyl (30)

A mixture of compound **2** (1.15 g, 4.04 mmol) in 2M Na_2CO_3 (35 ml) and DME (35 ml) was flushed with N_2 for 30 min. $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol) and compound **29** (1.6 g, 4.79 mmol) were added to the mixture, which was heated under reflux for 16 h (until GLC / TLC analysis revealed a complete reaction). The product was extracted into ether (twice). The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed and the residue was purified by column chromatography [silica gel / hexane-DCM, 1:1] to give a colourless solid, which was recrystallised from ethanol to yield colourless crystals which were dried *in vacuo* over phosphorus pentoxide.

Yield: 0.74 g, 37%.

Transitions (°C): Cr 56.1 SmC 101.9 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.05 (9H, s), 0.89 (2H, t), 0.92 (2H, m), 1.27- 1.35 (9H, m), 1.47 (2H, quintet), 1.81 (2H, t), 2.68 (2H, m), 4.01 (2H, t), 6.98 (2H, d, *J* = 8.98), 7.22 (2H, m), 7.30 (2H, d, *J* = 8.43), 7.49 (2H, dd, *J* = 6.23, *J* = 1.47), 7.52 (2H, dd, *J* = 6.42, *J* = 1.47)

^{13}C NMR (100 MHz, $CDCl_3$) -1.75, 14.09, 18.61, 22.66, 26.05, 29.25, 29.36, 29.81, 31.82, 68.07, (alkyl chains, 11 required, 10 found); 114.60, 124.30 (dd, *J* = 3.84, *J* = 3.84), 124.50 (dd, *J* = 3.84, *J* = 3.84), 128.03, 128.73(d, *J* = 3.07), 129.20 (x2, dd, *J* = 9.99, *J* = 3.84), 129.96 (x2), 131.91, 145.41, 148.44 (dd, *J* = 250, J= 13.84), 148.60 (dd, *J* = 250, J= 8.46), 159.15 (aromatic carbons, 14 required, 14 found)

MS *m/z* 494 (M^+)

HPLC 99.8%

Elemental analysis: $C_{31}H_{40}SiOF_2$ requires C 75.26%, H 8.15%; found C 75.53%, H 8.38%

2',3'-Difluoro-4-heptyl-4''-(trimethylsilylethyl)terphenyl (31)

Quantities: compound **5** (1.09 g, 4.3 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol), compound **29** (1.73 g, 5.18 mmol). The experimental procedure was as described for the preparation of compound **30**, except that the residue was purified by column chromatography [silica gel / hexane] to yield colourless crystals.

Yield: 1.20 g, 60%.

Transitions (°C) Cr 58.9 SmC 61.7 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.04 (9H, s), 0.89 (3H, t), 0.92 (2H, m), 1.25- 1.38 (8H, m), 1.66 (2H, quintet), 2.65 (2H, t), 2.69 (2H, m), 7.22 (2H, m), 7.27 (2H, d, *J* = 8.06), 7.30 (2H, d, *J* = 8.06), 7.51 (4H, 2 x d, *J* = 7.70)

^{13}C NMR (100 MHz, $CDCl_3$) -1.75, 14.10, 18.61, 22.68, 29.19, 29.35, 29.81, 31.4, 31.82, 35.72, (alkyl chains, 10 required, 10 found); 124.51 (x2, dd, *J* = 3.84, *J* = 3.07), 128.04, 128.65, 128.72 (x2, dd, *J* = 7.69, *J* = 1.54), 129.43, 129.51, 131.88, 131.97,

143.05, 145.44, 148.52 (x2, dd, *J* = 250, *J*= 15.4) (aromatic carbons, 14 required, 14 found)

MS *m/z* 464 (M^+)

HPLC 99.4%

Elemental analysis: $C_{30}H_{38}SiF_2$ requires C 77.54%, H 8.24%; found C 77.83%, H 8.28%

Scheme 10

4-Benzyloxy-4'-bromobiphenyl (39)

Quantities: 4-bromo-4'-hydroxybiphenyl (40.0 g, 0.161 mol), benzyl chloride (25.2 g, 0.20 mol), potassium carbonate (48 g, 0.35 mol), butanone (300 ml). The experimental procedure was as described for the preparation of compound **2**, except that the residue was recrystallised from ethanol to yield colourless crystals which were dried *in vacuo* over phosphorus pentoxide.

Yield: 25.0 g (44%)

Melting Point (°C): 152

^{1}H NMR (400 MHz, $CDCl_3$) 5.10 (2H, s), 7.03 (2H, d), 7.33- 7.42 (5H, m), 7.45 (2H, m), 7.48 (2H, d), 7.53 (2H, d)

MS *m/z* 340 (M^+), 338 (M^+)

4-Benzyloxy-4'- (trimethylsilylethynyl)biphenyl (33)

Quantities: *n*-butyllithium (2.5M in hexanes, 35.5 ml, 0.088 mol), (trimethylsilyl)acetylene (8.67 g, 0.088 mol), zinc chloride (15 g, 0.11 mol), $Pd(PPh_3)_4$ (5 g, 4.3 mmol), compound **39** (25 g, 0.0737 mol). The experimental procedure was as described for the preparation of compound **27,** to yield colourless crystals.

Yield: 18.5 g (70%)

Melting Point (°C): 159

^{1}H NMR (400 MHz, $CDCl_3$) 0.27 (9H, s), 5.13 (2H, s), 7.06 (2H, d), 7.35- 7.48 (5H, m), 7.51 (4H, d), 7.53 (2H, d)

MS *m/z* 356 (M^+)

4-Hydroxy-4'- (trimethylsilylethyl)biphenyl (34)

10% Palladium in charcoal (3 g) was added to a solution of compound **33** (18.3 g, 0.0514 mol) ethanol (300 ml). The mixture was hydrogenated overnight. (GC analysis

indicated absence of starting material). The catalyst was filtered off and the solvent was removed *in vacuo* to give a colourless solid.

Yield: 10.7 g (78%)

Melting Point (°C): 112.4

^{1}H NMR (400 MHz, $CDCl_3$) 0.03 (9H, s), 0.91 (2H, m), 2.65 (2H, m), 6.89 (2H, d), 7.26 (2H, d), 7.45 (2H, d), 7.47 (2H, d)

MS *m/z* 270 (M^+)

4'-(Trimethylsilylethyl)biphenyl triflate (35)

Triflic anhydride (6.26 g, 0.022 mol) was added dropwice to a stirred cooled (0 °C) solution of compound **34** (5 g, 0.0185 mol) in dry pyridine (80 ml) under dry nitrogen. The mixture was stirred at room temperature overnight and poured into water. The product was extracted into ether (twice). The combined extracts were washed successively with water, 10% hydrochloric acid (twice) water and brine and dried ($MgSO_4$). The solvent was removed and the crude product was purified by column chromatography [silica gel / hexane-DCM, 3:1] to give a colourless oil.

Yield: 6.8 g (91%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.04 (9H, s), 0.90 (2H, m), 2.67 (2H, m), 7.27 (2H, d), 7.29 (2H, d), 7.44 (2H, d), 7.59 (2H, d)

MS *m/z* 402 (M^+)

2,3-Difluoro-4''-(trimethylsilylethyl)-4-octyloxyterphenyl (36)

Quantities: compound **16** (1.63 g, 4.05 mmol), 2M Na_2CO_3 (35 ml), DME (35ml) $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol), compound **35** (1.4 g, 4.86 mmol). The experimental procedure was as described for the preparation of compound **30**, except that lithium chloride (0.55 g, 12.9 mmol) was added to the mixture, to yield colourless crystals.

Yield: 0.6 g, 30%.

Transitions (°C) Cr 78.8 SmC 118.6 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.06 (9H, s), 0.91 (3H, t), 0.94 (2H, m), 1.33 (8H, m), 1.51 (2H, quintet), 1.86 (2H, quintet), 2.70 (2H, m), 4.08 (2H, t), 6.82 (1H, ddd, *J* = 9.07, *J* = 9.07, *J* = 1.88), 7.14 (1H, ddd, *J* = 8.44, *J* = 8.44, *J* = 2.19), 7.31 (2H, d, *J* = 8.44), 7.56 (2H, d, *J* = 8.13), 7.58 (2H, dd, *J* = 5.94, *J* = 1.25), 7.68 (2H, d, *J* = 8.61)

^{13}C NMR (100 MHz, $CDCl_3$) -1.74, 14.08, 18.67, 22.64, 25.88, 29.18 (x2), 29.29, 29.70,31.79, 69.88 (alkyl chains, 11 required, 11 found), 109.50 (d, *J* = 3.84), 122.58 (dd, *J* = 10.76, *J* = 0.77), 123.44 (dd, *J* = 3.84, *J* = 3.84), 126.91, 127.03, 128.26, 129.00 (d, *J* = 3.07), 133.53, 137.76, 140.38, 141.91 (dd, *J* =246.75, *J* = 14.61), 144.72, 147.87 (dd, *J* = 8.46, *J* = 3.07), 148.97 (dd, *J* = 249.06, *J* = 11.53) (aromatic carbons, 14 required, 14 found)

MS *m/z* 494(M^+)

HPLC 99.3%

Elemental analysis $C_{31}H_{40}SiOF_2$ requires C 75.26%, H 8.15%; found C 75.43%, H 8.24%

2,3-Difluoro-4-heptyl-4''-(trimethylsilylethyl)terphenyl (37)

Quantities: compound **20** (1.43 g, 5.6 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol), compound **35** (1.73 g, 4.31 mmol). The experimental procedure was as described for the preparation of compound **30**, except that lithium chloride (0.55 g, 12.9 mmol) was added to the mixture, to yield colourless crystals.

Yield: 0.9 g, (45%)

Transitions (°C) Cr 66.7 SmC 78.9 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.05 (9H, s), 0.91 (3H, t), 0.93 (2H, m), 1.26- 1.37 (8H, m), 1.67 (2H, quintet), 2.66- 2.72 (4H, m), 7.02 (1H, ddd, *J* = 8.25, *J* = 8.25, *J* = 1.88), 7.16 (1H, ddd, *J* = 8.61, *J* = 8.61, *J* = 2.20), 7.30 (2H, d, *J* = 8.25), 7.51 (2H, d, *J* = 8.25), 7.56 (2H, dd, *J* = 8.25, *J* = 1.47), 7.63 (2H, d, *J* = 8.25)

^{13}C NMR (100 MHz, $CDCl_3$) -1.75, 14.09, 18.68, 22.66, 28.79, 29.09, 29.27, 29.71, 30.05, 31.79, (alkyl chains, 10 required, 10 found); 124.13 (dd, *J* = 3.07, *J* = 3.07), 124.73 (dd, *J* = 4.61, *J* = 4.61), 126.94, 127.03, 128.28, 129.14 (d, *J* = 3.07), 130.83,

130.69, 133.60 (d, *J* = 1.54), 137.75, 140.66, 144.77, 148.01 (dd, *J* = 247.52, *J* = 12.30), 149.54 (dd, *J* = 239.84, *J*= 6.92) (aromatic carbons, 14 required, 14 found)

MS *m/z* 464 (M^+)

HPLC 99.3%

Elemental analysis $C_{30}H_{38}SiF_2$ requires C 77.54%, H 8.24%; found C 77.88%, H 8.22%

Scheme 11

1-Bromo-2,3-difluorobenzene (40)

Solid *N*-bromosuccinimide (78.3 g, 0.44 mol) was added to a stirred suspension of compound **26** (35 g, 022 mol) in acetonitrile (300 ml) under dry nitrogen. The mixture was stirred under reflux for 16 h (until GLC and TLC analysis revealed a complete reaction) and poured into lots of water. The product was extracted into hexane twice, and the combined organic extracts were washed with aqueous $NaHSO_3$, and dried ($MgSO_4$). The solvent was distilled off at atmospheric pressure (68 °C) with a long column. Finally the product was transferred into 100 ml flask and distilled off.

Yield: 30. g (70%)

Boiling Point (°C): 158

^{1}H NMR (400 MHz, $CDCl_3$) 6.98 (1H, dddd), 7.11 (1H, dddd), and 7.29 (1H, dddd)

MS *m/z* 194 (M^+), 192 (M^+)

1,2-Difluoro-3-(trimethylsilylethynyl)benzene (41)

Quantities: *n*-butyllithium (2.5M in hexanes, 74.8 ml, 0.187 mol), (trimethylsilyl)acetylene (18.3 g, 0.187 mol), zinc chloride (31.8 g, 0.234 mol), $Pd(PPh_3)_4$ (10 g, 8.66 mmol), compound **40** (30 g, 0.156 mol). The experimental procedure was as described for the preparation of compound **27**, to yield colourless crystals.

Yield: 30 g (92%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.26 (9H, s), 6.98 (1H, dddd), 7.10 (1H, dddd), 7.18 (1H, dddd)

MS *m/z* 210 (M^+)

1,2-Difluoro-3-(trimethylsilylethyl)benzene (42)

10% Palladium in charcoal (5 g) was added to a solution of compound **41** (30 g, 0.142 mol) ethanol (300 ml). The mixture was hydrogenated overnight. (GC analysis indicated

absence of starting material). The catalyst was filtered off and the solvent was removed *in vacuo* to give a colourless liquid.

Yield: 21.16 g (70%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.07 (9H, s), 0.87 (2H, m), 2.71 (2H, m), 6.95- 7.02 (3H, m)

MS *m/z* 214 (M^+)

2,3-Difluoro-4-(trimethylsilylethyl)phenylboronic acid (43)

Quantities: *n*-butyllithium (2.5M in hexanes, 37.5 ml, 0.093 mol), compound **42** (20 g, 0.093 mol), trimethyl borate (19.5 g, 0.19 mol). The experimental procedure was as described for the preparation of compound **16**, to yield colourless crystals.

Yield: 18 g (75%)

^{1}H NMR (400 MHz, DMSO-D_6) 0.15 (9H, s), 0.99 (2H, m), 2.78 (2H, m), 7.21 (1H, ddd), 7.39 (1H, ddd), 8.41 (2H, s)

2,3-Difluoro-4-(trimethylsilylethyl)-4''-octyloxyterphenyl (44)

Quantities: compound **22** (1.43 g, 3.96 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol), compound **43** (1.23 g, 4.75 mmol). The experimental procedure was as described for the preparation of compound **30**, except that the residue was purified by column chromatography [silica gel / hexane] to yield colourless crystals.

Yield: 0.85 g, (43%)

Transitions (°C) Cr 81.0 SmC 141.5 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.09 (9H, s), 0.92 (5H, m), 1.28- 1.43 (8H, m), 1.52 (2H, quintet), 1.84 (2H, quintet), 2.78 (2H, m), 4.02 (2H, t), 7.00 (2H, d, *J* = 8.76), 7.05 (1H, ddd, *J* = 6.25, *J* = 6.25, *J* = 2.19), 7.17 (1H, ddd, *J* = 6.25, *J* = 6.25, *J* = 1.88), 7.58 (2H, d, *J* = 8.76), 7.61 (2H, dd, *J* = 7.82, *J* = 0.94), 7.63 (2H, d, *J* = 8.44)

^{13}C NMR (100 MHz, $CDCl_3$) -1.84, 14.10, 17.35, 22.66, 23.08, 26.07, 29.28 (x2), 29.38, 31.83, 68.07, (alkyl chains, 11 required, 11 found); 114.82, 123.93 (dd, *J* = 4.61, *J* =

4.61), 124.17 (dd, *J* = 3.07, *J* = 3.07), 126.71, 128.03, 129.14 (d, *J* = 2.31), 132.77, 133.23, 133.31 (dd, *J* = 12.30, *J* = 2.31), 140.33, 147.91 (dd, *J* = 251.37, *J* = 16.14), 149.32 (dd, *J* = 247.52, *J* = 15.37), 158.92 (aromatic carbons, 14 required, 13 found)

MS *m/z* 494(M^+)

HPLC 100%

Elemental analysis: $C_{31}H_{40}SiOF_2$ requires C 75.26%, H 8.15%; found C 75.15%, H 8.44%

2,3-Difluoro-4''-heptyl-4-(trimethylsilylethyl)terphenyl (45)

Quantities: compound **25** (1.43 g, 4.32 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol), compound **43** (1.23 g, 4.75 mmol). The experimental procedure was as described for the preparation of compound **30**, except that the residue was purified by column chromatography [silica gel / hexane] to yield colourless crystals.

Yield: 0.77 g, (38%)

Transitions (°C) Cr 57.5 SmC 106.1 SmA 119.5 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.09 (9H, s), 0.92 (5H, m), 1.28- 1.43 (8H, m), 1.69 (2H, quintet), 2.68 (2H, t), 2.74 (2H, m), 7.05 (1H, ddd, *J* = 6.88, *J* = 6.88, *J* = 1.88), 7.17 (1H, ddd, *J* = 6.88, *J* = 6.88, *J* = 1.25), 7.30 (2H, d, *J* = 8.29), 7.58 (2H, d, *J* = 7.82), 7.62 (2H, dd, *J* = 8.44, *J* = 1.25), 7.69 (2H, d, *J* = 6.57)

^{13}C NMR (100 MHz, $CDCl_3$) -1.84, 14.11, 17.35, 22.68, 23.08, 29.20, 29.35, 31.50, 31.83, 35.63, (alkyl chains, 10 required, 10 found); 123.93 (dd, *J* = 4.61, *J* = 4.61), 124.17 (dd, *J* = 3.07, *J* = 3.07), 126.89, 127.03, 128.88, 129.14 (d, *J* = 2.31), 133.36 (dd, *J* = 10.76, *J* = 2.31), 133.62 (d, *J* = 2.31), 137.83, 140.63, 142.37, 147.92 (dd, *J* = 250.60, *J* = 15.37), 149.29 (dd, *J* = 246.75, *J* = 14.61) (aromatic carbons, 14 required, 13 found)

MS *m/z* 464 (M^+)

HPLC 100%

Elemental analysis: $C_{30}H_{38}SiF_2$ requires C 75.54%, H 8.24%; found C 77.54%, H 8.24%

Scheme 12

1,2-Difluoro-3-(3,3-dimethylbut-1-ynyl)benzene (48)

Quantities: *n*-butyllithium (2.5M in hexanes, 74.8 ml, 0.187 mol), 3,3-dimethylbut-1-yne (15.35 g, 0.187 mol), zinc chloride (31.8 g, 0.23 mol), $Pd(PPh_3)_4$ (8 g, 0.0069 mol), compound **40** (30 g, 0.156 mol). The experimental procedure was as described for the preparation of compound **27,** to yield colourless crystals.

Yield: 28g, (93%)

^{1}H NMR (400 MHz, $CDCl_3$) 1.33 (9H, s), 6.96 (1H, dddd), 7.05 (1H, dddd), and 7.12 (1H, dddd)

MS *m/z*: 194 (M^+)

1,2-Difluoro-3-(3,3-dimethylbutyl)benzene (49)

10% Palladium in charcoal (5 g) was added to a solution of compound **48** (27 g, 0.139 mol) in ethanol (500 ml). The mixture was hydrogenated overnight. (GC analysis indicated absence of starting material). The catalyst was filtered off and the solvent was removed *in vacuo* to give a colourless liquid.

Yield: 21g, (76%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.96 (9H, s), 1.48 (2H, m), 2.62 (2H, m), 6.89- 6.97 (3H, m)

MS *m/z*: 198 (M^+)

1,2-Difluoro-4-(3,3-dimethylbutyl)phenylboronic acid (50)

Quantities: *n*-butyllithium (2.5M in hexanes, 40 ml, 0.10 mol), compound **49** (20 g, 0.10 mol), trimethyl borate (20.78 g, 0.2 mol). The experimental procedure was as described for the preparation of compound **16**, to yield colourless crystals.

Yield: 15 g, (62%)

^{1}H NMR (400 MHz, DMSO-D_6) 0.81 (9H, s), 1.32 (2H, m), 2.41 (2H, m), 6.95 (1H, ddd), 7.16 (1H, ddd), 8.19 (2H, s)

2,3-Difluoro-4-(3,3-dimethylbutyl)-4''-octyloxyterphenyl (51)

Quantities: compound **22** (2.27 g, 6.28 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), and compound **50** (1.822 g, 7.53mmol). The experimental procedure was as described for the preparation of compound **30**, except that the residue was purified by column chromatography [silica gel / hexane] to yield colourless crystals.

Yield: 2.1 g, (58%)

Transitions: (°C): Cr 95.0 SmC 156.0 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.91 (3H, t), 1.00 (9H, s), 1.28- 1.40 (8H, m), 1.45- 1.56 (4H, m), 1.82 (2H, quintet), 2.67 (2H, m), 4.01 (2H, t), 6.99 (2H, d, *J* = 8.80), 7.02 (1H, ddd, *J* = 6.23, *J* = 6.23, *J* = 0.37), 7.15 (1H, ddd, *J* = 6.23, *J* = 6.23, *J* = 1.10), 7.57 (2H, d, *J* = 8.80), 7.59 (2H, dd, *J* = 8.80, *J* = 1.01), 7.64 (2H, d, *J* = 8.61)

^{13}C NMR (100 MHz, $CDCl_3$) 14.10, 22.66, 24.26, 26.07, 29.17, 29.26, 29.30, 29.38, 30.61, 31.82, 44.56, 68.07, (alkyl chains, 12 required, 12 found), 114.82, 124.19 (dd, *J* = 3.07, *J* = 3.07), 124.55 (dd, *J* = 3.84, *J* = 3.84), 126.70, 128.02, 129.13 (d, *J* = 1.54), 131.50 (dd, *J* = 7.69, *J* = 2.31), 132.76, 133.20 (d, *J* = 1.54), 140.33, 148.12 (dd, *J* = 251.37, *J* = 16.14), 149.50 (dd, *J* = 247.52, *J* = 15.37), 158.92 (aromatic carbons, 14 required, 13 found)

MS *m/z* 478 (M^+)

HPLC 99.9%

Elemental analysis: $C_{32}H_{40}OF_2$ requires C 80.30%, H 8.42%; found C 80.36%, H 8.41%

2,3-Difluoro-4''-heptyl-4-(3,3-dimethylbutyl)terphenyl (52)

Quantities: Compound **25** (2.28 g, 6.6 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), compound **50** (1.9 g, 8.03 mmol). The experimental

procedure was as described for the preparation of compound **30**, except that the residue was purified by column chromatography [silica gel / hexane] to yield colourless crystals.

