Connective-Pummerer Cyclisations and SmI_2-Mediated Cascade Reactions for the Synthesis of Nitrogen-Containing Heteroacenes

A thesis submitted to The University of Manchester for the degree of Doctor of Philosophy

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Abstract

This thesis describes work towards a range of novel nitrogen containing polyaromatic heterocycles for use as organic semiconductors. A route to benzo[*b*]carbazole end-capped oligothiophenes has been developed; relying on two key steps; namely a connective-Pummerer cyclisation and a SmI_2-mediated cleavage–cyclisation cascade. A route to extended dibenzoindolo[3,2-*b*]carbazole-based aza-heptacenes has also been developed, by employing the same key steps in a two-directional manner. The physical and electronic properties of the resulting materials has been assessed, and the utility of the materials in OFET devices has been demonstrated.

Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Part of this work has been published in peer reviewed journals:

Levick, M. T.; Coote, S. C.; Grace, I.; Lambert, C.; Turner, M. L.; Procter, D. J.; Phase Tag-Assited Synthesis of Benzo[*b*]carbazole End-Capped Oligothiophenes; Org. Lett., 2012, 14, 5744-5747.

Rumer, J. W.; Levick, M. T.; Dai, S. Y.; Rossbauer, S.; Huang, Z.; Biniek, L.; Anthopoulous, T. D.; Durrant, J. R.; Procter, D. J.; McCulloch, I.; BPTs: thiophene-flanked benzodipyrrolidone conjugated polymers for ambipolar organic transistors; Chem. Comm., 2013, 49, 4465-4467.

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II Contents

IV Abbreviations and Definitions

Ac	acetyl
BHT	butylated hydroxytoluene
Bn	benzyl
BPT	thiophene-flanked benzodipyrrolidone
brsm	based on recovered starting material
CAN	ceric (IV) ammonium nitrate
COSY	correlation spectroscopy
d	doublet
DAST	diethylaminosulfur trifluoride
DBIC	dibenzoindolo[3,2-*b*]carbazole
DBM	dibenzoylmethane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
o-DCB	*ortho*-dichlorobenzene
DDQ	dichloro dicyano quinone
DEPT	distortionless enhancement by polarisation transfer
DFT	density functional theory
DIPA	diisopropylamine
DMF	dimethylformamide
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone
DPID	Dihydropyrroloindoledione
dppf	1,1'-*bis*(Diphenylphosphino)ferrocene
DSC	differential scanning calorimetry
EDCI	1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
Et	ethyl
eq.	equivalents
FCC	flash column chromatography
FTIR	Fourier transform infra-red
FSPE	fluorous solid phase extraction
h	hour(s)
HFIP	hexafluoro-2-propanol

HMPA	hexamethylphosphoramide
HMQC	heteronuclear multiple quantum coherence
HOBt	1-hydroxybenzotriazole
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
Hz	Hertz
g	gram(s)
LA	Lewis acid
LDA	lithium diisopropylamide
LHMDS	lithium *bis*(trimethylsilyl)amide
LUMO	lowest unoccupied molecular orbital
M	molar
m	multiplet
m	*meta*
*m*CPBA	*meta* chloroperbenzoic acid
Me	methyl
MeCN	acetonitrile
min	minute(s)
mL	millilitre(s)
mmol	millimole(s)
mp	melting point
MS	molecular sieves
MW	microwave
n	normal
NMR	nuclear magnetic resonance
o	*ortho*
OFET	organic field effect transistor
OLED	organic light emitting diode
OSC	organic semiconductor
OTFT	organic thin film transistor
OTS	octadecyltrichlorosilane
p	*para*

PMB	*para*-methoxy benzyl
PMMA	polymethyl methylmethacrylate
Tf	trifluoromethanesulfonyl
POM	polarised optical microscopy
Py	pyridine
q	quartet
R_F	$CH_2CH_2C_8F_{17}$
s	singlet
t	tertiary
t	triplet
TBAH	tetrabutylammonium hydroxide
TCE	trichloroethylene
TFAA	trifluoroacetic anhydride
TFE	2,2,2-trifluoroethanol
Tf_2O	triflic anyhdride
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TLC	thin layer chromatography
Ts	tosyl
μ	charge carrier mobility
V_T	threshold voltage
X	undefined group
XRD	X-ray diffraction

1 Introduction to organic semiconductors

The field of organic semiconductor research has expanded greatly over the past few decades from a purely academic research activity into a real industry with products on the market. Applications of organic semiconductors include organic field effect transistors (OFETs),[1] light-emitting diodes (OLEDs),[2] and photovoltaic cells (OPVs).[3]

The electronics industry is dominated by inorganic semiconductors, primarily based on silicon. Inorganic semiconductors are very well established and generally offer higher performance than organic semiconductors, it is therefore not expected that organic semiconductors will replace conventional inorganic semiconductors. Instead organic semiconductors have unique properties which open up new opportunities. The unique properties of organic semiconductors relative to their inorganic counterparts means they have the potential to deliver large area and low-cost devices by solution processing (spin coating, stamping, inkjet printing), thus avoiding the expensive lithography and vacuum deposition associated with the fabrication of inorganic based devices.[4] These milder fabrication procedures also make organic semiconductors more compatible with plastic substrates and allow for flexible devices. The other key advantage of organic semiconductors is their near-infinite tunability through chemical modifications. Organic materials can be readily designed and tuned through structural modification to meet the specific requirements of their intended applications.