Yield: 2.3 g, (63%)

Transitions: (°C): Cr 86.0 SmC 125.0 SmA 129.6 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.91 (3H, t), 0.98 (9H, s), 1.34 (8H, m), 1.56 (2H, m), 1.70 (2H, quintet), 2.67 (2H, t), 2.69 (2H, m), 7.03 (1H, ddd, *J* = 6.23, *J* = 6.23, *J* = 0.90), 7.17 (1H, ddd, *J* = 6.23, *J* = 6.23, *J* = 0.92), 7.29 (2H, d, *J* = 8.43), 7.57 (2H, d, *J* = 8.43), 7.62 (2H, dd, *J* = 8.43, *J* = 1.10), 7.61 (2H, d, *J* = 8.61)

^{13}C NMR (100 MHz, $CDCl_3$) 14.11, 22.69, 24.28, 29.16, 29.22, 29.37, 30.59, 31.49, 31.85, 35.64, 44.55, (alkyl chains, 11 required, 11 found), 124.21 (dd, *J* = 3.07, *J* = 3.07), 124.55 (dd, *J* = 3.84, *J* = 3.84), 126.87, 127.00, 127.92 (dd, *J* = 6.92, *J* = 3.07), 128.86, 129.12, 131.51 (dd, *J* = 8.46, *J* = 5.38), 133.57, 137.80, 140.62, 142.34, 148.13 (dd, *J* = 250.61, *J* = 115.37), 149.51 (dd, *J* = 246.75, *J* = 14.61) (aromatic carbons, 14 required, 14 found)

MS *m/z* 448 (M^+)

HPLC 100%

Elemental analysis: $C_{31}H_{38}F_2$ requires C 82.99, H 8.54%; found C 82.70%, H 8.50%

Scheme 13

1-Bromo-4-(3,3-dimethylbut-1-ynyl)benzene (53)

n-Butyllithium (2.5M in hexanes, 60 ml, 0.15 mol) was added dropwise to a stirred, cooled (-5 to 0 °C) solution of 3,3-dimethylbut-1-yne (12.3 g, 0.15 mol) in dry THF (150 ml), under dry nitrogen. This mixture was stirred for 10 min and zinc chloride (25 g, 0.18 mol) was added. The mixture was stirred at room temperature for 15 min and $Pd(PPh_3)_4$ (8 g, 0.0069 mol) was added. A solution of 1-bromo-4-iodobenzene (30 g, 0.10 mol) in dry THF (80 ml) was added dropwise. The mixture was stirred at room temperature overnight, (GLC analysis revealed a complete reaction) and poured into 10% hydrochloric acid. The product was extracted into ether (twice). The combined extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed and the crude product was purified by column chromatography [silica gel/ hexane] to give a white solid.

Yield: 10.4 g (44%)

Melting Point (°C): 51.7

^{1}H NMR (400 MHz, $CDCl_3$) 1.30 (9H, s), 7.22 (2H, d), 7.37 (2H, d)

MS *m/z* 238 (M^+), 236 (M^+)

2,3-Difluoro-4'-(3,3-dimethylbut-1-ynyl)biphenyl (54)

Quantities: Compound **53** (5 g, 0.021 mol), 2M Na_2CO_3 (125 ml), DME (125 ml), $Pd(PPh_3)_4$ (0.91 g, 0.78 mmol), compound **26** (5 g, 0.032 mol). The experimental procedure was as described for the preparation of compound **30**, to yield colourless crystals.

Yield: 5.35 g, (94%)

Melting Point (°C): 57.8

^{1}H NMR (400 MHz, $CDCl_3$) 1.31 (9H, s), 7.08- 7.18 (3H, m), 7.37 (4H, s)

MS *m/z* 270 (M^+)

2,3-Difluoro-4'-(3,3-dimethylbutyl)biphenyl (55)

10% Palladium in charcoal (1 g) was added to a solution of compound **54** (5 g, 0.0185 mol) in ethanol (500ml). The mixture was hydrogenated overnight. (GC analysis indicated absence of starting material). The catalyst was filtered off and the solvent was removed *in vacuo* to give a colourless liquid.

Yield: 5 g, (98%).

^{1}H NMR (400 MHz, $CDCl_3$) 0.98 (9H, s), 1.53 (2H, m), 2.61 (2H, m), 7.08 (2H, m), 7.16 (1H, m), 7.25 (2H, d), 7.43 (2H, dd)

MS *m/z* 274 (M^+)

2,3-Difluoro-4'-(3,3-dimethylbutyl)biphenyl-4-ylboronic acid (56)

Quantities: *n*-butyllithium (2.5M in hexanes, 7.3 ml, 0.018 mol), compound **55** (5 g, 0.018 mol), trimethyl borate (3.74 g, 0.036 mol). The experimental procedure was as described for the preparation of compound **16**, to yield colourless crystals.

Yield: 3 g, (52%)

^{1}H NMR (400 MHz, DMSO-D_6) 0.86 (9H, s), 1.39 (2H, m), 2.41 (2H, m), 7.18 (1H, ddd), 7.23 (2H, d), 7.31 (1H, ddd), 7.39 (2H, dd), 8.34 (2H, s)

2',3'-Difluoro-4-(3,3-dimethylbutyl)-4''-octyloxyterphenyl (57)

Quantities: compound **2** (1.3 g, 3.35 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.14 g, 0.13 mmol), compound **56** (1.3 g, 4.02 mmol). The experimental procedure was as described for the preparation of compound **30** to yield colourless crystals.

Yield: 1.13 g, (75%)

Transitions (°C) Cr 89.0 SmC 106.9 N 114.4 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 0.98 (9H, s), 1.32 (8H, m), 1.47 (2H, m), 1.54 (2H, t), 1.57 (2H, m), 1.81 (2H, quintet), 2.63 (2H, m), 4.01 (2H, t), 6.99 (2H, d, *J* =

8.80), 7.21 (2H, d, *J* = 6.23), 7.29 (2H, d, *J* = 8.43), 7.50 (2H, dd, *J* = 8.60, *J* = 1.01), 7.54 (2H, dd, *J* = 8.60, *J* = 1.01)

^{13}C NMR (100 MHz, $CDCl_3$) 14.10, 22.66, 26.06, 29.26, 29.32, 29.37, 30.56, 31.01, 31.82, 46.29, 68.04 (alkyl chains, 12 required, 10 found); 114.59, 124.29 (dd, *J* = 3.84, *J* = 3.84), 124.49 (dd, *J* = 3.84, *J* = 3.84), 126.78, 128.56, 128.73 (d, *J* = 3.07), 129.20 (x2, dd, *J* = 9.99, *J* = 9.99), 129.94 (d, *J* = 3.07), 131.95, 143.64, 148.44 (dd, *J* = 250.6, *J* = 11.53), 148.60 (dd, *J* = 251.37, *J* = 9.99), 159.15 (aromatic carbons, 14 required, 14 found)

MS *m/z* 478 (M^+)

HPLC 100%

Elemental analysis: $C_{32}H_{40}OF_2$ requires C 80.30%, H 8.42%; found C 80.47%, H 8.52%

2',3'-Difluoro-4-heptyl-4''-(3,3-dimethylbutyl)terphenyl (58)

Quantities: compound **5** (0.82 g, 3.2 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol), compound **56** (1.2 g, 3.84 mmol). The experimental procedure was as described for the preparation of compound **30** to yield colourless crystals.

Yield: 0.30 g, (21%)

Transitions (°C) Cr 60.0 SmC 76.0 N 77.7 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 0.98 (9H, s), 1.25- 1.38 (8H, m), 1.55 (2H, m), 1.66 (2H, quintet), 2.63 (4H, m), 7.21 (2H, dd, *J* = 4.77, *J* = 1.56), 7.27 (4H, 2 x d, *J* = 8.13), 7.50 (4H, 2 x d, *J* = 7.82)

^{13}C NMR (100 MHz, $CDCl_3$) 14.10, 22.68, 29.19, 29.32, 29.35, 30.57, 31.01, 31.41, 31.82, 35.72, 46.30, (alkyl chains, 11 required, 11 found); 124.52 (x2, dd, *J* = 3.84, *J* = 3.07), 128.69 (x4), 128.72 (x2, d, *J* = 6.92), 131.92, 131.96, 143.06, 143.70, 149.74 (x2, dd, *J* = 250.60, *J*= 15.37) (aromatic carbons, 14 required, 14 found)

MS *m/z* 448 (M+)

HPLC 99%

Elemental analysis: $C_{31}H_{38}F_2$ requires C 82.99%, H 8.54%; found C 82.89%, H 8.67%

Scheme 14

4-Benzyloxy-4'-(3,3-dimethylbut-1-ynyl)biphenyl (59)

Quantities: compound **53** (5 g, 0.021 mol), 2M Na_2CO_3 (125 ml), DME (125 ml), $Pd(PPh_3)_4$ (0.91 g, 0.78 mmol), compound **32** (7.18 g, 0.0315 mol). The experimental procedure was as described for the preparation of compound **30** except that the residue was purified by column chromatography [silica gel / hexane] to yield colourless crystals.

Yield: 6.83 g, (95%)

Melting Point (°C): 211

^{1}H NMR (400 MHz, $CDCl_3$) 1.32 (9H, s), 5.11 (2H, s), 7.04 (2H, d), 7.34- 7.48 (9H, m), 7.52 (2H, d)

MS *m/z* 340 (M^+)

4-Hydroxy-4'-(3,3-dimethylbutyl)biphenyl (60)

10% Palladium in charcoal (1 g) was added to a solution of compound **59** (6.8 g, 0.02 mol) in THF (300 ml) and ethanol (50 ml). The mixture was hydrogenated overnight. (GC analysis indicated absence of starting material). The catalyst was filtered off and the solvent was removed *in vacuo* to give a colourless solid.

Yield: 5 g, (98%)

Melting Point (°C): 144.5

^{1}H NMR (400 MHz, $CDCl_3$) 0.97 (9H, s), 1.53 (2H, m), 2.59 (2H, m), 6.88 (2H, d), 7.23 (2H, d), 7.43- 7.48 (4H, m), OH proton isn't visible.

MS *m/z* 254 (M^+)

4'-(3,3-Dimethylbutyl)biphenyl-4-yl triflate (61)

Quantities**:** triflic anhydride (5.31 g, 0.019 mol), compound **60** (4 g, 0.0157 mol), dry pyridine (80 ml). The experimental procedure was as described for the preparation of

compound **35** except that the residue was purified by column chromatography [silica gel / hexane-DCM, 1:1] to yield colourless crystals.

Yield: 5.4 g, (89%)

Melting Point (°C): 48.4

^{1}H NMR (400 MHz, $CDCl_3$) 0.97 (9H, s), 1.53 (2H, m), 2.59 (2H, m), 7.20 (2H, d), 7.24 (2H, d), 7.38 (2H, d), 7.54 (2H, d)

MS *m/z* 386 (M^+)

2,3-Difluoro-4''-(3,3-dimethylbutyl)-4-octyloxyterphenyl (62)

Quantities: compound **16** (0.95 g, 3.64 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml) $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol), compound **61** (1.17 g, 3.04 mmol). The experimental procedure was as described for the preparation of compound **30**, except that lithium chloride (0.4 g, 9.1 mmol) was added to the mixture, and the residue was purified by column chromatography [silica gel / hexane-DCM, 3:1] to yield colourless crystals.

Yield: 0.8 g, (55%)

Transitions (°C) Cr 81.3 SmC 131.0 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 0.98 (9H, s), 1.33 (8H, m), 1.55 (4H, m), 1.84 (2H, quintet), 2.62 (2H, m), 4.08 (2H, t), 6.81 (1H, ddd, *J* = 7.70, *J* = 7.70, *J* = 1.65), 7.14 (1H, ddd, *J* = 8.80, *J* = 8.80, *J* = 2.02), 7.27 (2H, d, *J* = 8.25), 7.55 (2H, d, *J* = 8.25), 7.57 (2H, dd, *J* = 8.25, *J* = 1.65), 7.65 (2H, d, *J* = 8.61)

^{13}C NMR (100 MHz, $CDCl_3$) 14.09, 22.65, 25.88, 29.18 (x2), 29.31 (x2),30.56, 30.90, 31.80, 46.38, 69.84 (alkyl chains, 12 required, 12 found), 109.52 (d, *J* = 2.31), 122.53 (dd, *J* = 10.76, *J* = 0.77), 123.43 (dd, *J* = 4.61, *J* = 4.61), 126.93, 127.02, 128.74, 129.00 (d, *J* = 3.07), 133.53, 137.79, 140.34, 141.88 (dd, *J* = 246.75, *J* = 16.14), 147.88 (dd, *J* = 8.46, *J* = 3.07), 148.96 (dd, *J* = 249.06, *J* = 11.53) (aromatic carbons, 14 required, 14 found)

MS *m/z* 478 (M^+)

HPLC 100%

Elemental analysis: $C_{32}H_{40}F_2$ requires C 80.30%, H 8.42%; found C 80.22%, H 8.07%

2,3-Difluoro-4-heptyl-4''-(3,3-dimethylbutyl)terphenyl (63)

Quantities: compound **20** (1.4 g, 5.36 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.17 g, 0.14 mmol), compound **61** (1.7 g, 4.46 mmol). The experimental procedure was as described for the preparation of compound **30**, except that lithium chloride (0.57 g, 13.4 mmol) was added to the mixture, and the residue was purified by column chromatography [silica gel / hexane-DCM, 3:1] to yield colourless crystals.

Yield: 1.45 g, (73%)

Transitions (°C) Cr 71.0 (G 56.4) SmC 101.0 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 0.98 (9H, s), 1.26- 1.42 (8H, m), 1.54 (2H, m), 1.63 (2H, quintet), 2.66 (2H, m), 2.67 (2H, t), 7.00 (1H, ddd, *J* = 8.25, *J* = 8.25, *J* = 1.47), 7.14 (1H, ddd, *J* = 8.61, *J* = 8.61, *J* = 1.83), 7.28 (2H, d, *J* = 8.25), 7.56 (2H, d, *J* = 8.25), 7.60 (2H, dd, *J* = 8.43, *J* = 1.47), 7.67 (2H, d, *J* = 8.61)

^{13}C NMR (100 MHz, $CDCl_3$) 14.10, 22.66, 28.79, 29.10, 29.28, 29.34, 30.05, 30.57, 30.92, 31.79, 46.39 (alkyl chains, 11 required, 11 found), 124.14 (dd, *J* = 3.07, *J* = 3.07), 124.72 (dd, *J* = 3.84, *J* = 3.84), 126.97, 127.03, 128.01 (dd, *J* = 9.99, *J* = 0.77), 128.79, 129.14 (d, *J* = 3.07), 130.87 (dd, *J* = 13.07, *J* = 0.77), 133.60 (d, *J* = 3.07), 137.80, 140.63, 143.00, 148.11 (dd, *J* = 248.29, *J* = 13.07), 149.54 (dd, *J* = 239.07, *J* = 6.15) (aromatic carbons, 14 required, 14 found)

MS *m/z* 448 (M^+)

HPLC 100%

Elemental analysis: $C_{31}H_{38}F_2$ requires C 82.99%, H 8.54%; found C 83.13%, H 8.20%

3.3.3 Monofluoroterphenyl Compounds

Scheme 15

3-Fluorophenylboronic acid (65)

Quantities: magnesium (8.38 g, 0.35 mol), 1-bromo-3-fluorobenzene (55 g, 0.314 mol), 1,2-dibromoethane (5 drops), trimethyl borate (65.2, 0.628 mol). The experimental procedure was as described for the preparation of compound **32**, to yield colourless crystals.

Yield: 30 g (68%)

^{1}H NMR (400 MHz, DMSO-D_6) 7.17 (1H, dddd), 7.34 (1H, m), 7.46 (1H, ddd), 7.56 (1H, dd), 8.18 (2H, s)

4'-Bromo-3-fluorobiphenyl (66)

Quantities: 1-bromo-4-iodobenzene (35 g, 0.124 mol), 2M Na_2CO_3 (150 ml), DME (150 ml), $Pd(PPh_3)_4$ (6 g, 5.19 mmol), compound **65** (26 g, 0.186 mol). The experimental procedure was as described for the preparation of compound **38**, to yield a colourless oil.

Yield: 7.3 g (24%)

Boiling Point °C: 100-110 at 0.2 mmHg

^{1}H NMR (400 MHz, $CDCl_3$) 7.08 (1H, dddd), 7.26 (1H, ddd), 7.32 (1H, ddd), 7.39 (1H, ddd), 7.42 (2H, d), 7.57 (2H, d)

MS *m/z* 251 (M^+), 249 (M^+)

3-Fluoro-4'-(trimethylsilylethynyl)biphenyl (67)

Quantities: *n*-butyllithium (2.5M in hexanes, 13.5 ml, 0.034 mol), (trimethylsilyl)acetylene (3.3 g, 0.034 mol), zinc chloride (5.7 g, 0.042 mol), $Pd(PPh_3)_4$ (3 g, 2.6 mmol), compound **66** (7 g, 0.028 mol). The experimental procedure was as described for the preparation of compound **27**, to give a colourless liquid.

Yield: 5.1g (68%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.31 (9H, s), 7.05 (1H, dddd), 7.27 (1H, ddd), 7.34- 7.42 (2H, m), 7.51 (2H, d), 7.56 (2H, d)

MS *m/z* 268 (M^+)

3-Fluoro-4'-(trimethylsilylethyl)biphenyl (68)

10% Palladium in charcoal (1 g) was added to a solution of compound **67** (5 g, 0.018 mol) in ethanol (500 ml). The mixture was hydrogenated overnight. (GC analysis indicated absence of starting material). The catalyst was filtered off and the solvent was removed *in vacuo* to yield a colourless liquid.

Yield: 4 g (81%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.08 (9H, s), 0.93 (2H, m), 2.70 (2H, m), 7.05 (1H, m), 7.31 (3H, m), 7.39 (2H, d), 7.52 (2H, d)

MS *m/z*: 272 (M^+)

3-Fluoro-4'-(trimethylsilylethyl)biphenyl-4-boronic acid (69)

Quantities: *sec*-butyllithium (2.5M in hexanes, 10.5 ml, 0.026 mol), compound **68** (4 g, 0.0147 mol), trimethyl borate (3.05 g, 0.029 mol). The experimental procedure was as described for the preparation of compound **16**, to yield colourless crystals.

Yield: 3 g (68%)

^{1}H NMR (400 MHz, DMSO-D_6) 0.10 (9H, s), 0.95 (2H, m), 2.75 (2H, m), 7.41 (2H, d), 7.49 (1H, dd), 7.56 (1H, dd), 7.71 (3H, m), 8.29 (2H, s)

2'-Fluoro-4''-(trimethylsilylethyl)-4-octyloxyterphenyl (70)

Quantities: A mixture of compound **2**(0.89 g, 3.15 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol) and compound **69** (1.19 g, 3.15 mmol). The experimental procedure was as described for the preparation of compound **30**, to yield colourless crystals.

Yield: 1.13 g, 75%.

Transitions (°C) Cr 62.7 SmC 110.5 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.04 (9H, s), 0.89 (5H, m), 1.26- 1.40 (8H, m), 1.47 (2H, quintet), 1.81 (2H, quintet), 2.66 (2H, m), 4.01 (2H, t), 6.98 (2H, d, *J* = 8.80), 7.29 (2H,d, *J* = 8.80), 7.36 (1H, dd, *J* = 12.28, *J* = 1.83), 7.42 (1H, dd, *J* = 7.88, *J* = 1.83), 7.46 (1H, dd, *J* = 7.88, *J* = 7.88), 7.52 (2H, dd, *J* = 8.88, *J* = 1.65), 7.53 (2H, d, *J* = 8.80)

^{13}C NMR (100 MHz, $CDCl_3$) -1.74, 14.11, 18.63, 22.67, 26.07, 29.26, 29.29, 29.39, 31.83, 67.97, (alkyl chains, 11 required, 10 found); 114.30 (d, *J* = 23.83), 114.46, 122.56 (d, *J* = 3.07), 126.72, 127.05 (d, *J* = 13.07), 127.64, 128.32, 129.96 (d, *J* = 3.07), 130.53 (d, *J* = 4.61), 136.75 (d, *J* = 4.61), 141.54 (d, *J* = 8.46), 145.04, 158.79, 159.98 (d, *J* = 246.75) (aromatic carbons, 14 required, 14 found)

MS *m/z* 476 (M^+)

HPLC 99.6%

Elemental analysis: $C_{31}H_{41}SiOF$ requires C 78.10%, H 8.67%; found C 78.3%, H 8.81%

2'-Fluoro-4-heptyl-4''-(trimethylsilylethyl)terphenyl (71)

Quantities: compound **5** (0.86 g, 3.4 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol), compound **69** (1.3 g, 4.03 mmol). The experimental procedure was as described for the preparation of compound **30**, except that lithium chloride (0.4 g, 9.1 mmol) was added to the mixture, and the residue was purified by column chromatography [silica gel / hexane-DCM, 3:1] to yield colourless crystals.

Yield: 1 g, 77%.

Transitions (°C) Cr 64.5 SmC 77.5 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.04 (9H, s), 0.89 (3H, t), 0.92 (2H, m), 1.26- 1.40 (8H, m), 1.66 (2H, quintet), 2.65 (2H, t), 2.67 (2H, m), 7.27 (2H, d, *J* = 8.61), 7.29 (2H, d, *J* = 8.61), 7.37 (1H, dd, *J* = 12.10, *J* = 1.83), 7.43 (1H, dd, *J* = 7.88, *J* = 1.83), 7.48 (1H, dd, *J* = 7.88, *J* = 7.88), 7.51 (2H, dd, *J* = 8.25, *J* = 1.47), 7.54 (2H, d, *J* = 8.61)

^{13}C NMR (100 MHz, $CDCl_3$) -1.73, 14.11, 18.64, 22.69, 29.22, 29.37, 29.73, 31.45, 31.84, 35.72; (alkyl chains, 10 required, 10 found); 114.28 (d, *J* = 23.83), 122.59 (d, *J* =

3.07), 126.78, 127.34 (d, *J* = 13.84), 128.34, 128.51, 128.76 (d, *J* = 3.07), 130.77 (d, *J* = 3.84), 132.81, 136.75 (d, *J* = 2.31), 141.92 (d, *J* = 7.69), 142.47, 145.12, 145.12, 160.05 (d, *J* = 247.52) (aromatic carbons, 14 required, 14 found)

MS *m/z* 446 (M^+)

HPLC 100%

Elemental analysis: $C_{30}H_{39}SiOF$ requires C 80.66%, H 8.80%; found C 80.69%, H 8.78%

3.3.4 Trifluoroterphenyl Compounds

Scheme 16

4-Octyloxyphenylboronic acid (72)

Quantities: *n*-butyllithium (2.5M in hexanes, 70 ml, 0.175 mol), compound **2** (50 g, 0.175 mol), trimethyl borate (36.46 g, 0.35 mol). The experimental procedure was as described for the preparation of compound **16**, to yield colourless crystals.

Yield: 34 g (78%)

^{1}H NMR (400 MHz, DMSO-D_6) 0.83 (3H, t), 1.25 (10H, m), 1.68 (2H, quintet), 3.94 (2H, quintet), 6.82 (2H, d), 7.67 (2H, d), 7.78 (2H, s)

4-Heptylphenylboronic acid (73)

Quantities: *n*-butyllithium (2.5M in hexanes, 78 ml, 0.196 mol), compound **5** (50 g, 0.196 mol), trimethyl borate (40 g, 0.39 mol). The experimental procedure was as described for the preparation of compound **16**, to yield colourless crystals.

Yield: 26.7 g (75%)

^{1}H NMR (400 MHz, DMSO-D_6) 0.76 (3H, t), 1.18 (8H, m), 1.48 (2H, quintet), 2.48 (2H, t), 7.05 (2H, d), 7.60 (2H, d), 7.84 (2H, s)

3-Fluoro-4-hydroxy-4'-octyloxybiphenyl (75)

A mixture of 4-bromo-2-fluorophenol (15.9 g, 0.83 mol), potassium fluoride (16.8 g, 0.29 mol), **72** (25 g, 0.1 mol), and $Pd(PPh_3)_4$ (3.2 g, 2.8 mmol), THF (300 ml), was heated under reflux under N_2 for 20 h (until GLC / TLC analysis revealed a complete reaction). The product was extracted into ether (twice). The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed and the residue was purified by column chromatography [silica gel / hexane-gradual change to DCM] to give colourless crystals.

Yield: 22 g (84%)

Melting Point (°C): 118.5

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.24- 1.40 (8H, m), 1.46 (2H, quintet), 1.80 (2H, quintet), 3.98 (2H, t), 6.94 (2H, d), 7.03 (1H, t), 7.21 (1H, ddd), 7.26 (1H, dd), 7.43 (2H, d)

MS *m/z* 316 (M^+)

3-Fluoro-4-hydroxy-4'-heptylbiphenyl (76)

Quantities: 4-bromo-2-fluorophenol (18.1 g, 0.094 mol), potassium fluoride (19.84 g, 0.34 mol), compound **73** (25 g, 0.11 mol), and $Pd(PPh_3)_4$ (3.76 g, 3.0 mmol). The experimental procedure was as described for the preparation of compound **75**, to yield colourless crystals.

Yield: 18.22 g (68%)

Melting Point (°C): 98.8

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22-1.38 (8H, m), 1.64 (2H, quintet), 2.64 (2H, t), 7.04 (1H, t), 7.23 (2H, d), 7.25 (1H, m), 7.28- 7.32 (1H, dd), 7.43 (2H, d)

MS *m/z* 286 (M^+)

3-Fluoro-4'-octyloxybiphenyl-4-yl triflate (77)

Quantities: triflic anhydride (5.5 g, 0.019 mol), compound **75** (5 g, 0.015 mol), dry pyridine (80 ml). The experimental procedure was as described for the preparation of compound **35**, except that the residue was purified by column chromatography [silica gel / hexane-DCM, 4:1] to yield colourless crystals.

Yield: 6.0 g (90%)

Melting Point (°C): 49.0

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 1.24- 1.38 (8H, m), 1.46 (2H, quintet), 1.81 (2H, quintet), 3.99 (2H, t), 6.97 (2H, d), 7.35 (2H, t), 7.41 (1H, m), 7.47 (2H, d)

MS *m/z* 448 (M^+)

3-Fluoro-4'-heptylbiphenyl-4-yl triflate (78)

Quantities: triflic anhydride (5.9 g, 0.02 mol), compound **76** (5 g, 0.0175 mol), dry pyridine (80 ml). The experimental procedure was as described for the preparation of compound **35**, except that the residue was purified by column chromatography [silica gel / hexane-DCM, 4:1] to yield colourless liquid.

Yield: 6.5 g (89%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 1.22-1.38 (8H, m), 1.64 (2H, quintet), 2.64 (2H, t), 7.26 (2H, d), 7.36 (2H, m), 7.25 (1H, m), 7.43 (2H, m)

MS *m/z* 418 (M^+)

2,2',3-Trifluoro-4-(trimethylsilylethyl)-4''-octyloxyterphenyl (79)

Quantities: compound **77** (1.75 g, 3.9 mmol), 2M Na_2CO_3 (35 ml), of DME (35 ml), $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol), compound **43** (1.2 g, 4.68 mmol). The experimental procedure was as described for the preparation of compound **30**, except that lithium chloride (0.5 g, 11.7 mmol) was added to the mixture, to yield colourless crystals.

Yield: 1.6 g, (80%)

Transitions (°C) Cr 74.1 SmC 100.3 SmA 104.7 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.06 (9H, s), 0.89 (5H, m), 1.26- 1.38 (8H, m), 1.47 (2H, quintet), 1.83 (2H, quintet), 2.71 (2H, m), 4.00 (2H, t), 6.98 (2H, d, *J* = 8.80), 7.05 (2H, m), 7.35 (1H, m), 7.40 (2H, m), 7.54 (2H, d, 8.80)

^{13}C NMR (100 MHz, $CDCl_3$) -1.87, 14.09, 17.31, 22.66, 23.12, 26.06, 29.26 (x2), 29.38, 31.82, 68.07, (alkyl chains, 11 required, 11 found); 113.62, 113.85, 114.89, 120.59 (dd, *J* = 16.14, *J* = 3.07), 122.14 (d, *J* = 3.07), 122.48 (d, *J* = 13.07), 123.78 (dd, *J* = 4.61, *J* = 4.61), 125.25 (dd, *J* = 2.31, *J* = 2.31), 127.99, 131.60 (m), 134.14 (d, *J* = 13.07), 143.03 (d, *J* = 7.69), 148.10 (dd, *J* = 249.83, *J* = 13.84), 149.06 (dd, *J* = 245.22, *J* = 12.30), 159.31, 160.03 (d, *J* = 249.06) (aromatic carbons, 16 required, 16 found)

MS *m/z* 512 (M^+)

HPLC 100%

Elemental analysis: $C_{31}H_{39}SiOF_3$ requires C 72.62%, H 7.67%; found C 72.89%, H 7.63%

2,2',3-Trifluoro-4''-heptyl-4-(trimethylsilylethyl)terphenyl (80)

Quantities: compound **78** (1.73 g, 4.15 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.18 g, 0.15 mmol), compound **43** (1.28 g, 4.15 mmol). The experimental procedure was as described for the preparation of compound **30**, except that lithium chloride (0.53 g, 12.4 mmol) was added to the mixture, to yield colourless crystals.

Yield: 1.1 g, (55%)

Transitions (°C) Cr 45.8 SmC 71.6 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.06 (9H, s), 0.89 (5H, m), 1.25- 1.36 (8H, m), 1.65 (2H, quintet), 2.65 (2H, t), 2.71 (2H, t), 7.05 (1H, m), 7.10 (1H, m), 7.28 (2H, d, *J* = 8.25), 7.39 (1H, m), 7.43 (2H, m), 7.53 (2H, d, *J* = 8.25)

^{13}C NMR (100 MHz, $CDCl_3$) -1.86, 14.11, 17.32, 22.69, 23.15, 29.26 (x2), 31.45, 31.84, 35.64 (alkyl chains, 10 required, 10 found); 114.00, 114.23, 121.05 (dd, *J* = 15.37, *J* = 2.31), 122.47 (dd, *J* = 10.76, *J* = 3.07), 123.79 (dd, *J* = 4.61, *J* = 4.61), 125.27, 126.82, 128.99, 131.62, 134.19 (d, *J* = 13.07), 136.69 (d, *J* = 1.54), 143.01, 143.44 (d, *J* = 7.69), 148.13 (dd, *J* = 250.60, *J* = 13.84), 149.30 (dd, *J* = 239.45, *J* = 13.07), 160.03 (d, *J* = 249.06) (aromatic carbons, 16 required, 16 found)

MS *m/z* 482 (M^+)

HPLC 100%

Elemental analysis: $C_{30}H_{37}SiF_3$ requires C 74.65%, H 7.73%; found C 73.42%, H 7.70%

2,2',3-Trifluoro-4-(3,3-dimethylbutyl)-4''-octyloxyterphenyl (81)

Quantities: compound **77** (1.8 g, 4.03 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.17g, 0.15 mmol), compound **50** (1.17 g, 4.84 mmol). The experimental

procedure was as described for the preparation of compound **30**, except that lithium chloride (0.51 g, 12.24 mmol) was added to the mixture, to yield colourless crystals.

Yield: 1.6 g, (80%)

Transitions (°C) Cr 98.5 SmC 110.1 SmA 113.6 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.89 (3H, t), 0.99 (9H, s), 1.28- 1.38 (8H, m), 1.51 (2H, quintet), 1.54 (2H, m), 1.81 (2H, quintet), 2.67 (2H, m), 4.00 (2H, t), 6.98 (2H, d, *J* = 8.80), 7.01 (1H, ddd, , *J* = 8.06, *J* = 8.06, *J* = 1.28), 7.08 (1H, m), 7.35 (1H, m), 7.40 (2H, m), 7.54 (2H, d, *J* = 8.80)

^{13}C NMR (100 MHz, $CDCl_3$) 14.08, 22.66, 23.31, 24.31, 26.05, 29.14, 29.26, 29.38, 30.59, 31.82, 44.50, 68.07, (alkyl chains, 12 required, 12 found); 113.61, 113.84, 114.89, 120.57 (dd, *J* = 15.37, *J* = 2.31), 122.13 (d, *J* = 3.07), 122.58 (d, *J* = 12.30), 124.39 (dd, *J* = 4.61, *J* = 4.61), 125.25 (m), 127.98, 131.57 (m), 132.32 (d, *J* = 13.07), 143.03 (d, *J* = 7.69), 148.14 (dd, *J* = 249.83, *J* = 13.84), 149.38 (dd, *J* = 245.99, *J* = 13.07), 159.31, 160.02 (d, *J* = 249.06) (aromatic carbons, 16 required, 16 found)

MS *m/z* 496 (M^+)

HPLC 100%

Elemental analysis: $C_{32}H_{39}OF_3$ requires C 77.39%, H 8.92%; found C 77.6%, H 8.89%

2,2',3-Trifluoro-4''-heptyl-4-(3,3-dimethylbutyl)terphenyl (82)

Quantities: compound **78** (1.79 g, 4.29 mmol), 2M Na_2CO_3 (35 ml), DME (35 ml), $Pd(PPh_3)_4$ (0.18 g, 0.15 mmol), compound **50** (1.24 g, 5.14 mmol). The experimental procedure was as described for the preparation of compound **30**, except that lithium chloride (0.55 g, 12.9 mmol) was added to the mixture, to yield colourless crystals.

Yield: 1.34 g, (67%)

Transitions (°C) Cr 56.0 SmC 67.3 SmA 75.3 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.88 (3H, t), 0.99 (9H, s), 1.25- 1.38 (8H, m), 1.53 (2H, m), 1.65 (2H, quintet), 2.66 (4H, m), 7.01 (1H, ddd, *J* = 6.60, *J* = 6.60, *J* = 1.47), 7.08 (1H, m), 7.27 (2H, d, *J* = 8.43), 7.41 (3H, m), 7.53 (2H, d, *J* = 8.43)

^{13}C NMR (100 MHz, $CDCl_3$) 14.10, 22.68, 23.33, 29.16 (x2), 29.34, 30.60, 31.44, 31.83, 35.63, 44.52 (alkyl chains, 11 required, 11 found); 114.00, 114.23, 121.06 (dd, *J* = 15.37, *J* = 2.31), 122.51 (d, *J* = 3.07), 124.41 (dd, *J* = 3.84, *J* = 3.84), 125.28 (m), 126.82, 128.99, 131.62 (m), 132.39 (d, *J* = 13.07), 136.68 (d, *J* = 1.54), 143.02, 143.35 (d, *J* = 7.69), 148.16 (dd, *J* = 249.83, *J* = 13.84), 149.40 (dd, *J* = 245.99, *J* = 13.07), 160.02 (d, *J* = 249.06) (aromatic carbons, 16 required, 16 found)

MS *m/z* 466 (M^+)

HPLC 100%

Elemental analysis: $C_{31}H_{37}F_3$ requires C 79.79%, H 7.99%; found C 79.96%, H 8.24%

3.3.5 Chiral Difluoroterphenyl Compounds

Scheme 17

1-Bromo-4'-ethanoylbiphenyl (83)

Quantities: acetyl chloride (47g, 0.6 mol), aluminium chloride (48.06 g, 0.36 mol), DCM (300 ml), 4-bromobiphenyl (70 g, 0.30 mol). The experimental procedure was as described for the preparation of compound **24**, except that the residue was purified by column chromatography [silica gel / DCM] to yield off white crystals.

Yield: 42 g (51%)

Melting Point (°C): 127.6

^{1}H NMR (400 MHz, $CDCl_3$) 2.64 (3H, s), 7.50 (2H, d), 7.60 (2H, d), 7.66 (2H, d), 8.03 (2H, d)

MS *m/z* 275 (M^+), 273 (M^+)

4'-Bromobiphenyl-4-carboxylic acid (84)

A solution of sodium hypobromite was prepared at 0 °C by dissolving bromine (83.44 g, 0.715 mol) in a solution of sodium hydroxide (71.5 g, 1.78 mol) in water (350 ml). The hypobromite solution was added with stirring to a solution of the compound **83** (41 g, 0.149 mol) in dioxan (300 ml). The mixture was stirred at 35-40 °C for 15 mins. The suspension was treated with enough aqueous sodium thiosulphate pentahydrate to declourise the excess of hypobromite. Water (500 ml) was added and the majority of the dioxan was distilled off. The residual suspension was acidified with concentrated hydrochloric acid and cooled (stir vigorously to convert all of the salt to the acid). The free acid was filtered off and crystallised from isopropanol and ethanol. It was filtered off and left in 60 °C oven overnight to yield off white crystals.

Yield: 37 g (90%)

^{1}H NMR (400 MHz, $CDCl_3$) 6.85 (4H, m), 6.89 (2H, d), 7.31 (2H, d)

MS *m/z* 277 (M^+), 275 (M^+)

Ethyl 4'-bromobiphenyl-4-carboxylate (85)

A few drops of conc. sulphuric acid were added to a mixture of compound **84** (37 g, 0.133 mol), and ethanol (500 ml). The mixture was heated under reflux for 20 h. The now homogenous solution was allowed to cool and the ester filtered off. The product was washed with enough cool ethanol to wash out traces of acid and dried *in vacuo* over phosphorus pentoxide to yield off white crystals.

Yield: 22.4 g (55%)

Melting Point (°C): 77.0

^{1}H NMR (400 MHz, $CDCl_3$) 1.41 (3H, t), 4.40 (2H, q), 7.49 (2H, d), 7.59 (2H, d), 7.62 (2H, d), 8.11 (2H, d)

MS *m/z* 306 (M^+), 304 (M^+)

Ethyl 2,3-difluoro-4-(trimethylsilylethyl)terphenyl-4''-carboxylate (86)

Quantities: compound **85** (11 g, 0.036 mol), 2M Na_2CO_3 (250 ml), DME (250 ml), $Pd(PPh_3)_4$ (1.21 g, 1.05 mmol), compound **43** (14 g, 0.054 mol). The experimental procedure was as described for the preparation of compound **30**, except that the mixture was heated for just 5 h to yield off white crystals.

Yield: 10 g, (63%).

Melting Point (°C): 125.0

^{1}H NMR (400 MHz, $CDCl_3$) 0.07 (9H, s), 0.89 (2H, m), 1.42 (3H, t), 2.70 (2H, m), 4.41 (2H, q), 7.05 (1H, ddd), 7.15 (1H, ddd), 7.65 (2H, d), 7.70 (2H, d), 7.72 (2H, d), 8.14 (2H, d)

MS *m/z* 438 (M^+)

Ethyl 2,3-difluoro-4-(3,3-dimethylbutyl)terphenyl-4''-carboxylate (87)

Quantities: compound **85** (8.5 g, 0.028 mol), 2M Na_2CO_3 (250 ml), DME (250 ml), $Pd(PPh_3)_4$ (0.87 g, 0.757 mmol), compound **50** (10 g, 0.041 mol). The experimental

procedure was as described for the preparation of compound **30**, except that the mixture was heated for just 5 h to yield off white crystals.

Yield: 7 g, (59%)

Transitions (°C) Cr 152 SmA 166 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.99 (9H, s), 1.43 (3H, t), 1.54 (2H, m), 2.70 (2H, m), 4.41 (2H, q), 7.02 (1H, ddd), 7.17 (1H, ddd), 7.64 (2H, d), 7.70 (2H, d), 7.72 (2H, d), 8.13 (2H, d)

MS *m/z* 422 (M^+)

2,3-Difluoro-4-(trimethylsilylethyl)terphenyl-4''-carboxylic acid (88)

Compound **86** (9.5 g, 0.021 mol) was added to a mixture of sodium hydroxide (1.735 g, 0.043 mol) dissolved in water (10 ml) and ethanol (200 ml). The stirred mixture was heated under reflux for 1 h. A precipitate was obtained by adding water (500 ml) and conc. HCl (10 ml) to the still warm mixture and stirred until cold. The precipitate was filtered and washed with copious amounts of water. The powder was dried *in vacuo* over phosphorus pentoxide to yield colourless crystals.

Yield: 7.8 g, (91%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.06 (9H, s), 0.90 (2H, m), 2.56 (2H, m), 7.13 (1H, ddd), 7.23 (1H, ddd), 7.65 (2H, d), 7.75 (2H, d), 7.78 (2H, d), 8.08 (2H, d)

MS *m/z* 410 (M^+)

2,3-Difluoro-4-(3,3-dimethylbutyl)terphenyl-4''-carboxylic acid (89)

Quantities: Compound **87** (7 g, 0.016 mol), sodium hydroxide (1.327 g, 0.033 mol). The experimental procedure was as described for the preparation of compound **88**, to yield colourless crystals.

Yield: 5.5 g, (84%)

^{1}H NMR (400 MHz, $CDCl_3$) 0.99 (9H, s), 1.50 (2H, m), 2.70 (2H, m), 7.15 (1H, ddd), 7.27 (1H, ddd), 7.67 (2H, d), 7.78 (2H, d), 7.83 (2H, d), 8.06 (2H, d)

MS *m/z* 394 (M^+)

2,3-Difluoro-4-(trimethylsilylethyl)terphenyl-4''-carbonyl chloride (90)

Dry DCM (30 ml) was added to compound **88** (7 g, 0.017 mol) in a flask fitted with a nitrogen bubbler. Oxalyl chloride (1.1 ml) was added *via* syringe and 1 drop of DMF. After adding the DMF the nitrogen supply was turned off and the reaction monitored by the rate of evolution of CO/CO_2. When bubbling of gas ceased, solvent was evaporated, the crude acid chloride was used immediately in the esterification step.

2,3-Difluoro-4-(3,3-dimethylbutyl)terphenyl-4''-carbonyl chloride (91)

Quantities: compound **89** (5 g, 0.0127 mol), oxalyl chloride (1.1 ml), DMF (1 drop). The experimental procedure was as described for the preparation of compound **90**, and the crude acid chloride was used immediately in the esterification step.

(*R*)-1-Amino-1-oxopropan-2-yl 2'',3''-difluoro-4''-(2-(trimethylsilyl)ethyl)terphenyl-4-carboxylate (93)

(*R*)-(+)-Lactamide (2.18 g, 0.025 mol) was dissolved in pyridine (20 ml). Compound **90** (7 g, 0.016 mol) in dry THF (60 ml) was added to the above solution dropwise with the help of dropping funnel under nitrogen atmosphere while stirring. The mixture was left stirring for 20 h, and poured in to a solution of HCl (120 ml), water, and ice. It was filtered off, and recrystallised from ethyl acetate, and dried *in vacuo* over phosphorus pentoxide to yield colourless crystals.

Yield: 2.7 g, (35%)

Melting Point (°C): 191.0

^{1}H NMR (400 MHz, $CDCl_3$) 0.06 (9H, s), 0.91 (2H, m), 1.63 (2H, d), 2.70 (2H, m), 5.43 (1H, q), 7.08 (1H, ddd), 7.17 (1H, ddd), 7.66 (2H, d), 7.74 (2H, d), 7.76 (2H, d), 8.18 (2H, d)

MS *m/z* 481(M^+)

(*R*)-1-Amino-1-oxopropan-2-yl 4''-(3,3-dimethylbutyl)-2'',3''-difluoroterphenyl-4-carboxylate (94)

Quantities: (*R*)-(+)-Lactamide (1.6 g, 0.018 mol), compound **91** (5 g, 0.012 mol). The experimental procedure was as described for the preparation of compound **93** to yield colourless crystals.

Yield: 3.6 g, (65%)

Melting Point (°C): 200.0

^{1}H NMR (400 MHz, $CDCl_3$) 1.00 (9H, s), 1.53 (2H, m), 1.62 (2H, d), 2.68 (2H, m), 5.41 (1H, q), 7.05 (1H, ddd), 7.18 (1H, ddd), 7.65 (2H, d), 7.73 (2H, d), 7.76 (2H, d), 8.18 (2H, d)

MS *m/z* 465 (M^+)

(*R*)-1-Cyanoethyl 2'',3''-difluoro-4''-(2-(trimethylsilyl)terphenyl-4-carboxylate (95)

$POCl_3$ (3.19 g, 20.7 mmol) was added dropwise to a stirred, cooled (-5 to 0 °C) dry DMF (40 ml) under dry nitrogen. This mixture was stirred for 20 min and compound **93** (2 g, 4.15 mmol) was added in portions. The mixture was then stirred at room temperature for 20 h. Solution was poured in ice and water mixture. A precipitate was filtered and washed with water. The dry product was recrsytalised through toluene, and dried *in vacuo* over phosphorus pentoxide to yield colourless crystals.

Yield: 0.70 g, (36%)

Transitions (°C) Cr 132.5 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.06 (9H, s), 0.90 (2H, m), 1.80 (2H, d), 2.71 (2H, m), 5.69 (1H, q), 7.06 (1H, ddd, *J* = 7.70, *J* = 7.70, *J* = 1.28), 7.18 (1H, ddd, *J* = 8.06, *J* = 8.06, *J* = 1.28), 7.65 (2H, dd, *J* = 8.43, *J* = 1.28), 7.71 (2H, d, *J* = 8.43), 7.74 (2H, d, *J* = 8.43), 8.14 (2H, d, *J* = 8.25)

^{13}C NMR (100 MHz, $CDCl_3$) -1.90, 17.27, 18.89, 23.05,57.72; (alkyl chains, 5 required, 5 found); 117.55, 124.09 (x2, m), 127.01, 127.08, 127.33, 129.35 (d, *J* = 3.07), 130.48, 133.77 (x2), 135.10, 138.87, 145.92, 147.84 (dd, *J* = 252.90, *J* = 16.91), 149.21 (dd, *J* =

247.52, *J* = 14.61) (aromatic carbons, 14 required, 14 found, nitrile carbon, 1 required, 1 found); 164.46 (carbonyl carbon, 1 required, 1 found)

MS *m/z* 463 (M^+)

HPLC 100%

Elemental analysis: $C_{27}H_{27}SiO_2NF_2$ requires C 69.95%, H 5.87%, N 3.02%; found C 69.74%, H 5.89%, N 3.01%

(*R*)-1-Cyanoethyl 2'',3''-difluoro-4''-(3,3-dimethylbutyl)terphenyl-4-carboxylate (96)

Quantities: $POCl_3$ (3.30 g, 21.5 mmol, compound **94** (2 g, 4.3 mmol). The experimental procedure was as described for the preparation of compound **95** to yield colourless crystals.

Yield: 0.58 g, (30%)

Transitions (°C) Cr 170 I

^{1}H NMR (400 MHz, $CDCl_3$) 0.99 (9H, s), 1.52 (2H, m), 1.80 (2H, d), 2.67 (2H, m), 5.69 (1H, q), 7.02 (1H, ddd, *J* = 8.06, *J* = 8.06, *J* = 1.28), 7.16 (1H, ddd, *J* = 8.06, *J* = 8.06, *J* = 1.28), 7.65 (2H, dd, *J* = 8.25, *J* = 1.28), 7.72 (2H, d, *J* = 8.25), 7.74 (2H, d, *J* = 8.25), 8.14 (2H, d, *J* = 8.25)

^{13}C NMR (100 MHz, $CDCl_3$) 18.96, 24.28, 29.15, 30.61, 44.53, 57.75, (alkyl chains, 6 required, 6 found); 117.58, 124.18 (dd, *J* = 3.07, *J* = 3.07), 124.73 (dd, *J* = 3.07, *J* = 3.07), 127.05, 127.16, 127.40, 129.41 (d, *J* = 3.07), 130.55, 132.03 (x2), 135.16, 138.97, 146.02, 148.09 (dd, *J* = 252.14, *J* = 16.14), 149.47 (dd, *J* = 248.29, *J* = 15.37) (aromatic carbons, 14 required, 14 found, nitrile carbon, 1 required, 1 found); 164.52 (carbonyl carbon, 1 required, 1 found)

MS *m/z* 447 (M^+)

HPLC 100%

Elemental analysis: $C_{28}H_{27}SiO_2NF_2$ requires C 75.15%, H 6.08%, N 3.13%; found C 75.38%, H 6.10%, N 3.12%

3.4 References

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4 Experimental Discussion

This chapter discusses the experimental strategy both in term of the chosen synthetic routes and the experimental techniques used to obtain the compounds shown in the figure 4.1.

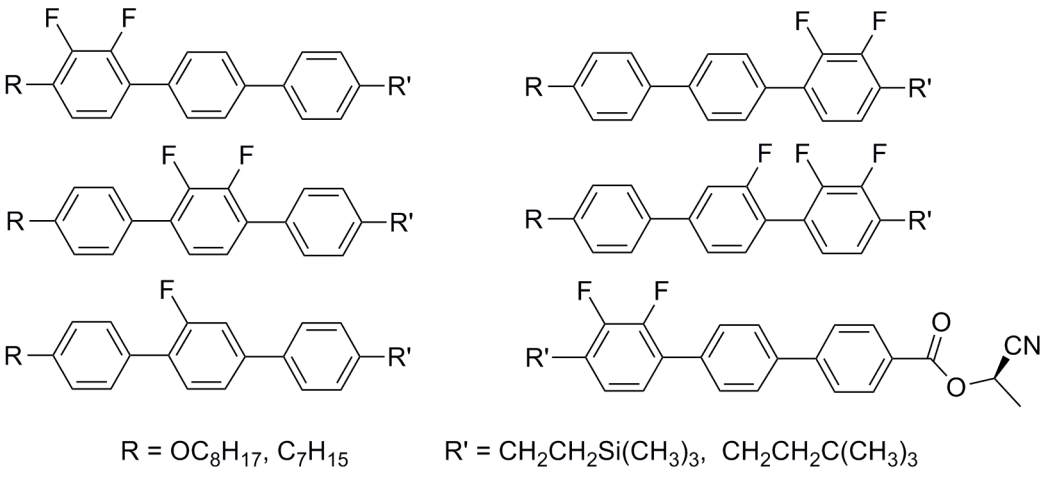


Figure 4.1. General structures of the compounds prepared.

The targeted materials have all been designed to perform a very specific function in liquid crystal mixtures for use in display devices. The aims of phase separation to circumvent layer shrinkage and confer a bookshelf alignment can be tackled by using structural units in the material which can disrupt the intermolecular forces of attraction at the ends of the molecules. The intention was to study the effect of the bulky end group on melting point and mesophase morphology of the compounds and also to assess how these compounds affect the switching times of mixtures in which they are included. Accordingly, the structural composition of these novel compounds is somewhat more complex than most liquid crystals. In this case, such complexity of the targeted structures necessitated careful consideration of the synthetic routes and methods to be used.

The general preparation of multi-aryl core compounds with two terminal chains and several lateral fluoro substituents cannot possibly be accomplished from the core unit directly. The introduction of structural units into a phenyl ring is most often achieved using electrophilic substitution reaction. The range of units that can be introduced is

somewhat limited, however subsequent functional group interconversions can give a vast array of substituents. The electrophilic substitutions in an aryl ring are directed and rate-determined by the already present substituents. Hence, as the number of substituents required in an aryl ring is increased, the chance that a substituent will be directed to an undesired position becomes ever greater. Additionally, steric hindrance will limit the chances of a substituent being directed to a desired position in the ring. In biphenyls and terphenyls, the scope for electrophilic substitution is very restricted because the positions in the bay regions of the core (*i.e.*, the 2- and 2'- positions) are sterically hindered by the ring structure itself, hence in these positions substitution is very unlikely. The introduction of a terminal chain such as an alkyl or alkoxy chains (which are used in this work as terminal chains) into a biphenyl or a terphenyl core will activate positions in the terminal rings to further substitution.

With all these facts in mind, alternative methods were required for preparing the terphenyl materials with lateral fluoro substituents. The alternative methods involve the initial synthesis of the individual ring units and the subsequent systematic linking of these units to provide the desired multi-aryl final product materials. Many methods of generating carbon-carbon bonds between aryl units have now been developed to a suitable standard of high product yields and operational simplicity to allow their widespread use in synthetic organic chemistry. Most such methods use two aryl units, one having a leaving group or substituent and the other aryl unit is an organometallic unit. The two aryl units can then be coupled together in the presence of a transition metal catalyst which contains suitable ligands. One of the most useful catalysts is tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$. Iodo, bromo and chloro can be leaving groups as well as triflate and tosylate, these latter two are formed from phenols or enols which greatly enhance the scope of the methodology. The arylboronic acids are the most successful organometallic units in the synthesis of liquid crystals because of:

1. Boronic acids non-toxicity
2. Lack of significant homocoupling
3. Their ease of preparation especially at low temparature
4. Compatibility with a wide range of other functional groups

The use of arylboronic acids in metal-catalysed cross-couping reactions was developed by Suzuki and co-workers in 1981[1]. Since this time, Suzuki and many other chemists[2-7]

have further developed the methodology and obtained excellent results with a wide range of different substrates. 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[8]. The palladium-catalysed cross-coupling reaction is generally carried out in DME, the substrate containing the leaving group is added to a mixture of DME and 2M aqueous sodium carbonate, under dry nitrogen and then the palladium catalyst is added followed by 15-20% excess of the boronic acid.

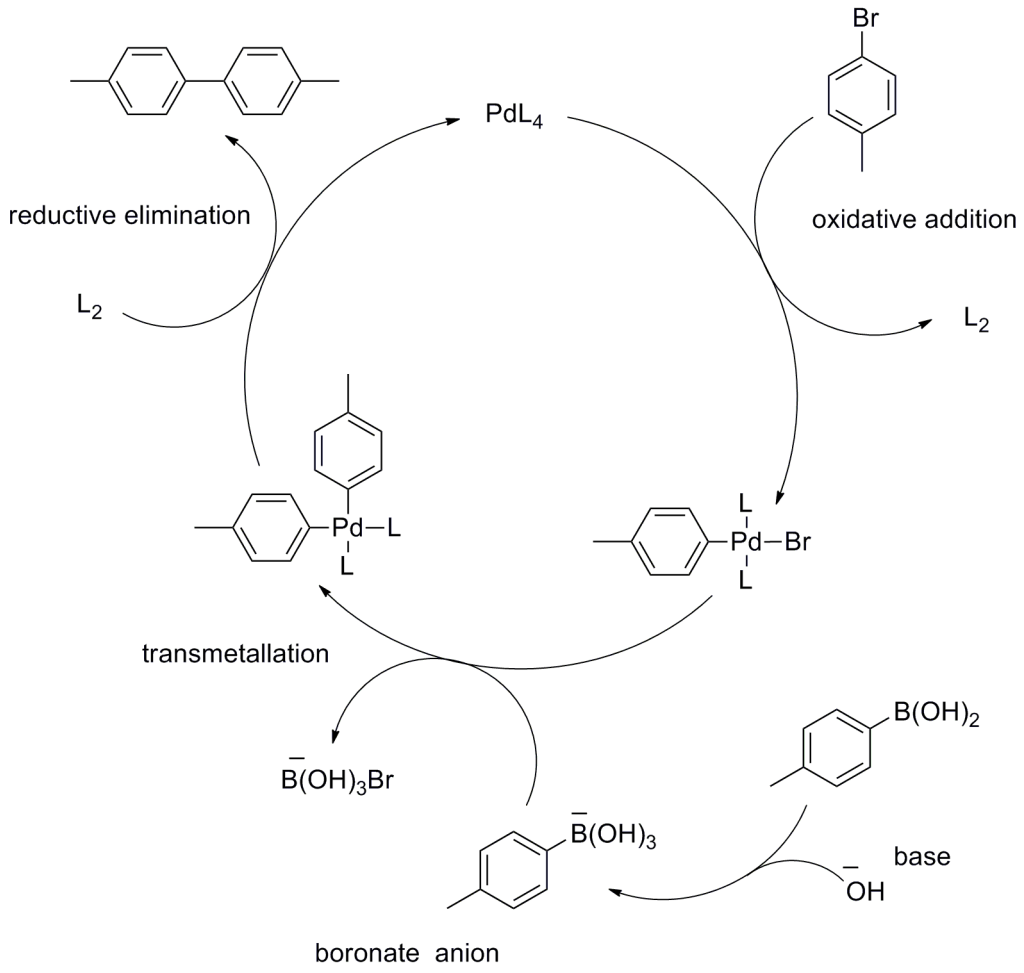


Figure 4.2. Proposed mechanism of the catalytic cycle for the palladium cross-coupling.

The mechanism of the Suzuki coupling catalytic cycle has been proposed[9-11] to be that in figure 4.2, but many variations have been reported. The basic steps in the cross-coupling reaction include oxidative addition of the aryl or vinyl halide (or triflate) to Pd(0), followed by transmetallation of an organic ligand from an organometallic to the

resulting Pd(II) intermediate. The disubstituted Pd(II) intermediate then undergoes reductive elimination, which gives the product by carbon bond formation and regenerates the catalytically active Pd(0) oxidation level. Ligands and anions play a crucial role in determining the rates and equilibria of various steps by controlling the detailed coordination environment at palladium[12].

For this thesis, the synthetic schemes and experimental section are arranged in two parts, and the second part is then further sub-categorised as follows:

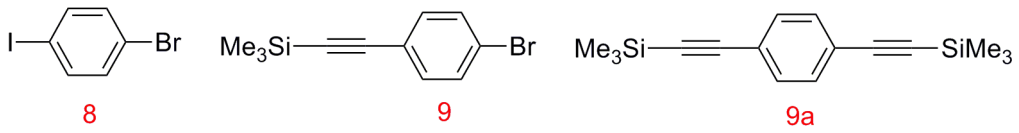
1. Synthesis of required intermediate compounds (schemes 1 – 6)
2. Use of intermediate compounds to synthesise desired final products
    a. Difluoroterphenyl products (schemes 7 – 14)
    b. Monofluoroterphenyl products (scheme 15)
    c. Trifluoroterphenyl products (scheme 16)
    d. Chiral difluoroterphenyl products (scheme 17)

Note that in the schemes, some unsuccessful routes, and the connected proposed routes to final products, have been included in order to put the research into context.

4.1 Required Intermediate Compounds

Scheme 1 shows the synthesis of two intermediates, 1-bromo-4-octyloxybenzene (**2**) and 1-bromo-4-heptylbenzene (**5**). 4-Bromophenol (**1**) was *O*-alkylated with 1-bromooctane to produce satisfactory results (yields >80%) of compound **2**, which is a very common intermediate in the synthesis of liquid crystals. During the reaction, the potassium carbonate abstracts the phenolic proton (Williamson ether synthesis)[13] resulting in the formation of the corresponding phenolate anion which then attaches to alkyl bromide in a typical S_N2 reaction to generate the desired aryl-alkyl ether (**2**). 1-Bromo-4-heptylbenzene (**5**) was prepared using the general method of introducing an alkyl chain into an aromatic unit which involves a Friedel-Crafts acylation followed by Wolff-Kishner reduction[11] of the resulting ketone. Two steps are necessary to generate compound **5** because any direct alkylation of compound **3** would lead to a rearrangement of the alkyl chain and multiple substitutions[13]. A yield of around 80% of compound **5** was obtained.

Scheme 2 shows the attempted preparation of 1-bromo-4-(trimethylsilylethynyl)benzene (**9**). The original synthetic strategy for this part of the work was to use compound **9** in appropriate coupling reactions (see schemes 7 and 8) to eventually generate final products (**30**, **31**, **36**, and **37**). In the first attempt at the synthesis of compound **9**, the reaction was carried out as a selective coupling using a palladium catalyst. One equivalent of *n*-butyllithium was used to remove the acidic proton of (trimethylsilyl)acetylene, then 1.5 equivalent of fresh zinc chloride was added to form the unstable intermediate (compound **7**) which was treated with the catalyst and then with 0.8 equivalent of 1-bromo-4-iodobenzene, the mixture was stirred at room temperature overnight. Unfortunately, the reaction did not go to completion, ^{1}H NMR analysis shows a mixture of the starting compound **8** and the product (compound **9**). A second attempt involved gentle heating (30 °C) overnight but unfortunately without the necessary success. Figure 4.3 shows the ^{1}H NMR for the aromatic protons of the crude product from this second attempt, and reveals a mixture of the starting compound **8**, some of desired product compound **9**, and the double coupled compound **9a** in an approximate ratio of 2:3:2.



8 9 9a

Purification of the desired compound **9** from the starting compound **8** is very difficult since both the desired compound and undesired compounds have very similar physical properties.

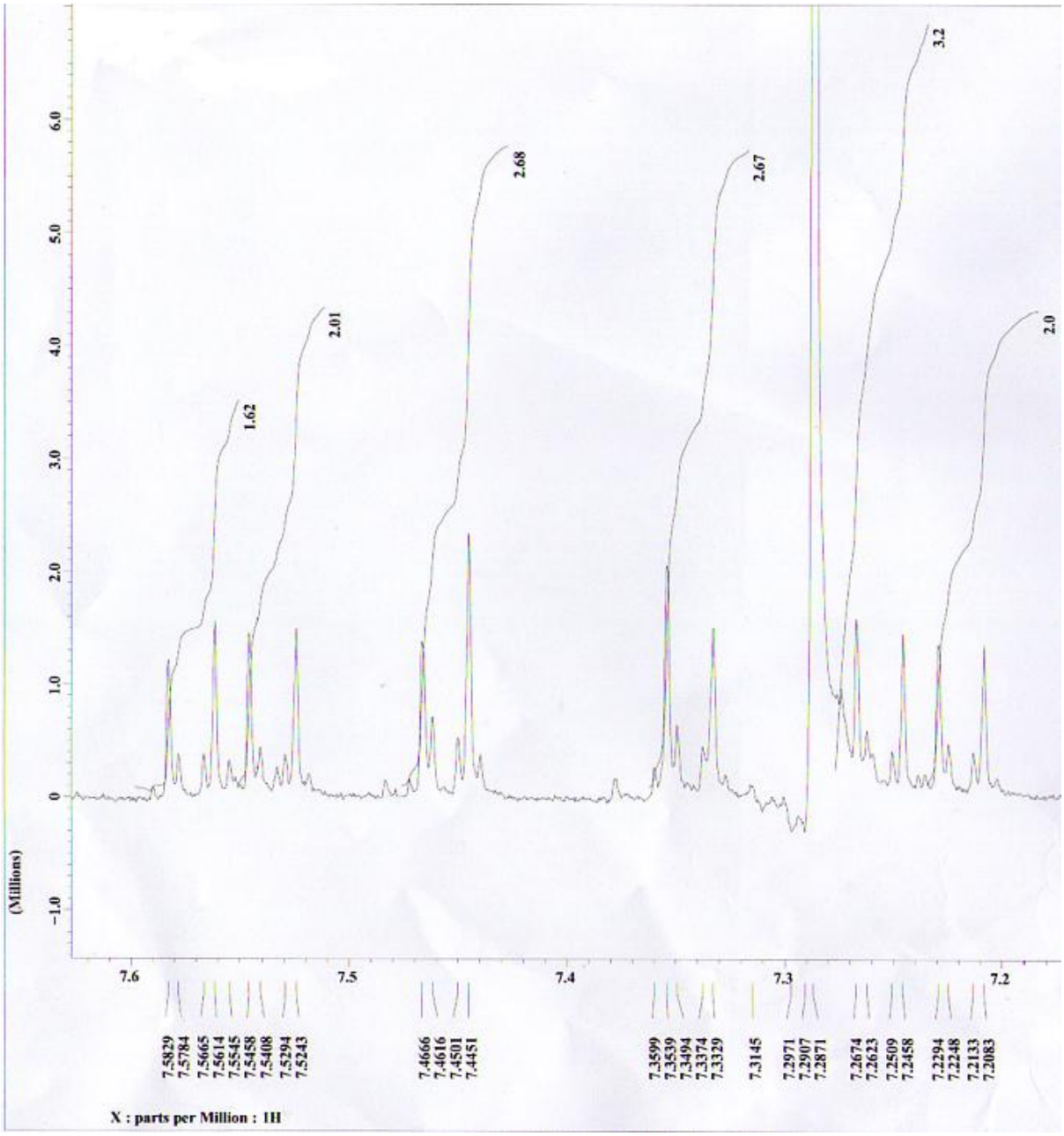


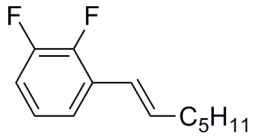
Figure 4.3. ^{1}HNMR spectrum of compound **9**, attempted synthesis (Method 2).

The proposed aim of scheme 3 was to prepare an alternative material to compound **9**. Compound **13** was planned to be used as an alternative material to compound **9**, and indeed would not require a selective coupling. It was expected that the benzyl group would be removed and the triple bond hydrogenated of compound **11** in one step, however, debenzylation of this substrate was not possible. The hydroxyl group in compound **1** was protected using benzyl chloride in an *O*-alkylation reaction to give a satisfactory yield (73%) of compound **10**. The acidic proton of (trimethylsilyl)acetylene was removed by *n*-butyllithium at low temperature, followed by treatment with zinc chloride to generate the unstable intermediate compound **7**, which was coupled with compound **10** to provide an excellent yield (> 70%) of compound **11**. Several hydrogenation methods using 10% palladium on carbon as catalyst were attempted to hydrogenate compound **11** in order to generate compound **12**. The first hydrogenation was attempted by using ethyl acetate as solvent and the reaction mixture was stirred overnight, but ^{1}H NMR showed that triple bond had been hydrogenated, but the benzyl group remained. Some more attempts to hydrogenate compound **11** were done using different a solvent system, and increasing the amount of the catalyst every time. Each time the ^{1}H NMR showed that the benzyl group remained. Hence yet another approach would be necessary (see scheme 9 and 10).

Scheme 4 details the synthesis of a difluorophenyl-alkyl ether *i.e.*, compound **16**, again a common intermediate in the synthesis of liquid crystals. Compound **16** was needed to synthesise the final compounds **36** and **37** with two fluoros in an end ring (see scheme 10). The synthesis begins with an *O*-alkylation of difluorophenol (**14**), using potassium carbonate in butanone to give the 1,2-difluoro-3-octyloxybenzene (**15**) in order to eventually generate the boronic acid (**16**). The treatment of compound **15** with *n*-BuLi generated the aryllithium intermediate *via* hydrogen-metal interconversion, which upon quenching with trimethyl borate yielded the boronic acid **16**. The reaction was carried out at a low temperature (−78 °C) to avoid benzyne formation by loss of LiF.

The introduction of a terminal alkyl chain into a ring containing lateral fluoro substituents (scheme 5) is more lengthy and involved than for an alkoxy terminal chain (scheme 4). The usual method of placing an alkyl chain into an aromatic unit involves a Friedel-Crafts acylation followed by a Wolff-Kishner reduction of resulting ketone, as used in scheme 1. However, in this case, the presence of the fluoro substituents directs

the acylation into the undesirable 4-position. Accordingly, in order to obtain the 1,2-difluoro-3-heptylbenzene (**19**), a different route was required which would exploit the acidic protons of 1,2-difluorobenzene (**17**). Generation of the mono-lithium salt of compound **17** as described previously (scheme 4), followed by addition of heptanal at low temperature (−78 °C) and acidification with ammonium chloride solution gave the benzylic alcohol (**18**). Dehydration of this alcohol **18** was effected using phosphorus(V) oxide to yield the alkene **18a** (not isolated) which was subsequently hydrogenated at room temperature over 10% Pd/C to give a yield of 67% from 1,2-difluoro-3-heptylbenzene (**19**).



18a

Lithiation of the remaining acidic proton on the substituted ring allowed the conversion of compound **19** into the corresponding boronic acid **20** using the procedures described for preparing compound **16** (scheme 4), to give a yield of 50%.

Scheme 6 shows very similar chemistry to scheme 1, 1-bromo-4-octyloxybenzene (**2**) and 1-bromo-4-heptylbenzene (**5**) were prepared in scheme 1, while scheme 6 shows the preparation of the two-ring analogues, 4-bromo-4'-octyloxybiphenyl (**22**) and 4-bromo-4'-heptylbenzene (**25**). The procedures for the preparation of compound **22** were as described for the preparation of compound **2**. The overall alkylation of 4-bromobiphenyl (**23**) was achieved by the conventional two-step process of acylation, followed by Wolff-Kishner reduction[11]. A yield of around 60% of compound **25** was obtained. The procedure for preparing compound **24** in scheme 6 was slightly different from that used for preparing compound **4** in scheme 1. The acylation of compound **23** was attempted using an excess of heptanoyl chloride, and the reaction was carried out at room temperature to avoid further alkylation.

4.2 Use of Intermediate Compounds to Synthesise Desired Final Products

In attempting to successfully synthesise laterally fluoro-substituted terphenyl materials, it is necessary to carefully consider all possible synthetic routes to the desired materials and to evaluate any possible problems that may be encountered. The target final materials which prepared in this work are mono, di, or trifluoroterphenyls with different terminal groups, with different positions for the fluorine on the benzene rings. The position of the lateral fluoro-substituents on the benzene rings is the main factor of choosing the suitable route to go with, in another words, the position of the lateral fluoro-substituents on the benzene rings would give the order that the coupling reactions would be attempted. The discussion here will be divided into four parts, the first part will cover all the strategies and methods which were used for preparing the difluorophenyls, this part will be also subdivided into three parts. The second part will concern the synthetic scheme for preparing the mono fluoroterphenyls. The third part will concern synthesising the trifluoroterphenyls. The first three parts will be focus on preparing achiral materials while the fourth part will centre on the preparation of the difluorophenyl chiral materials.

4.2.1 Difluoroterphenyl Compounds (Schemes 7 – 14)

4.2.1.1 Schemes 7, 9, and 13

Route 1 (figure 4.4) was applied for preparing compounds **30** and **31** detailed in scheme 9, and this route also was applied to the uncompleted syntheses detailed in scheme 7. The basis of the synthesis of these compounds was the sequential exploitation of the acidic protons of 1,2-difluorobenzene (**17**) *via* hydrogen-metal interconversion[4, 14]. 1,2-Difluorobenzene (**17**) has two equivalent protons *ortho* to a fluoro substituent which are acidic due to the electron-withdrawing effect of the adjacent fluoro substituent[15-17]. Metallation of 1,2-difluorobenzene with 1 mol equivalent of *n*-BuLi occurs at –78 °C to give the mono-lithium derivative. The low temperatures are required in order to stabilise the *ortho*-fluoroaryllithium intermediates as at higher temperatures the *ortho*-fluoroaryllithium intermediates will decompose violently with elimination of lithium fluoride to form the reactive benzyne species[18]. Adding the trimethyl borate slowly to mono-lithium derivative at –78 °C and gradual warming to room temperature, gave the

borate ester which was hydrolysed *in situ* with 10% hydrochloric acid to yield the boronic acid **26**. In general Grignard reagents can be used for preparing boronic acids, however, it is worth noting that when an *ortho* fluoro substituent is present, Grignard reagents cannot be used because at the high temperature required to form the Grignard reagent the *ortho* fluorine atom would eliminate lithium fluoride to form a benzyne[15].

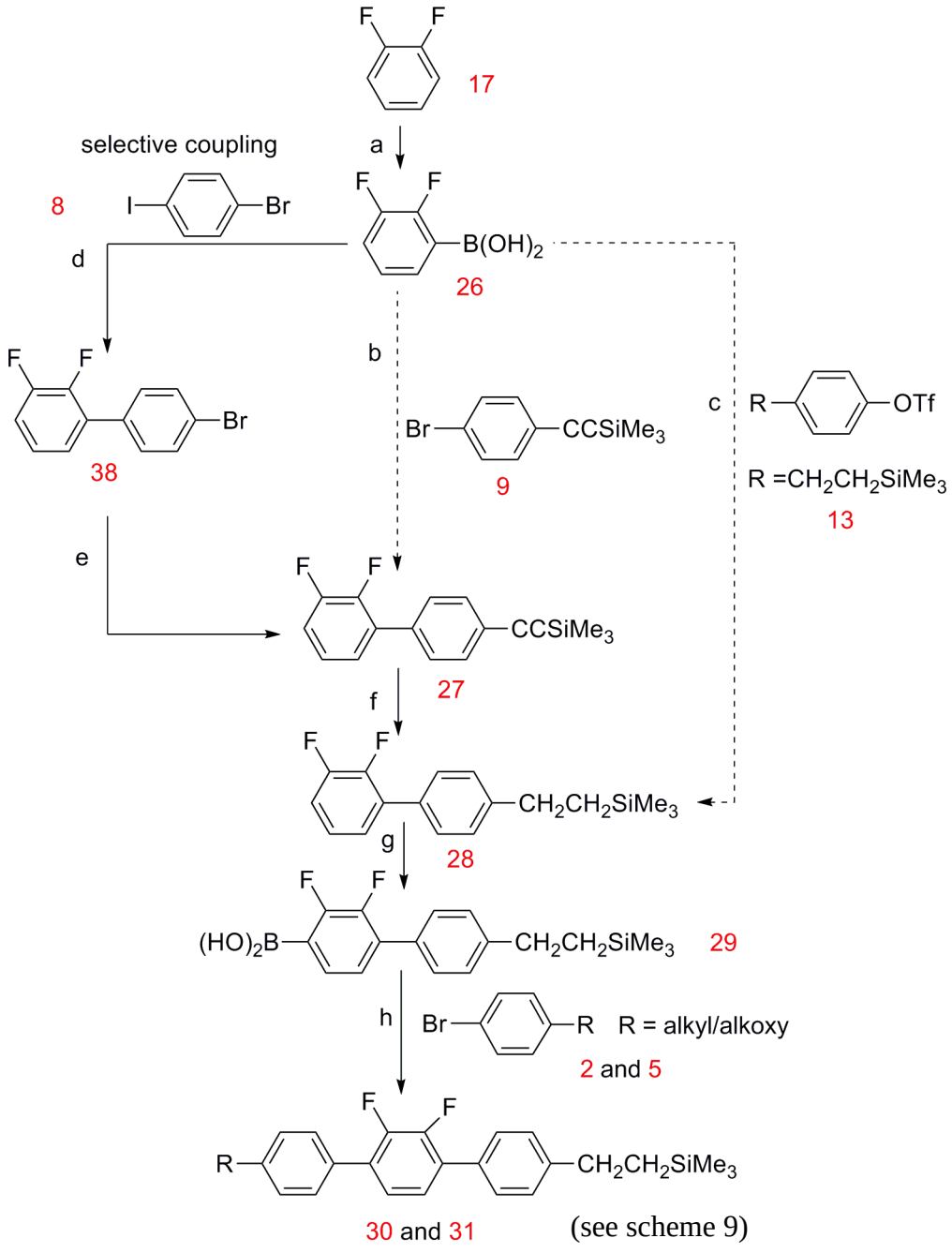


Figure 4.4. Synthetic Route 1.

As summorised in figure 4.4, three different strategies were attempted to synthesise the difluorobiphenyl **28** from the boronic acid **26**. The main planned strategy (steps b and f) was to couple compound **26** to compound **9** to give compound **27** which on planned hydrogenation would give compound **29**. Unfortunately this route detailed in scheme 7 did not progress because of the failure of preparing compound **9**, as discussed previously (see scheme 2). However, somewhat surprisingly, this strategy was successful for the dimethylbutyl family of materials (see scheme 13). The first alternative plan (step c) was to couple the triflate compound **13** to the boronic acid **26** to give compound **28**, this also could not be successful since compound **13** could not be prepared as discussed previously (see scheme 3). The second alternative planned route involved compound **26** to compound **28** (steps d, e, and f) which was successful, as detailed in scheme 9. Boronic acid **26** was coupled selectively to bromoiodobenzene **8** at the more reactive iodo site to generate biphenyl **38**. These selective couplings are of great synthetic value because they enable a separate subsequent coupling reaction to be carried out, however some double coupling can occur which often limits the product yield. Purification of the desired bromobiphenyl (**38**) from the terphenyl, formed by double coupling of the arylboronic acid at both the iodo and bromo positions, was difficult since both the desired biphenyl and double coupled terphenyl have very similar physical properties.

Compound **38** was alkylated in two steps. Firstly the bromo site was coupled to trimethylsilylethynyl group (-CCSiMe$_3$), the acidic terminal hydrogen of the alkyne was removed by *n*-BuLi at low temperature (–5 to 0 °C), subsequent addition of solid zinc chloride gave the unstable zinc chloride derivative which was coupled to compound **38** using Pd(PPh$_3$)$_4$ to give compound **27**. In the second step, hydrogenation using palladium on charcoal gave the desired saturated trimethylsilyldimethylene chain.

Before discussing the final reaction in route 1 (step h), one of the most important facts about boronic acids needs to be clarified. The fact is that boronic acids are prone to hydrodeboronation under the aqueous basic conditions of the coupling process, particularly in the presence of electron-withdrawing substituents[19-21], *e.g.*, *ortho* fluoro substituents, which renders the boron atom susceptible to nucleophilic attack from the aqueous base[14]. If there is no steric hindrance of either the boronic acid or the aryl halide, and a large enough excess of boronic acid is used, then the efficiency of the coupling will not be affected and high yields will result[14]. However, if either component

is sterically hindered[22], the rate of coupling, *i.e*, the transmetallation step, is reduced and the rate of hydrodebroronation becomes significant, resulting in low product yields.

The final coupling process (step h) in route 1 is relatively unhindered and consequently an excess of compounds **29**, was sufficient to generate good yields of compounds **30** and **31**. Although hydrodeboronation of the boronic acid **29** results in an involved purification process, and does reduce the yield of the desired terphenyl product.

Scheme 7 shows the original planned pathway for preparing compounds **30** and **31**, The strategy of scheme 7 was to couple the trimethylsilylethynyl group (-CCSiMe$_3$) selectively to 1-bromo-4-iodobenzene (**8**) at the iodo site, (scheme 2), then couple the resulting compound **9** to the boronic acid **26** in order to prepare compound **27**. Scheme 7 could not continue beyond the preparation of boronic acid **26** because as discussed previously for compound **9** could not be synthesized. The 2,3-difluorophenylboronic acid (**26**) was prepared by exploiting the acidic proton in 1,2-difluorobenzene with *n*-butyllithium at very low temperature (−78 °C), followed by quenching with trimethyl borate and subsequent acidification. The boronic acid **26** has a soft-waxy appearance, two reasons could explain this, firstly, boronic acids have a tendency to co-ordinate with THF and often this accounts for their soft-waxy nature as well as apparent yields greater than 100% and, secondly, boronic acids appear to be a mixture of acid and its dimeric, trimeric and sometimes polymeric anhydrides[14, 23].

An alternative synthetic route was proposed for the eventual synthesis of compounds **30** and **31**, which involved preparing triflate **13** (scheme 3). Triflate compound **13** was planned to be coupled to boronic acid **26** to give compound **27**, unfortunately, compound **13** could not be prepared, as was mentioned earlier in the discussion for scheme 3. Hence another alternative synthetic route was planned and this rout brough success (see scheme 9) for the preparation of compound **27** and to eventual synthesis of compounds **30** and **31**.

In scheme 9, the strategy involved the selective coupling of boronic acid **26** to compound **8** at the iodo site, and then the alkynyl group was added to the bromo site in the resulting biphenyl compound **38**. The synthesis shown in scheme 9 started by selective palladium catalysed coupling at standard coupling reaction temperature between boronic acid **26** and bromoiodobenzene **8**, a 60% yield of the biphenyl **38** was

collected as colourless oil after a distillation under reduced pressure. The bromo site in biphenyl **38** was then coupled to the trimethylsilylethynyl group as described previously to give a yield of 70% of compound **27**. The triple bond of the terminal alkynyl chain in compound **27** was saturated during the hydrogenation reaction using palladium on charcoal, to give a good yield (57%) of the saturated alkyl biphenyl **28**. Lithiation of the remaining acidic proton on the substituted ring allowed the conversion of compound **28** into corresponding boronic acid **29** as described previously. Palladium-catalysed cross-coupling reactions between compound **29** and the intermediate aryl bromides **2** and **5** were performed and the terphenyls **30** and **31** were collected at yields of 40% from compound **30**, and of 60% from compound **31** after purification by column chromatography and recrystalliation. All the final products such as compounds **30** and **31** were subjected to a purification by column chromatography, filtration of the materials using filtration papers after dissolving material in suitable solvent to remove any silica gel which may present with the material after column chromatography, and then further purification by recrystallization.

The original strategy of route 1 (steps a, b, f, g, and h) was unsuccessful for preparing the final compounds **30** and **31**, it was discussed before that because of the purification difficulties of compound **9** (scheme 2) from its mixture with the starting material **8** and a side product **9a**, an alternative route was performed successfully (steps d, e, f, g, and h, in route 1, and scheme 9) for preparing the desired final compounds **30** and **31**, however, steps a, b, f, g, and h in route 1 were applied successfully in scheme 13 for preparing their carbon analogues *i.e.*, compounds **57** and **58**. Scheme 13 shows the interesting synthesis of final liquid crystals compounds **57** and **58**, the synthesis started from the commercially available 3,3-dimethylbut-1-yne which was treated with *n*-BuLi at low temperature to remove the acidic terminal hydrogen, zinc chloride was added and the 1-bromo-4-iodobenzene was added to the resultant zinc chloride alkynide to form compound **53** in reasonably good yield >40%. The preparation of compound **53** was a challenge since the similar style compound **9** could not be prepared in this work. A Suzuki cross-coupling reaction was performed involving boronic acid **26** (see scheme 7) with compound **53** to give the biphenyl compound **54**. The remaining reactions of scheme 13 are very similar to those described previously.

4.2.1.2 Schemes 8, 10, and 14

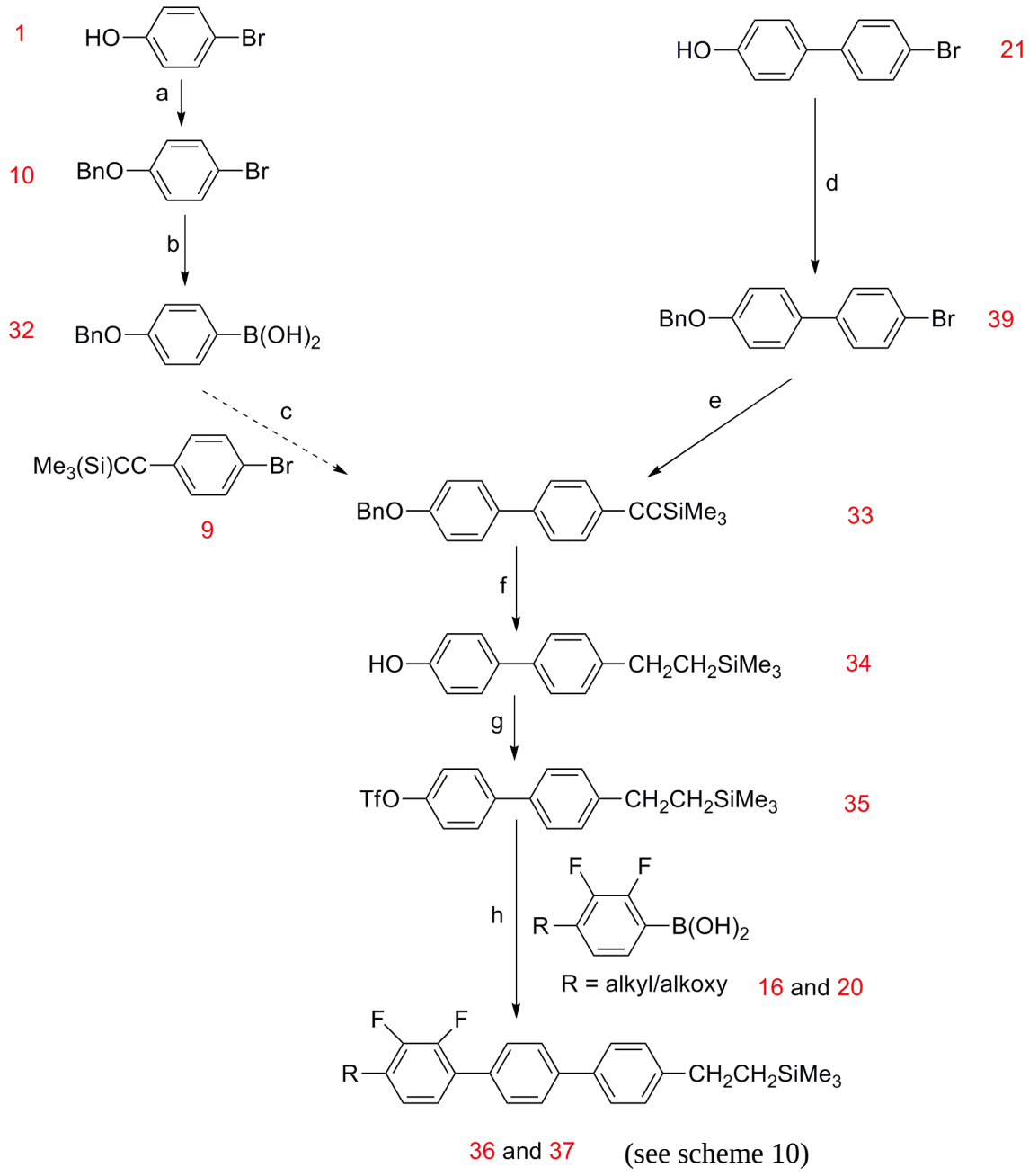


Figure 4.5 Synthetic Route 2.

Route 2 (figure 4.5) shows a summary of all the strategies and methods considered for preparing compounds **36** and **37** (detailed in schemes 8 and 10). The synthesis of the carbon analogues (compounds **62** and **63**) as detailed in scheme 14. The synthesis started from the commercially available 4-bromophenol (**1**). Compound **1** was *O*-alkylated with benzyl chloride in order to protect the hydroxyl group, the phenolic proton could destroy one equivalent of a strongly basic organometallic reagent which

would be used in the following reaction[11]. In order to generate the boronic acid (**32**) from the bromo-compound (**10**) (step b), it would be possible to use two methods, a Grignard reaction using magnesium, or a lithiation using *n*-butylithium (*n*-BuLi) which was been used several times before in this research. However, treating compound **10** with *n*-BuLi requires low temperature (–78 °C) to prevent addition of a butyl chain of the lithiated site, 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 good yield of the boronic acid **32** was obtained[6].

The synthesis of compounds **36** and **37** (terphenyls with trimethylsilylethyl end group) using the original planned pathway (scheme 8 and steps a, b, and c in route 2), progressed only to step c because of the unsuccessful preparation of the required bromo compound **9** (scheme 2), which was needed to couple to the boronic acid to give the biphenyl compound **33**. An alternative strategy (scheme 10 and steps d, and e in route 2) was designed to circumvent the problem, starting from protecting the hydroxyl group of 4-bromo-4'-hydroxybiphenyl (**21**) followed by the alkynylation of the bromo site of the resulting hydroxyl-protected bromobiphenyl **39** would give the compound **33**. The benzyl protecting group was then removed *via* hydrogenolysis using 10% palladium on carbon as catalyst, and in the same step the alkynyl group was reduced to an alkyl group affording the phenol **34**.

Because hydroxide is a very poor leaving group, the preparation of sulfonate esters from alcohols or phenols is an effective way of installing a reactive leaving group on an alkyl chain or aryl ring. The reaction is very general, and complications arise only if the resulting sulfonate ester is sufficiently reactive to require special precautions. *p*-Toluenesulfonate (tosylate) and methanesulfonate (mesylate) esters are the most frequently used groups for preparative work, but the very reactive trifluoromethanesulfonates (triflates) are useful especially when a very good leaving group is required[11]. The triflate of the hydroxybiphenyl **34** (*i.e.*, compounds **35**) was prepared by the reaction with trifluoromethanesulfonic anhydride in the presence of pyridine[24]. The method of the palladium-catalysed cross-coupling reaction between the aryl triflate **35** and the boronic acids **16** and **20** are very similar to that used previously

for aryl halides and boronic acids, except for the use of lithium chloride. The need for lithium chloride can be understood by looking to the mechanism of this reaction which has been proposed[12] to be that shown in figure 4.6.

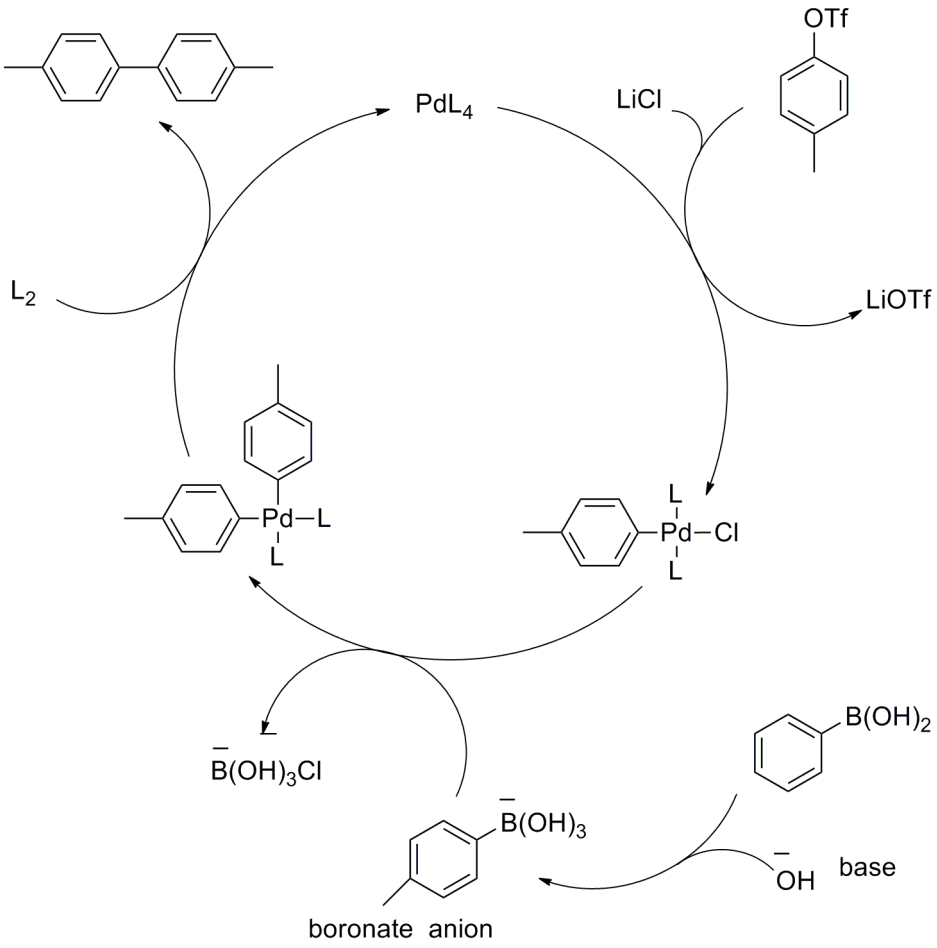


Figure 4.6. Proposed mechanism of the catalytic cycle for the palladium-catalyzed cross-coupling between a phenyl triflate and a boronic acid.

Scheme 8 employs the original strategy to that of route 2 (steps a, b, c, f, g, and h), toward the preparation of compounds **36** and **37**. Unfortunately, this scheme could not progress beyond the boronic acid **32**, because of the failure to synthesize compound **9**.

Scheme 10 was proposed as an alternative pathway (steps d and e in route 2) for preparing 4-benzyloxy-4'- (trimethylsilylethynyl)biphenyl (**33**), and proved to be successful. The new strategy begins with biphenyl compound **21**, the hydroxyl was masked using benzyloxy group, then the resulting compound **39** was converted to the required biphenyl akynyl **33** in two steps, as performed for preparing compound **27** in

scheme 9. The hydrogenation of compound **33** using palladium on charcoal deprotected the hydroxyl group in the same step as the reduction of the triple bond of the terminal alkynyl chain. The resulting compound **34** from the hydrogenation step was the treated with triflic anhydride in the presence of pyridine to give compound **35**, which was then coupled to boronic acids **16** and **20** to give final products **36** and **37** in yields of 30% and 40% after thorough purification.

Final liquid crystal compounds **62** and **63** (scheme 14) were prepared using strategies and methods planned for their silicon analogues **36** and **37** (scheme 8, and steps a, b, c, f, and g of route 2), however, while the strategy of steps a, b, and c was unsuccessful for the silicon family because of the purification difficulties of compound **9** (scheme 2), they were very successful for their carbon family analogues. The successful preparation of compound **53** (scheme 13) and boronic acid **32** (scheme 8) eased the synthesis in this scheme which was started by a cross-coupling reaction between these two compounds to form compound **59**, which was then hydrogenated to remove the benzyl protecting group and reduce the alkynyl unit to a saturated alkyl chain in a single step. The rest of steps are similar to those discussed previously in scheme 10, and yields of 50-70% of compounds **62** and **63** were obtained after thorough purification.

4.2.1.3 Schemes 11 and 12

Schemes 11 and 12 represent the most straight forward pathway employed, and generated the final compounds **44**, **45**, **51**, and **52**. The route employed in both schemes was performed successfully without the need of any alternative pathways. The synthetic strategy in schemes 11 and 12 could be similar to that used in route 1, the basis of the synthesis was the sequential exploitation of the acidic protons of 1,2-difluorobenzene **17** (schemes 5 and 7).

It was mentioned previously that the positions of the lateral fluoro-substituents on the benzene rings of the desired final compounds would dictate the order that the coupling reactions would be attempted, lateral fluoro-substituents in compounds **44**, **45**, **51**, and **52** are *ortho* to bulky terminal chain. The synthetic strategy was then started from compound **26**, a bromo substituent was introduced onto the aromatic ring of 1,2-difluorobenzene from the brominolysis of boronic acid **26** to give 1-bromo-2,3-difluorobenzene (**40**) in good yield. Kuivila and co-workers have studied the kinetics of brominolysis in aqueous acetic acid and found that bases catalyse the reaction[25], this

observation and further kinetic studies of brominolysis of ten arylboronic acids[26] are consistent with a proposed mechanism (Figure 4.7) involving the usual weakening effect of the C-B bond through formation of a boronate anion[23].

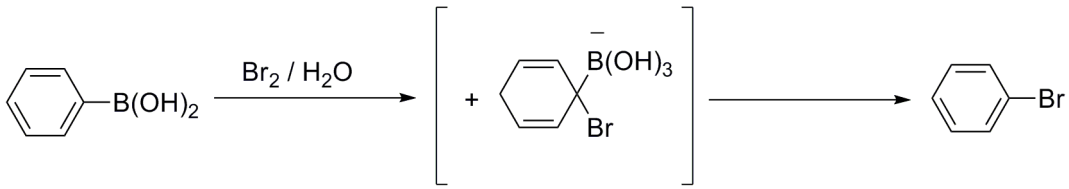


Figure 4.7. Proposed mechanism of brominolysis of arylbornic acids.

Compound **40** was converted to the required phenyl alkynyls **41** (scheme 11) and **48** (scheme 12) in two steps reaction similar to that used for performing similar materials in the previous schemes, and in similar ways the resulting alkynyl unit was hydrogenated to give compounds **42** and **49**. Lithiation of the remaining acidic proton on the substituted ring allowed the conversion of compounds **42** and **49** into corresponding boronic acids **43** and **50**, each boronic acid was then coupled to alkyl / alkoxy biphenyls **22** and **25**, to give the final liquid crystal terphenyls **44**, **45**, **51**, and **52**.

4.2.2 Monofluoroterphenyl Compounds (Scheme 15)

Two monofluoroterphenyl compounds (**70** and **71**) were prepared in this section of the research, they were synthesised for comparison with the difluoroterphenyls previously prepared. Scheme 15 shows the pathway used to synthesise 2'-fluoro-4-octyloxy-4"-(trimethylsilylethyl)terphenyl (**70**), and 2'-fluoro-4-heptyl-4"-(trimethylsilylethyl)terphenyl (**71**). The synthetic strategy applied in this scheme is somewhat similar to that used in scheme 9. Boronic acid **65** was prepared from 1-bromo-3-fluorobenzene (**64**), and a subsequent selective Suzuki coupling gave bromo biphenyl **66**. A further coupling of trimethylsilylethynylzinc chloride (**7**) to biphenyl **66** introduced the bulky end unit. Hydrogenation reduced the triple bond to provide the desired alkyltrimethylsilyl terminal chain (compound **68**).

In the preparation of the boronic acid **69**, lithiation of compound **68** must be selective due to the fact that the difluorobiphenyl **68** has two acidic protons *ortho* to the fluoro substituent. By using a more reactive, sterically hindered lithiating agent, *i.e.*, *sec*-BuLi, the mono-lithium salt was formed at the unhindered acidic proton position. The

procedure of lithiation compound **68** using *sec*-BuLi was similar to that when using *n*-BuLi for preparing a boronic acid, a good yield was collected of the boronic acid **69**. This scheme was completed by two Suzuki coupling reactions between boronic acid **69** and compound **2** in the first reaction and with compound **5** in the second one, the final monoterphenyls **70** and **71** were collected in yields of 75% after thorough purification.

4.2.3 Trifluoroterphenyl Compounds (Scheme 16)

Scheme 16 represents the final series of the achiral systems, the trifluoroterphenyl products were synthesised for comparison with the difluoroterphenyls prepared previously. Trifluoroterphenyl compounds **79**, **80**, **81**, and **82** were synthesised according to this scheme *via* four steps reactions, the availability of the intermediate materials **2**, **5**, **43** and **50** from previous syntheses eased the synthesis by reducing the number of the reactions required for preparing the targeted materials in this scheme. The strategy in scheme 16 was to prepare a biphenyl containing a lateral fluoro substituent, alkyl or alkoxy terminal chain, and good leaving group to undergo another cross-coupling reaction, a third benzene ring containing two lateral fluoro substituents and the appropriate bulky end group *ortho* to fluoro substituents would be attached to the leaving group site of the biphenyl to form the desired trifluoroterphenyls.

Lithiation of compounds **2** and **5** using similar methods as previously described, followed by a Suzuki cross-coupling reaction between the resulting boronic acids **72** and **73**, with the commercially available phenol **74** to give the biphenyls **75** and **76**. The advantages of 4-bromo-2-fluorophenol (**74**) is that having a bromo site *para* to the hydroxyl group, the bromo site can couple to another benzene ring, and the hydroxyl group can be converted to a triflate group to undergo another coupling reaction to a different benzene ring group. The four trifluoroterphenyl compounds (**79**, **80**, **81** and **82**) were collected in yields of 60-80% after the coupling reactions between the triflates *i.e*, compounds **77** and **78**, and each of the boronic acids **43** and **50**.

4.2.4 Chiral Difluoroterphenyl Compounds (Scheme 17)

The synthetic routes of the chiral materials in terms of the core unit are identical to their non-chiral analogues. The introduction of chirality into a liquid crystal system is nearly always performed through a terminal chain[8]. The reaction conditions need to be carefully chosen when preparing a chiral material where the reaction site involves a

chiral centre, there is a chance of complete chirality inversion from one isomer to another or racemisation to give a mixture of the two isomers.

Scheme 17 represents the synthesis of two chiral system compounds, incorporating the chiral (*R*)-(+)-lactamide moiety. Chiral compounds such as (*R*)-(+)-lactamide 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. The (*R*)-1-cyanoethyl 2",3"-difluoro-4"-(2-(trimethylsilyl)terphenyl-4-carboxylate (**95**) and (*R*)-1-cyanoethyl 2",3"-difluoro-4"-(3,3-dimethylbutyl)terphenyl-4-carboxylate (**96**) were prepared in acceptable yields (30 - 36%), compounds **95** and **96** were synthesised to use as chiral dopants in ferroelectric mixtures.

The synthesis in scheme 17 was started from 4-bromobiphenyl which is commercially available. The methyl ketone **83** was synthesised using a Friedel-Crafts acylation, and compound **83** was then oxidised using the haloform reaction to give the carboxylic acid **84**. The following steps of scheme 17 involved protection of the carboxylic end group, coupling to the biphenyl boronic acids **43** and **50**, and hydrolysis to generate the 3 rings carboxylic acids **88** and **89**. Since an acyl chloride is the most reactive of the carboxylic acid derivatives, carboxylic acids **88** and **89** were treated with oxalyl chloride to form the acyl chlorides **90** and **91**. The esters **93** and **94** were then synthesised by the reaction of each acyl chloride with the (*R*)-(+)-lactamide, this reaction occurred rapidly with the help of the pyridine to remove the HCl that forms. The amide groups of compounds **93** and **94** were then dehydrated to give the final chiral nitrile compounds **95** and **96**.

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5 Results and discussions

It has been shown in the aims section that one of the viable ways of generating appropriate ferroelectric liquid crystal mixtures is to use achiral host materials doped with a suitable chiral material to introduce the essential reduced symmetry properties to the mixture. This section of the thesis concerns the mesomorphic studies of novel *ortho*-difluoroterphenyl materials prepared in this work, based on the *ortho*-difluoroterphenyl materials that are well-established as excellent host materials for ferroelectric mixtures[1]. In addition to the many novel *ortho*-difluoroterphenyl systems synthesised, a few analogous novel trifluoroterphenyls and two novel mono fluoroterphenyls have been prepared to show the effect of fluoro substitution on melting points, transition temperatures and mesophase morphologies.

It has been shown in the introduction part that a single lateral fluoro substituent has a detrimental effect on the overall liquid crystal phase stabilities of terphenyl mesogens, particularly smectic phase stabilities. However, the most important implication of lateral fluoro substitution is the effect on the overall mesophase morphology, in particular the generation of tilted smectic phases, such as the smectic C phase[2-5]

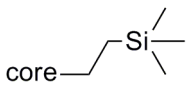
Incorporation of a second lateral fluoro substituent into the terphenyl core, strategically placed adjacent (*ortho*) to the original, produces the 2,3- and 2',3'-difluoroterphenyls[1, 6], which are a vast improvement as ferroelectric host materials over the monofluoro substituted terphenyls, the reasons are that: firstly the second fluoro substituent does not lead to an increase in the molecular breadth since the two fluoro substituents are inherently fixed on one side of the molecule[7], so, the overall liquid crystal phase stabilities are not significantly reduced, as a result liquid crystal phase transition temperatures are upheld. The second reason is that in terms of physical properties, the viscosity tends to be relatively low because of the minimized molecular breadth, and the large lateral dipole generated by the additive combination of the two fluoro substituents which tends to favour the tilted smectic C phase [8].

In the discussions that follow, the effect of replacing one of the terminal chains with a short bulky end unit (*i.e.,* tertiarybutyl group or trimethylsilyl group) on the melting points, transition temperatures and mesophase morphology of the materials will be

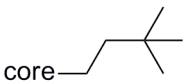
examined. As was mentioned in the aims and objectives section, the bulky terminal chain will be incompatible with the conventional unbranched terminal chain causing phase separation, so several terphernyls with one of the two short bulky end groups were prepared in this work and either octyloxy or heptyl on the other side of the core. The discussions will study the effect of the bulky units on the melting points, transition temperatures, and mesophase morphology of the materials with lateral fluoro substituents in different rings of the core. These discussions will also cover the effect of increasing the number of the fluoro substituents in the core unit of the materials on mesophase morphology.

5.1 Difluoroterphenyl Compounds

A wide range of difluoroterphenyls having two terminal chains and two lateral fluoro substituents have been prepared, these terminal chains include alkyl or alkoxy in one side of the terphenyl core and a short bulky unit (*i.e.*, tertiarybutyl group or trimethylsilyl group) in the other side of the core. The two fluoro substituents are strategically positioned in different positions of the core. Since these materials are intended for use as ferroelectric host materials, or at least additives to ferroelectric mixtures, the difluoroterphenyls were required to have reasonably low melting points and reasonably high smectic C phase stabilities combined with a low viscosity.



trimethylsilyl



tertiarybutyl

A total of twelve novel *ortho*-difluoroterphenyl materials were prepared which enable a comprehensive investigation of initially melting point, mesophase morphology and transition temperatures in comparison with the known analogues with conventional terminal chains. The melting points, transition temperatures and mesophase morphologies of the novel compounds are presented systematically in tables 5.1, 5.2 and 5.3. To gain some appreciation of the significance of their melting points, transition temperatures and mesophase morphology, discussion will involve comparison of the different classes of novel compounds, and also some comparisons will be drawn with known materials of identical core structure[1]. The difluoroterphenyl analogues (compounds **5.1**, **5.2**, **5.3**, **5.4**, **5.5**, and **5.6**) have been chosen as parent systems for the

twelve novel difluoroterphenyls. The structures of the novel difluoroterphenyls are different from their difluoroterphenyls analogues (compounds **5.1**, **5.2**, **5.3**, **5.4**, **5.5**, and **5.6**) in having the short bulky group in one of the terminal chains (*i.e.*, tertiarybutyl group or trimethylsilyl group), when in the parent system, it is a longer unbranched group (*i.e.*, *n*-pentyl group). By comparing the novel difluoro substituted terphenyls (tables 5.1, 5.2, and 5.3) with their difluoroterphenyls analogues (compounds **5.1**, **5.2**, **5.3**, **5.4**, **5.5**, and **5.6**), it is possible to evaluate the effect on transition temperatures and mesophase morphology of the short bulky terminal group occupying the 4- or 4''-positions.

All of the novel compounds exhibit the smectic C phase, but the smectic A phase, and particularly the nematic phase, so prominent in the parent difluoroterphenyls (compounds **5.1**, **5.2**, **5.3**, **5.4**, **5.5**, and **5.6**)[1], do not generally feature, nevertheless, these mesophase headings have been included in all the tables for this very emphasis. This effect of the short bulky end-groups on eliminating the smectic A phase and nematic phase is due, in part, to the bulky end-group, because of its steric hindrance, depresses the mesophase stabilities but it suppresses the nematic and smectic A phases more than the smectic C phase. However, in general previous work, the effect of the branch in a terminal chain is to cause a disruption in the molecular packing which often reduces melting points and reduces the liquid crystal phase stability particularly smectic[9].

As would be expected, the dominance of the smectic C phase results from the molecular phase separation due to the bulky end-groups, as mentioned in the aims and the strong tendency to molecular tilting because of the strong lateral dipole of the *ortho*-difluorophenyl moiety, particularly when an alkoxy terminal chain is also present. The short bulky end group will help the molecules to stand in a small positional order which is required to form the smectic C phase[10].

The two bulky end groups used in this work (*i.e.*, tertiarybutyl group or trimethylsilyl group) are mainly chosen to disrupt the intermolecular forces of attraction. The branch is located very close to the core in order to effect the maximum influence on the molecular properties. By comparing the two bulky end groups used in this work with each other, it can be found that, since carbon (C) is a smaller atom than silicon (Si), less disruption of the intermolecular forces of attraction confers higher melting points and

higher transition temperatures on the 'C' series of compounds (tertiarybutyl terminal chain) when compared with the 'Si' series of compounds (trimethylsilyl terminal chain).

As would be expected, those compounds with a terminal alkoxy chain (**a**) have higher transition temperatures, and usually higher melting points, than analogous compounds with a terminal alkyl chain (**b**)[11]. This trend is due to the oxygen being in conjugation with the aromatic core, which extends the length of the rigid core, and enhances the polarisability anisotropy[9]. Additionally, the alkoxy chain is more linear than the alkyl chain since the bond angle at the ring to oxygen to alkyl chain unit is larger than the angle for the ring to CH_2 to alkyl chain unit.

The following discussions will classify the twelve novel *ortho*-difluoroterphenyl compounds according to the positions of the two fluoro-substituents, and will be allocated to three groups. The first group is that with fluoro substituents in the end ring containing the bulky terminal unit (table 5.1), second one is that with fluoro substituents in the other end ring containing the alkyl-alkoxy chains (table 5.2), and the third group is with fluoro substituents in the middle ring (table 5.3). Each table also contains known 'parent' compounds for comparison.

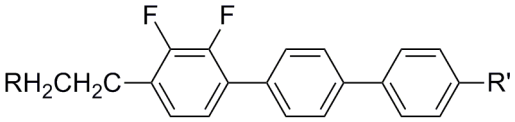
5.1.1 Transition Temperatures (°C) for the 2,3-difluoro-4''-alkoxy and alkylterphenyls (compounds 44, 45, 51, and 52)

Table 5.1 shows the mesomorphism of the four novel *ortho*-difluoroterphenyl compounds with the fluoro substituents in the end ring containing the bulky terminal unit, and known compounds for comparison. The effect of introducing the bulky terminal units into the *ortho*-difluoroterphenyl is seen by comparing each compound with its known analogue (*e.g.*, compound **51** to **5.1**), the analogous *ortho*-difluoroterphenyl compounds are different in containing a smaller unbranched group *i.e.*, *n*-pentyl group. The comparison will also cover the difference in the transition temperatures and melting points between the 'Si' series of the novel compounds and their 'C' series analogues.

Compound **51** (table 5.1) has the highest mesophase stability of the novel compounds, which is in keeping with the parent system (compound **5.1**)[1], and is due to the outer-ring location of the lateral fluoro substituents and the alkoxy chain being part of the untwisted biphenyl section of the terphenyl core. The arrangement of *ortho* fluoro

substituents in an outer-ring allows two important structural features to dominate mesogenicity. Firstly, only one interannular twist occurs and a normal, untwisted, unsubstituted biphenyl region remains. This gives an enhanced polarisability which enhances transition temperatures generally, whilst secondly, the fluoro substituent at the 'outer-edge' position tends to fill space with a polar unit, facilitating the side-to-side intermolecular forces of attraction, and hence upholding the smectic phase stability[5, 8, 12, 13]. Unfortunately the same attributes confer a high melting point (95 °C), particularly high no doubt because of the conformationally stiff short bulky terminal chain.

Table 5.1. The mesomorphism of those compounds with the fluoro substituents in the end ring containing the bulky terminal unit, and known compounds for comparison.



compound			transition temperatures (°C)								
no.	R	R'	Cr		SmC		SmA		N		I
51	Me_3C	**a**	•	95.0	•	156.0	—	—	—	—	•
52	Me_3C	**b**	•	86.0	•	125.0	•	129.6	—	—	•
44	Me_3Si	**a**	•	81.0	•	141.5	—	—	—	—	•
45	Me_3Si	**b**	•	57.5	•	106.1	•	119.5	—	—	•
5.1	C_3H_7	**a**	•	89.0	•	155.5	•	165.0	•	166.0	•
5.2	C_3H_7	**b**	•	65.5	•	118.5	•	135.0	•	137.0	•

a = $C_8H_{17}O$, **b** = C_7H_{15} except where indicated, all alkyl chains are unbranched

The SmC phase stability of compound **51** and its known analogue compound **5.1** is controlled by the relative strengths and positioning of the lateral molecular dipoles[2]. The arrangement of dipole moments in compounds **51** and **5.1** is such that the tilt-inducing, strong lateral dipole from the *ortho* difluorophenyl unit is complemented by ether oxygen at the other end of the molecule to generate an extremely high SmC phase stability (155.5 °C). The presence of an untwisted alkoxy-substituted biphenyl section aids mesomorphic properties by enhancing the longitudinal polarisability of the core and hence, enables a SmA phase to be revealed in compound **5.1**. The bulky tertiarybutyl group as part of the terminal chain in compound **51** has depressed the overall liquid crystallinity when compared with the parent system (compound **5.1**), which is to be expected considering the steric bulk. However, the nematic and smectic A phase stabilities have been reduced to the point of elimination, and the smectic C phase stability (156.0 °C) is virtually identical to that of the parent system (155.5 °C); hence indicating the bulky tertiarybutyl group can be better accommodated with the molecules being tilted than when they are orthogonal within the smectic phase.

As would be expected, the overall smectic tendency and in general, mesophase stabilities of the alkyl analogue (compound **52**) are somewhat reduced in comparison to compound **51**. The lower polarizability of compound **52** compared to compound **51**, confers reduced mesophase stability, and a slightly lower melting point. Figure 5.1 provides a good illustration of the differences between alkyl-alkoxy compounds (*e.g.*, compound **51**), and dialkyl compounds (*e.g.*, compound **52**). The tertiarybutyl-2,3-difluorophenyl section can be said to confer relatively good overall smectic character to both compounds **51** and **52**. However, compound **51** has the alkoxy-unsubstituted biphenyl unit which confers good smectic C character, hence no smectic A phase is exhibited in this material; compound **52** however, has an alkyl- unsubstituted biphenyl unit which is less effective for the tilted smectic C phase, hence despite the good smectic A phase stability of compound **52**, the smectic C phase stability is much reduced. In another words, the lack of an ether oxygen in compound **51** means a lower tendency towards molecular tilting, and the smectic C phase stability is lower (by 31 °C) than for compound **51**, which allows a smectic A phase to be exhibited.

Despite this lower smectic C phase stability compared with compound **51**, the smectic C phase stability of compound **52** is actually 7.5 °C higher than that of the comparable

parent system (compound **5.2**)[1], which emphasizes the remarkable ability of the short bulky terminal chain to maximize the tendency towards molecular tilting. The melting point is 21 °C higher than that of the parent system (compound **5.2**) and this is again because of the conformationally rigid short bulky terminal chain.

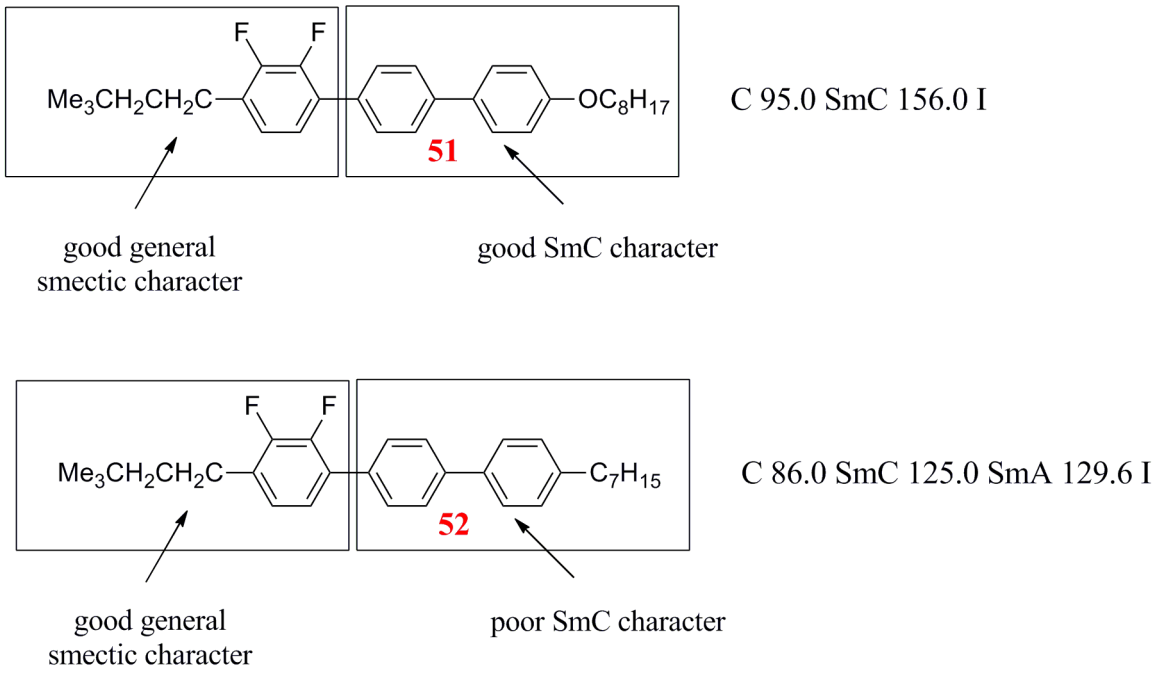


Figure 5.1. The effect of the terminal chains on the relative stabilities of the SmC and SmA phases.

The nematic stability for compound **52** has been reduced to the point of elimination just as for compound **51**, and the smectic A phase stability (129.6 °C) is 5.4 °C lower than that of the parent system (135.0 °C), compound **5.2**. The smectic A phase range is narrow (4.6 °C), which again can be explained by that the bulky tertiarybutyl group can be better accommodated with the molecules being tilted than when they are orthogonal within the smectic phase.

A similar pattern is seen for the trimethylsilyl compounds (**44** and **45**), except of course the larger silicon atom confers lower temperatures throughout. In the alkoxy compound **44**, the larger silicon atom reduces the smectic C phase stability by 14 °C, yet in the

alkyl compounds **45**, it is reduced by 19 °C. However, for the latter compound (**45**) the smectic A phase stability is reduced by just 10 °C.

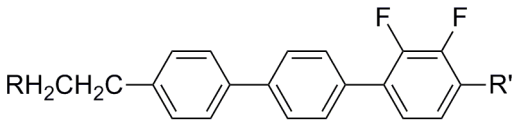
These lower temperatures caused by the larger silicon atom are also translated to the melting points, and the lack of an ether oxygen in compound **45** ensures a significantly lower melting point, yet the smectic C phase stability is still usefully high to make this compound a particularly promising candidate for ferroelectric liquid crystals mixtures. However, it is worth remembering that in formulating mixtures, melting points are depressed significantly and have the melting points of individual compounds can, to a degree, be relatively high. If a chosen chiral dopant is likely to depress the SmC phase stability, then the achiral host mixture must have a high SmC phase stabilities to accommodate the chiral dopant[13, 14].

One issue of importance in materials exhibiting the smectic C phase is the nature of the phase transition on cooling into the smectic C phase. Where a compound generates the smectic C phase on cooling from a smectic A phase, then the phase transition is usually second order. That is when determined by differential scanning calorimetry, there is no actual enthalpy change associated with the phase transition, just a simple entropy change, which is seen as a step in the baseline rather than a true peak. Where a compound generates the smectic C phase on cooling from the isotropic liquid phase or a nematic phase, then the phase transition is first order. That is when determined by differential scanning calorimetry, there is a genuine enthalpy change associated with the phase transition, which is seen as a peak, the area beneath which represents the enthalpy of transition[14].

All the novel compounds presented in this thesis that show a smectic A to smectic C transition on cooling exhibit second order behaviour, which is indicative of a gradual increase in tilt angle on cooling into the smectic C phase, and that the eventual maximum tilt angle is relatively low (around 22°). On the other hand, all the novel compounds that show either an isotropic liquid to smectic C transition or a nematic to smectic C transition on cooling exhibit first order behavior, which is indicative of a sudden generation of a molecular tilt angle, and that tilt angle is relatively large (around 40°).

5.1.2 Transition Temperatures (°C) for The 2,3-Difluoro-4-alkoxy and Alkylterphenyls (Compounds 36, 37, 62, and 63)

Table 5.2. The mesomorphism of those compounds with the fluoro substituents in the end ring containing the linear terminal unit, and known compounds for comparison.



compound			transition temperatures (°C)								
no.	R	R'	Cr		SmC		SmA		N		I
62	Me_3C	**a**	•	81.3	•	131.0	—	—	—	—	•
63	Me_3C	**b**	•	71.0	•	101.0	—	—	—	—	•
36	Me_3Si	**a**	•	78.8	•	118.6	—	—	—	—	•
37	Me_3Si	**b**	•	66.7	•	78.9	—	—	—	—	•
5.3	C_3H_7	**a**	•	93.5	•	144.0	•	148.0	•	159.0	•
5.4	C_3H_7	**b**	•	56.0	•	105.5	•	131.0	•	136.0	•

a = $C_8H_{17}O$, **b** = C_7H_{15} except where indicated, all alkyl chains are unbranched

Table 5.2 shows isomeric materials to those of table 5.1 with the two fluoro substituents in the end ring with the conventional unbranched chain. Compound **62** has the same mesophase morphology as the isomeric compound (**51**), but the smectic C phase stability is 25 °C lower. The very strong lateral dipole at one end of the molecule (compound **62**), afforded by the ether oxygen acting mesomerically with the *ortho* fluoro substituent,

induces tilt and ensures a high SmC phase stability, yet the overall mesomorphic properties are reduced due to lower polarisability of the untwisted biphenyl section of the terphenyl core (figure 5.2). The overall effect of this structural combination is to lower the smectic phase stability to the extent that SmC phase is generated with a lower phase stability (131.0 °C) than that of compound **51** (156.0 °C). For the same reason, the melting point of compound **62** (81.3 °C) is significantly lower than that of compound **51** (95.0 °C).

As discussed earlier, the reduced lateral dipole of the dialkyl materials in comparison to that of the alkyl-alkoxy materials means that, at higher temperatures, the tilting tendency is overcome by strong side-to-side lameller attractions resulting in the generation of the orthogonal SmA phase in these materials. However, comparing the dialkyl compound (**63**) to its alkyl-alkoxy analogue compound (**62**), the smectic A phase stability has been reduced by more than the smectic C phase stability, causing it to be eliminated, which again emphasizes the strong tendency of the short bulky terminal group to support the smectic C phase.

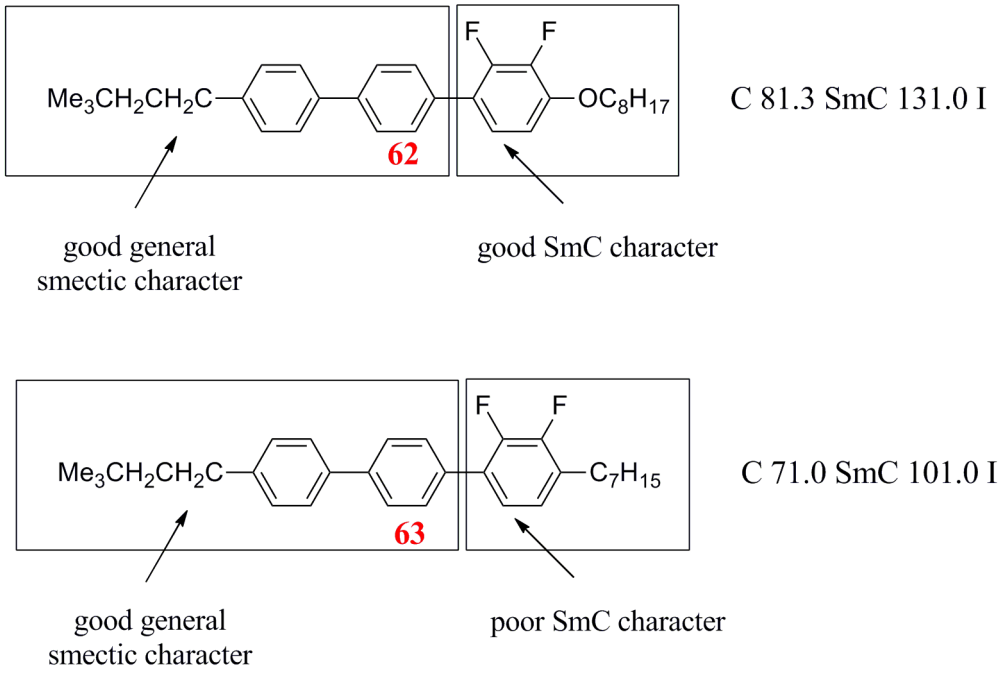


Figure 5.2. The effect of the terminal chains on the relative stabilities of the SmC.

Unlike the isomeric compounds (**51** and **52**) shown in table 5.1 where the bulky tertiarybutyl group conferred a higher smectic C phase stability in comparison to the

parent systems (**5.1** and **5.2**), in compounds **62** and **63**, it is slightly lower than seen in the parent systems (**5.3** and **5.4**)[1], which is due to the more disadvantageous structural feature of an alkyl chain as part of the untwisted biphenyl section of the terphenyl core (see figure 5.2).

By comparing the novel trimethylsilyl compounds (**36** and **37**) in table 5.2 with their tertiarybutyl analogues (compounds **62** and **63**); it is possible to evaluate the effect on melting points, transition temperatures and mesophase morphology of the larger size of silicon in comparison with carbon. Just as seen for the isomeric compounds in table 5.1, the trimethylsilyl compounds (**36** and **37**) in table 5.2 have lower transition temperatures than the tertiarybutyl analogues (compounds **62** and **63**), because of the larger size of silicon in comparison with carbon. Compound **36** with trimethylsilyl terminal group has a lower melting point and a much lower clearing point than compound **62** with a tertiarybutyl terminal group (2.5 and 12.4 °C respectively), figure 5.3 shows the focal conic fan texture and Schlieren texture of the smectic C liquid crystal phase of compound **36**. The melting point of compound **37** has been reduced by around 4.3 °C, compared to the tertiarybutyl analogue (compound **63**), but the smectic phase stability has been much more affected and is 21 °C lower than its tertiarybutyl analogue.

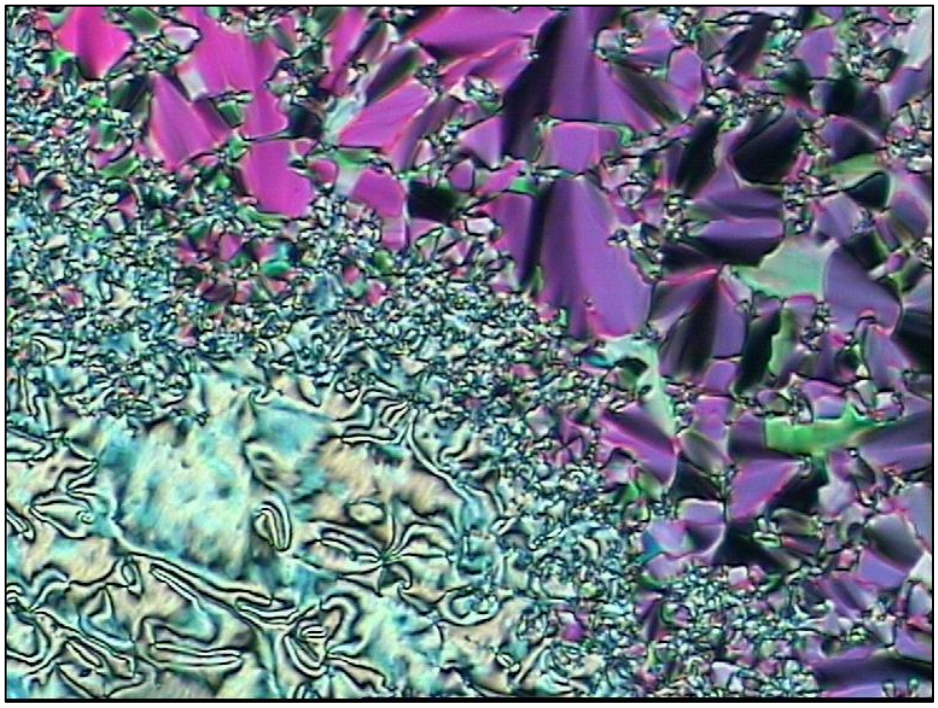
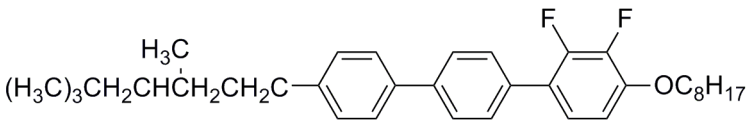


Figure 5.3. The focal conic fan texture and Schlieren texture of the smectic C liquid crystal phase of compound **36**, 112.1 °C

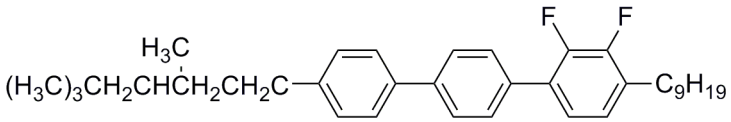
The comparison of compounds **36** and **37** with their isomeric compounds (**44** and **45**) in table 5.1 again shows reduced smectic C stabilities, the smectic phase stabilities of compounds **36** and **37** are reduced by 22.9 °C and 27.2 °C respectively. This reduction in the smectic phase stability is again as a result of the lower polarisability of the untwisted biphenyl section of the terphenyl core. For the same reason, the melting points of compound **36** (78.8 °C) is lower than that of compound **44** (81 °C), but the melting point of compound **37** (66.7 °C) surprisingly is higher than that of compound **45** (57.5 °C).

The effects of increasing the size of the terminal group is seen by comparing compounds **62** and **63** (table 5.2) with compounds **5.5** and **5.6**[15], which were synthesised by Guirec Cosquer[15], as a part of his study about the effect of the bulky end groups on the melting point and mesophase morphology. The terminal chain in compound **5.5** is longer than that in compound **62** with six atoms along the chain and a methyl branching at the 2-poistion in the chain, whereas compound **62** has four atoms along the chain. For compounds **63** and **5.6**, beside the longer bulkier terminal group in compound **5.6** compared to compound **63**, compound **5.6** has a longer alkyl chain in the other side of the terphenyls.



C 55.4 SmC 104.5 I

5.5



C 53.7 SmC 62.7 I

5.6

As discussed previously, the effect of the branch in a terminal chain is to cause a disruption in the molecular packing which reduces liquid crystal phase stability and melting points[9]. Hence, as would be expected, the overall smectic phase stabilities of the bulkier terminal group compounds **5.5** and **5.6** (104.5 and 62.7 °C respectively) is reduced in comparison to less bulkier compounds **62** and **63** (131.0 and 101.0 °C

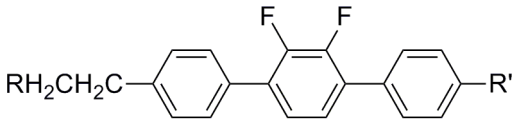
respectively). However, the melting points and the clearing points for compounds **5.5** and **5.6** are lower compared to less bulkier compounds **62** and **63**, which suggest that the greater the steric volume the lower the melting and clearing point.

5.1.3 Transition Temperatures (°C) for the 2',3'-difluoro-4-alkoxy and alkylterphenyls (compounds 30, 31, 57, and 58)

Table 5.3 shows isomeric materials to those shown in tables 5.1 and 5.2, here with the two fluoro substituents in the centre ring. These novel compounds in table 5.3 with the lateral fluoro substituents in the 'inner-core' location have a completely different mesomorphism and transition temperatures to the comparable compounds with the lateral fluoro substituents in the 'outer-edge' position. The compounds with fluoro substituent at the 'outer-edge' position have higher smectic phase stability, and less tendency toward nematic phase, than compounds with the fluorines in the centre ring.

It has already been shown in the introduction section that compounds with the fluoro substituent at the 'outer-edge' position (*i.e.*, compounds in tables 5.1 and 5.2) twist about one interannular bond and a normal biphenyl region remains, however, lateral fluoro substituents in the centre ring (*i.e.*, compounds in table 5.3) cause two interannular twistings, which effectively gives separate, non- coplanar, phenyl units which reduces polarizability, and hence liquid crystal phase stability is reduced, particularly smectic phase stability[7, 12, 16]. However, even with two interannular twisting, the strong, centrally located dipole is more conducive towards the tilted SmC phase. Hence, any imbalance in the molecular structure, such as that created by the use of two unequal terminal chains, promotes the generation of a smectic C phase.

Table 5.3. The mesomorphism of those compounds with the fluoro substituents in the centre ring, and known compounds for comparison.



compound			transition temperatures (°C)								
no.	R	R'	Cr		SmC		SmA		N		I
57	Me_3C	**a**	•	89.0	•	106.9	—	—	•	114.4	•
58	Me_3C	**b**	•	60.0	•	76.0	—	—	•	77.7	•
30	Me_3Si	**a**	•	56.1	•	101.9	—	—	—	—	•
31	Me_3Si	**b**	•	58.9	•	61.7	—	—	—	—	•
5.7	C_3H_7	**a**	•	48.5	•	95.0	—	—	•	141.5	•
5.8	C_3H_7	**b**	•	36.5	•	(24.0)	—	—	•	111.5	•

a = $C_8H_{17}O$, **b** = C_7H_{15} except where indicated, all alkyl chains are unbranched

Additionally, the increase in breadth being in the centre of the molecule tends to disrupt smectic phase stability by significantly more than nematic phase stability. The same reasoning also tends to confer low melting points for compounds with this location of lateral fluoro-substituents. This general tendency can be seen clearly by comparing the parent compounds **5.7** and **5.8** (table 5.3) with their isomeric analogues (**5.1**, **5.2**, **5.3** and **5.4**) with fluoro substituents in an outer-ring (tables 5.1 and 5.2)[1].

It is amazing to see the melting points, mesophase morphology and transition temperature of the novel compounds (**57**, **58**, **30**, **31**) shown in table 5.3, particularly the

latter two compounds (**30** and **31**) that contain the more bulky trimethylsilyl group at the terminus. Compound **57** melts at 89.0 °C which is 40 °C higher than the comparable parent system (compound **5.7**)[1], which is rather unfortunate. However, the smectic C phase stability is remarkably high, 12 °C higher than that of the parent system with the unbranched terminal chains (compound **5.7**)[1], but the nematic phase stability is 27 °C lower. Figure 5.3 shows the Schlieren texture of the nematic liquid crystal phase of compound **57**. This class of compound with a core that is least supportive towards liquid crystal phase stability, and particularly unsupportive towards the smectic C phase, actually gains most from a bulky terminal chain.

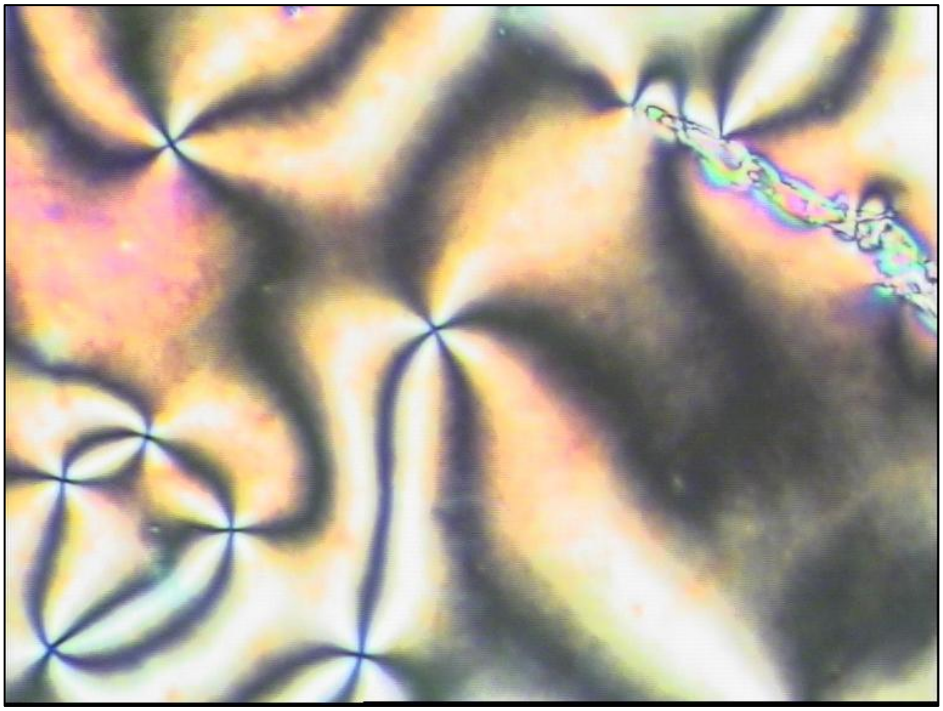


Figure 5.4. The Schlieren texture of the nematic liquid crystal phase of compound **57**, 114.0 °C.

As discussed previously, lateral fluoro substitution has a detrimental effect on liquid crystal phase stabilities, particularly smectic phase stabilities. However, it is the relative positioning of the lateral fluoro substituents on the molecular core that is of fundamental importance to mesomorphic behaviour;[1, 5, 7] inclusion of lateral fluoro substituents in inner-core positions has a more drastic effect on mesophase thermal stabilities due to the resultant interannular twisting of the core than fluorination on the outer-edge of the core.

Comparing the inner-core fluoro-substitueted compound **57** to its outer-edge analogues (compounds **51** and **62**) shows the effect of having the fluoro substituents in the inner-core rather than outer-edge, compound **57** has a lower smectic C stability (106.9 °C) compared to compound **51** (156.0 °C) and compound **62** (131.0 °C). The reduced smectic C stability of compound **57** allows the nematic phase to be generated to high temperature (114.4 °C). This effect of lateral fluoro substituents in inner-core and outer-core positions on the smectic C phase stability is illustrated in figure 5.5 for compounds **51**, **57**, and **62**.

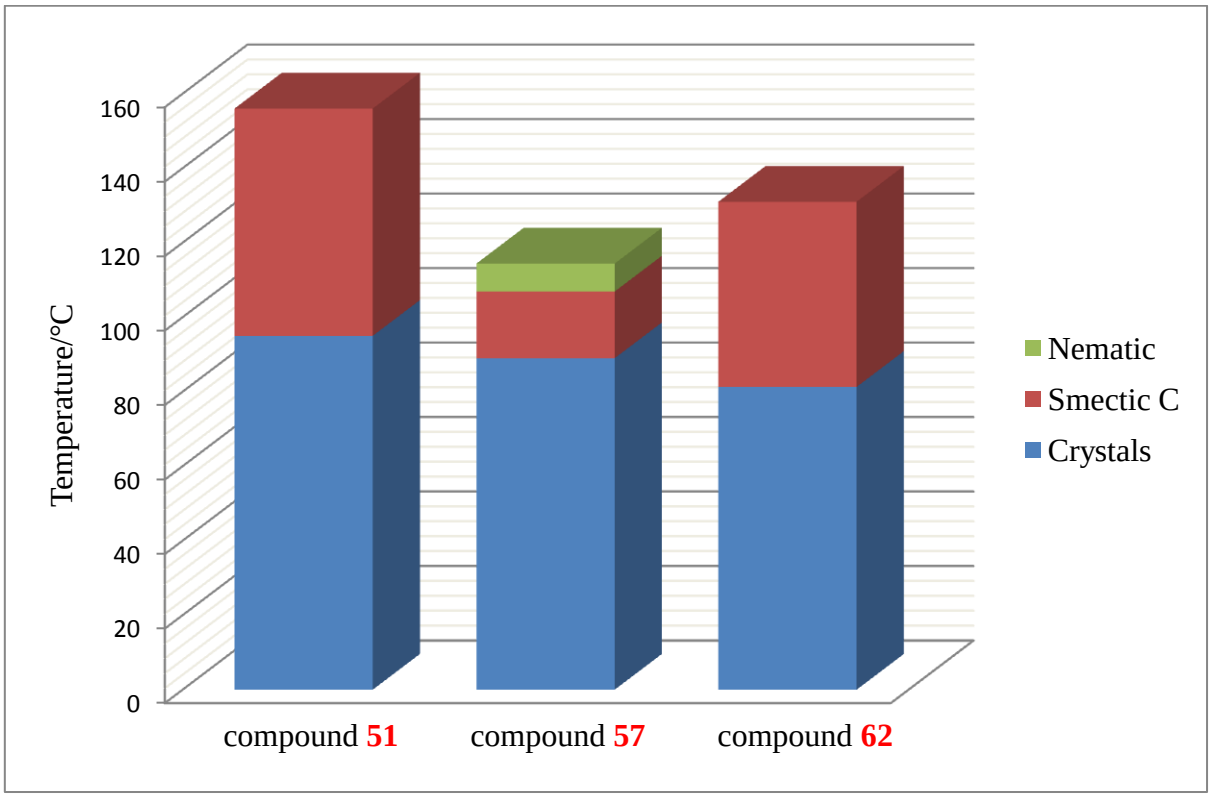


Figure 5.5. Effect on transition temperatures of relative positioning of the lateral fluoro substituents on the molecular core (*e.g.*, compounds **51**, **57**, and **62**)

For the dialkyl analogue (compound **58**), the disruption to the nematic phase stability is 34 °C. More significantly, the smectic C phase stability has increased by a massive 52 °C in comparison to the parent system with the unbranched chains (compound **5.8**)[1], which is mostly nematogenic in nature with a monotropic smectic C. The lack of smectic mesophases from this class of dialkyl material (*e.g.*, compound **5.8**) is expected because of a combination of both the overall reduced polarisability of the compounds due to the use two terminal alkyl chains, the presence of two interannular twists and the

lack of an outer-edge fluoro substituent which tends to promote smectic character. However, the introduction of a tertiarybutyl group does enhance molecular tilting which results in the generation of the smectic C phase over a range 16.0 °C. This is again showing how the bulky terminal chains affect this class of compound with a core that is least supportive towards smectic C phase stability.

The trimethylsilyl compounds **30** and **31** have lower smectic C phase stabilities (101.9 and 61.7 °C respectively) than their isomeric analogues, compounds **36**, **37**, **44**, and **45** (118.6, 78.9, 141.5, and 106.1 °C respectively), again due to the two interannular twistings. Interestingly, the larger trimethylsilyl unit, whilst not enhancing the smectic C phase stability certainly does not cause much of a further reduction that was seen for the other two classes of compound shown in tables 5.1 and 5.2.

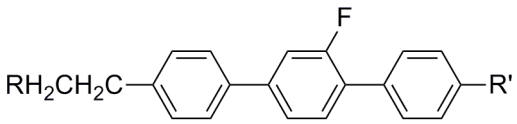
It is very surprising that the alkoxy compound **30** has a slightly lower melting point (56.1 °C) than its alkyl analogue compound **31** (58.9 °C). This reduction of the melting point is different from the trends which were seen before for isomeric analogous in tables 5.1 and 5.3, which show that the alkoxy compounds have higher melting points than their alkyl compounds. However, melting points are notoriously difficult to predict[12].

The greatest effect of the short bulky trimethylsilyl end group on melting points, transition temperatures and mesophase morphology can be seen clearly by comparing the novel compounds (**30** and **31**) with their parent systems (compounds **5.7** and **5.8**). Both parent system compounds show lower smectic C phase stabilities (95.0 ° C for compound **5.7** and a monotropic smectic C at 24.0 °C for compound **5.8**), compared to the two novel compounds **30** and **31** (101.9 and 61.7 °C respectively). Surprisingly, the nematic phase is not exhibited by compounds **30** and **31**, whilst, their parent system (compounds **5.7** and **5.8**) have high nematic phase tendency with clearing points of 141.5 and 111.5 °C respectively. The presence of the trimethylsilyl group eliminates the nematic phase showing a much greater support for the smectic C phase stability in comparison to the nematic phase stability, a completely anomalous situation to that seem for the parent systems (compounds **5.7** and **5.8**)[1].

5.2 Monofluoroterphenyl Compounds

Two novel monofluoroterphenyl compounds with the fluoro substituent in the centre ring were prepared for mesomorphic evaluation (compounds **70** and **71** table 5.4). Compounds **70** and **71**, have lower melting points (62.7 and 64.5 °C respectively) than their diflouro analogues compounds **30** and **31** in table 5.3 (56.1 and 58.9 °C respectively), due to the overall reduced polarity of the molecule afforded by the absence of the second fluoro substituent. Compound **70** melts at a slightly lower temperature than its alkyl analogue compound **71**, which is unusual, however, this is similar situation to their difluoro analogues compound **30** and **31**.

Table 5.4. The mesomorphism of the novel monofluoroterphenyl compounds with the fluoro substituents in the centre ring



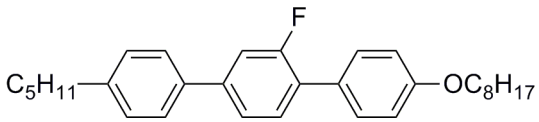
compound			transition temperatures (°C)								
no.	R	R'	Cr		SmC		SmA		N		I
70	Me_3Si	**a**	•	62.7	•	110.5	—	—	—	—	•
71	Me_3Si	**b**	•	64.5	•	77.5	—	—	—	—	•

a = $C_8H_{17}O$, **b** = C_7H_{15} except where indicated, all alkyl chains are unbranched

From table 5.4, it can be seen that the novel monofluoroterphenyl compounds **70** and **71** have a higher melting points, a greater mesophase stability and overall smectic character than the difluoro-substituted analogues compounds **30** and **31**. This is due to the fact that the interannular twisting of the core is caused by just one fluoro substituent in the centre ring, whilst, the *ortho* difluoro substituents in the centre ring cause increased

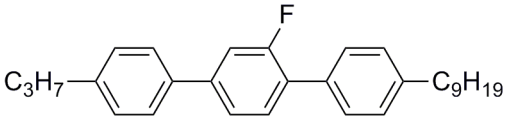
twisting about both interannular bonds which further disrupts the longitudinal polarisability of the mesogenic core giving effectively separate phenyl units.

Compound **5.9**, prepared by Chan and co-workers[3, 8], has a very similar structure to the novel compound **70**, which differs only in that the novel compound has the short bulky trimethylsilyl end group instead of the unbranched pentyl end group, however, as can be seen, they exhibit significantly different mesomorphic behaviour. Inclusion of the bulky group in compound **70** has resulted in a higher melting point (62.7 °C) compared to 47.0 °C for the parent system compound **5.9**, the underlying ordered smectic phases (SmI and SmA) being eliminated and the full extent of the smectic phase stability is exhibited as the tilted smectic C, but with a lower stability (110.5 °C) compared to the parent system compound **5.9** (116.5 °C). Additionally, the nematic phase is not exhibited by compound **70** and the clearing point of the novel compound (110.5 °C) is reduced, compared to compound **5.9** (155.0 °C). The interannular twisting in compound **5.9** is at a point which leaves a relatively untwisted biphenyl section that has a simple unbranched alkyl chain, whereas compound **70** has the situation that has a relatively untwisted biphenyl section with the short bulky trimethylsilyl, which confers a greater effect on the melting point and on the clearing point and acts to hinder the packing and molecular association of the molecules. This observation suggests that the bulky end group, because of its steric hindrance, depresses the mesophase stabilities but it suppresses the nematic and smectic A phases more than the smectic C phase.



C 47.0 (J 40.0) Smi 53.5 SmC 116.5 SmA 130.0 N 155.0 I

5.9



C 46.0 (SmB 35.0) SmC 52.2 SmA 89.0 N 126.5 I

5.10

Interestingly, compound **5.10**[3], having a longer alkyl terminal chain (C_9), has a smectic C phase stability of 52.2 °C whereas, compound **71**, despite a shorter alkyl terminal

chain (C_7), has a much higher smectic C phase stability (77.5 °C). Compound **5.10** exhibits three smectic phases and a wide temperature range nematic phase (37.5 °C), whilst, using a bulky group as a terminal chain in compound **71** has resulted in all the underlying ordered smectic phase B and the smectic phase A being eliminated and hence, the full extent of the smectic phase is exhibited as the tilted smectic C. Additionally, the nematic phase is not exhibited in compound **71** and the clearing point of the novel compound (77.5 °C) is reduced, compared to compound **5.10** (126.5 °C). This observation suggests again, that the bulky end group depresses the mesophase stabilities but it suppresses the nematic and smectic A phases more than the smectic C phase.

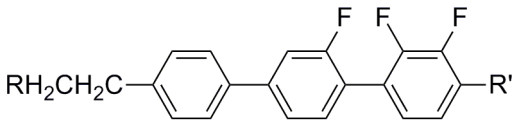
5.3 Trifluoroterphenyl Compounds

As mentioned before in the aims section, the trifluoroterphenyl compounds are known to generate low melting points, which is an aim for the novel materials with bulky terminal units and since such short units might be expected to give relatively high melting points, then four novel trifluoroterphenyl compounds were prepared for this mesomorphic evaluation (compounds **79**, **80**, **81**, and **82**, table 5.5). The third fluoro substituent is expected to add to, or usefully reinforce the lateral dipole generated by the two *ortho* fluoro substituents, whilst preferably still generating the smectic C phase. In particular, the third fluoro substituent has been located as close as possible to the existing fluoro substituents, across the bay region, to generate the 2,2',3-trifluoroterphenyls. This structural architecture was concentrated on because, although both steric and polar effects would suggest that the fluoro substituent in the 2'-position (*i.e.*, the bay region) would prefer to be as far apart as possible, therefore broadening the molecules. Hence, the molecular breadth of the 2,2',3-trifluoroterphenyls should be minimised since all three lateral fluoro substituents are held effectively on one side of the molecule, whilst the dipole of 2'-fluoro substituent should be mainly additive giving an enhanced lateral dipole to the molecule.

In comparison, the novel trifluoroterphenyls (compounds **81**, **82**, **79**, and, **80** table 5.5) than their parent system compounds **5.11** and **5.12** show higher smectic C phase stabilities and higher melting point. The alkoxy parent system (compound **5.11**) has a lower melting point compared to the novel compounds **81** and **79**, with a narrow smectic C phase temperature range (2.9 °C) and a wide nematic phase temperature range (60.1 ° C). The alkyl parent system (compound **5.12**) has a lower melting point compared to the novel compounds **82** and **80**, and is mostly nematogenic in character with a monotropic smectic C phase. The short bulky terminal chain in the novel compounds (**81**, **82**, **79**, and **80**) massively increases the smectic C phase stabilities, when compared with the parent system (compound **5.11** and **5.12**). However, unlike the parent system (compounds **5.11** and **5.12**), a narrow smectic A phase temperature range was exhibited in the novel compounds (**81**, **82**, and **79**), but the nematic phase has been reduced to the point of elimination. Compound **80** has the lowest melting point (45.8 °C) of the novel compounds, and exhibits just a smectic C phase, however, comparing compound **80** with the parent system (compound **5.12**), gives a situation where going from a short

unbranched propyl end group to a short trimethylsilyl end group as part of the unfluorinated ring, changes the material from nematogenic to smectogenic.

Table 5.5. The mesomorphism of trifluoro-substituted terphenyls, and known compounds[12, 16] for comparison.



compound			transition temperatures (°C)								
no.	R	R'	Cr		SmC		SmA		N		I
81	Me_3C	**a**	•	98.5	•	110.1	•	113.6	—	—	•
82	Me_3C	**b**	•	56.0	•	67.3	•	75.3	—	—	•
79	Me_3Si	**a**	•	74.1	•	100.3	•	104.7	—	—	•
80	Me_3Si	**b**	•	45.8	•	71.6	—	—	—	—	•
5.11	C_3H_7	**a**	•	47.3	•	50.2	—	—	•	110.3	•
5.12	C_3H_7	**b**	•	22.7	•	(8.2)	—	—	•	75.5	•

a = $C_8H_{17}O$, **b** = C_7H_{15} except where indicated, all alkyl chains are unbranched

By comparing the trifluoro substituted terphenyls (compound **81**, **82**, **79**, and, **80** table 5.5) with their 2,3-difluoro substituted analogues (compounds **62**, **63**, **36**, and **37**, table 5.2), it is possible to evaluate the effect on transition temperatures and mesophase morphology of a third fluoro substituent occupying the 2'-position in the presence of the short bulky end group at 4'-position. As would be expected, incorporation of the third

fluoro substituent in the 2'-position has reduced transition temperatures considerably. In general, the smectic C phase stabilities have been reduced by between 7 and 34 °C, which is a common result of lateral fluoro substitution within the core due to a disruption in lamellar packing of the constituent molecules. However, the lower smectic C stabilities allow narrow smectic A phase to be generated (compounds **81**, **82**, and **79** have SmA ranges of 3.5, 8.0, and 4.4 °C), figure 5.6 shows a typical focal-conic fan texure of the smectic A liquid crystal phase of compound **79**.

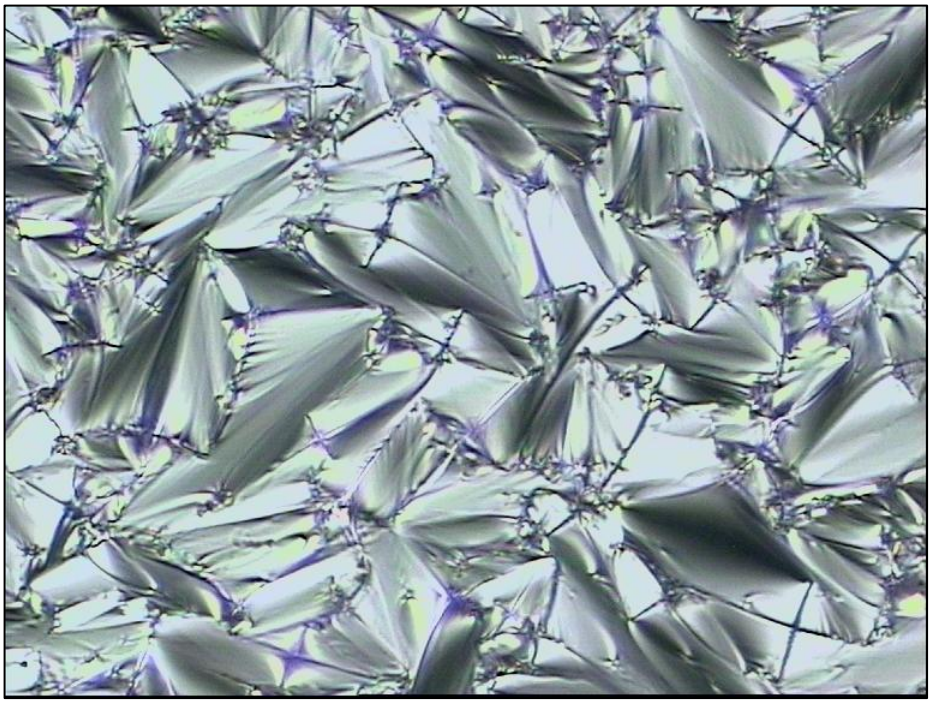


Figure 5.6. The focal-conic fan texure of the smectic A phase of compound **79**, 103.2 °C.

The detrimental effect of a third fluoro substituent in the 2'-position on the smectic phase stability is somewhat greater than might be anticipated. This is due, in part, to the 2'-fluoro substituent, which due to steric repulsion/crowding, causes an increased interannular twisting of the core. This not only results in a 'net-broaden' of the core but also a further reduction in the molecular polarisability. The increase in molecular breadth leads to a reduction in lamellar attractions between constituent molecules which consequently results in a reduction of the smectic phase stability.

Perhaps the most significant aspect of the trifluoroterphenyls is their lower melting points in comparison with the difluoroterphenyl analogues, apart from compound **81**, all the trifluoroterphenyls in table 5.5, including the parent systems, have lower melting

points compared to their difluoroterphenyl analogues in table 5.2. Given the high polarity of these materials (three fluoro substituents), there were a valid expectation, and a major worry, that the melting points would be at least as high as for the difluoroterphenyls, clearly if this was the case then most of the trifluoroterphenyl materials would be just nematogenic or even non-mesogenic. However, the third lateral fluoro substituent in the 2'-position reduces the packing capability of the molecules in the crystal state which, despite the overall increase in polarity of the molecules, leads to a considerable reduction in melting points.

It is interesting to look at the effect of introducing two further *ortho* fluoro substituents into monofluoroterphenyls, compounds **70** and **71** (table 5.4), by comparing them with the trifluoroterphenyls materials, compound **79** and **80** respectively. In such comparisons, the simultaneous effects of outer-edge and inner-core fluoro substituents are well illustrated. The most obvious effect of incorporating two *ortho* fluoro substituents into the terphenyl core is the reduced smectic C phase stability.

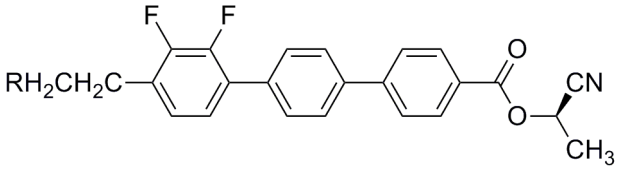
Compound **70** shows strong smectic C tendency relative to the tilting power of molecule, however, the introduction of the two *ortho* fluoro substituents (*i.e.*, compound **79**) decreases the smectic C phase stability, allowing the smectic A phase to be generated for a temperature range of 2.9 °C. The smectic C phase stability for the trifluoroterphenyl compound **80** is just 1 °C lower than that of its monofluoroterphenyl analogue compound **71**.

Obviously, a compromise situation in the 2,2',3-trifluoroterphenyl materials (*e.g.*, compounds **79** and **80**) appears to be occurring, the additional inner-core fluoro substituent in the 2'-position is tending to eliminate smectic phases by enhancing the interannular twisting of the core which results in a net-broadening of the molecule, whilst the outer-edge fluoro substituent is upholding the smectic phase stability by filling space. Thus a compromise or balance is reached between the steric effect of the fluoro substituent in the inner-core 2'-position which reduces smectic tendency, and the smectic enhancing outer-edge fluoro substituent in the 3-position.

5.4 Chiral Difluoroterphenyl Compounds

As was mentioned in the introduction section, chiral matched dopants are needed for addition to a host mixture for the formulation of FLC mixtures. In order to obtain good solubility and compatibility between the dopant and the host mixture, the chiral dopant should be matched or at least similar in structure to the ferroelectric host materials. This should not only eliminate solubility problems but should help maintain the properties of the host mixture.

Table 5.6. The mesomorphism of chiral *ortho* difluoroterphenyls and known compound for comparison.



compound		transition temperatures (°C)
No.	R	
95	Me_3C	C 170.0 I (recrystallized at 138.0)
96	Me_3Si	C 132.5 I (recrystallized at 125.6)
5.13	C_3H_7	C 103.2 (SmC* 102.8) SmA* 164.9 I

Two chiral compounds were prepared in this work (table 5.6), both containing bulky terminal units, tertiarybutyl (compound **95**) and the other containing trimethylsilyl (compound **96**). Both compounds possess a central terphenyl core and incorporate one chiral centre in the terminal carboxyl chain. In each compound, the chiral centres were introduced using commercially available (*R*)-(+)-lactamide for initial synthetic simplicity and their consistently high enantiomeric excess, however, the resulting 1-

amino-1-oxopropan-2-yl group was then dehydrated to form the desired (*R*)-1-cyanoethyl group.

As can be seen from Table 5.6, compounds **95** and **96** do not exhibit any mesomorphic behaviour since they possess a branched terminal group in one side of the terphenyl core, and a short bulky end group in the other terminal chain of the core. The steric effect of the chiral moiety and bulky terminal chain limits the capacity of the molecules to pack efficiently into any smectic or nematic structural arrangement. Both compounds have very high melting points, the trimethylsilyl compound (**96**) has a lower melting point because of the larger silicon. The difference in the melting points is being due to differences in the ability of the molecules to pack in the crystal state. The lack of any liquid crystal phases however, does not pose a problem since a chiral dopant need not necessarily be mesogenic as the chiral structure can still induce chirality into the achiral liquid crystal host mixture.

Compound **5.13**[17], which was chosen as a parent system of novel chiral *ortho* difluoroterphenyls (compounds **95** and **96**), differs only in having the unbranched pentyl end group instead of the bulky terminal chains in the novel materials. Compound **5.13** has a lower melting point (103.2 °C) compared to compounds **95** and **96**, and is a purely smectogenic material, exhibiting a monotropic SmC* phase and a SmA* phase to high temperature (164.9 °C). The bulky tertiarybutyl and trimethylsilyl end groups have rendered compounds **95** and **96** as non-mesogenic. This is again support the previous observation about the bulky end group depressing the mesophase stabilities.

5.5 Summary

A wide range of novel terphenyl materials with a bulky terminal chain (tertiarybutyl and trimethylsilyl) have been prepared which incorporate one, two, or three lateral fluoro substituents in various positions within the terphenyl core. From the results obtained, the following observation can be made:

- The smectic phase stability (particularly smectic C) is upheld by more than the nematic phase stability, and in most cases the smectic C phase stability is actually higher than comparable analogues with conventional unbranched terminal chains.
- The surprisingly high smectic C phase stability results from a phase separation effect due to the incompatibility of the spherical bulky group and the conventional unbranched terminal chain.
- The bulky end group suppresses the nematic phase.
- In general, the alkyl-alkoxy materials exhibit higher melting points and mesophase transition temperatures than the dialkyl systems.
- Since carbon (C) is a smaller atom than silicon (Si), less disruption of the intermolecular forces of attraction confers higher melting points and higher transition temperatures on the 'C' series of compounds (tertiarybutyl terminal chain) when compared with the 'Si' series of compounds (trimethylsilyl terminal chain).
- Introduction of the third fluoro substituent in an inner-core position generates materials with considerably reduced smectic phase stability.

5.6 References

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6 Conclusions

6.1 Achiral Compounds

A number of achiral compounds based on *ortho*-difluoroterphenyl mesogenic cores with a terminal chain at one end of the terphenyl core containing a bulky end group (tertiarybutyl or trimethylsilyl), and with atypical unbranched alkoxy or alkyl chain (octyloxy or heptyl) at the other end of the terphenyl, were synthesised to study how the unusual terminal groups influence the mesomorphology of the compounds. The investigation of all three possible *ortho*-difluoroterphenyl cores have provided for a total of 12 novel liquid crystals, and enabled a comprehensive investigation of initially melting point, mesophase morphology and transition temperatures in comparison with the known analogues with conventional terminal chains. Two mono- and four tri-fluoro systems were synthesised in order to investigate The effect on the mesomorphic behaviour of varying the degree of fluoro-substituents upon the multi-ring system[1].

The inclusion the bulky end groups in the terminal chain of the terphenyl core was found to depress the nematic phase and smectic A phase to the greatest extent but the stability of the smectic C phase was upheld, and in most cases the smectic C phase stability is actually higher than comparable analogues with conventional unbranched terminal chains. Most of the novel compounds only displayed the smectic C phase, therefore, bulky end groups can be used to favour the formation of the smectic C phase by a mesogenic core.

In agreement with the literature[2, 3], the alkyl-alkoxy compounds generally have higher melting points and higher phase transition temperatures than the dialkyl systems. Gray *et al*.[2] found that compounds with two fluorines in the end rings rather than in the centre ring have higher melting points and higher phase transition temperatures, with greater smectic tendencies, and also, compounds with two fluorines in the centre ring tend to be more nematic in character. However, in this work, similar results were observed about the novel compounds with two fluorins in the end rings, but, novel compounds with two fluorines in the centre ring tend to be more smectic in character.

6.2 Chiral Compounds

In addition to achiral systems synthesised in this work, two novel chiral *ortho* difluoro terphenyls were synthesised. Both chiral compounds (**95** and **96**) have very high melting points, and do not exhibit any mesomorphic behaviour. The bulky tertiarybutyl and trimethylsilyl end groups as part of the terminal chains have increased the melting points of both compounds to very high temperatures (170.0 and 132.5 °C), and hence, the two novel chiral compounds do not show any mesomorphic behaviour until they melt to isotropic liquid, however, chiral dopant need not necessarily be mesogenic as the chiral structure can still induce chirality into the achiral liquid crystal host mixture. The two novel chiral compounds were prepared, with similarity in structure to the achiral systems, to be used as chiral matched dopants for addition to a host mixture for the formulation of FLC mixtures, however, mixture studies were not carried out in this thesis, and could be part of a future PhD thesis.

6.3 References

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