1.1 Organic semiconductors in OFETs

The work described in this thesis focuses on the development of new methodology aimed towards the synthesis of new organic semiconductors, and the subsequent application and study of these new materials as the active layer in organic field effect transistors.

1.1.1 Device operation and mode of charge transport

Organic field effect transistors consist of a substrate and a gate electrode (typically heavily doped silicon wafer), a dielectric insulating layer (typically SiO_2), and an organic semiconducting material between a source and drain electrode (typically Au) (Figure 1).

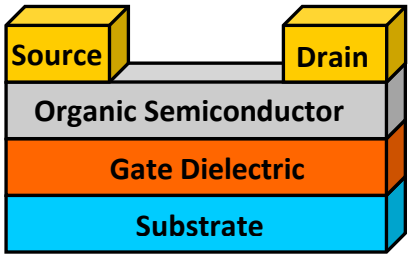


Figure 1 Typical device showing top-contact construction geometry.

In an ideal OFET, in the "off" state, the current between the source and drain electrodes will be zero when no voltage is applied to the gate electrode. The actual off current (I_{off}) observed is greatly dependant on the purity of the organic semiconductor, a high "off" current indicates the presence of additional unwanted charge carriers. Off currents are typically in the range 10^{-10} to 10^{-12} A for high performing materials of good purity.[5]

When a negative or positive voltage is applied to the gate electrode, an electric field is produced at the dielectric-semiconductor interface, charge carriers of opposite sign to the applied voltage are then injected from the source electrode and begin to accumulate at the dielectric-semiconductor interface (i.e. when a negative gate voltage is applied, radical cations accumulate at the dielectric/semiconductor interface).[6] As the charges accumulate a conducting channel will form and the OFET is then in the "on" state. When a voltage is applied between the source and drain electrodes electrons are then able to flow either from the source into the LUMO of the semiconductor (*n*-type transport) and

through the channel to the drain electrode, or holes are injected from the source electrode into the HOMO (*p*-type transport) which then travel through the channel to the drain electrode. The HOMO and LUMO energies of the material, the choice of dielectric, and the relative work functions of the source and drain electrodes all contribute to determine which type of charge is transported (*n*-type or *p*-type),[7] with a growing number of reports of ambipolar transport (*n*-type and *p*-type) .[8] The on/off current ratio (I_{on}/I_{off}) is used as a measure of the purity of the semiconductor, with impure materials giving a high "off" current leading to a low I_{on}/I_{off} ratio. High performing materials in the literature typically display I_{on}/I_{off} values of at least 10^5.[9] The voltage at which the device switches from the "off" state to the "on" state is referred to as the threshold voltage (V_T), and should ideally be as close to zero as possible.

One of the key parameters used to assess the performance of an organic semiconductor is charge mobility (μ), which is defined as the drift velocity of the charge carrier (cm s^{-1}) per unit applied field (V cm^{-1}), which can in turn be related to the rate of charge transfer through the material.[10]

The mode of charge transport in molecular organic semiconductors differs from inorganic semiconductors, whose properties are explained by conventional band theory (except in a few cases where band-like transport has been observed for specific organic materials in single crystals).[11] In small molecule organic semiconductors the large delocalised bands associated with inorganic semiconductors are not formed under normal operating temperatures; organic semiconductors in the solid state usually exist as polycrystalline materials in which the individual molecules are held together only by weak forces (Van der Waals, hydrogen bonding and π-stacking) rather than strong covalent bonds. Charge transport throughout the solid occurs via thermally activated hopping between adjacent neutral and charged molecules (*i.e.* charge transfer from a localised radical cation/anion to an adjacent neutral molecule).[12] The rate of charge transfer is described by semi-classical Marcus theory (Equation 1).

$$k_{ET} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi k_B T}} t^2 \exp\left(-\frac{\lambda}{4k_B T}\right)$$

Equation 1

The rate of charge transfer (k_{ET}) is determined by the transfer integral (t) and the reorganisational energy (λ), which are in turn both highly dependant on the electron cloud overlap between adjacent molecules and the overall crystal packing structure. When *p*-type transport is being described the transfer integral (t) is related to the energy level splitting of the HOMO which arises from the interaction of two adjacent molecules within the solid, a larger energy level splitting leads to a higher transfer integral, and ultimately a faster rate of charge transfer. The degree of splitting depends on the nature of the compound and on the orientation of the individual molecules relative to one another.[13] The reorganisational energy is the loss in energy which occurs when a charge carrier passes through a molecule, and is the sum of two different contributing factors of similar magnitude. The inner intramolecular contribution is related to energy changes which occur due to changes in the geometry of the two molecules which the charge is directly passing between as they go from ionised form to neutral and vice versa, and the outer contribution which is due to energy changes resulting from polarisation and relaxation of the surrounding area.[14]

The performance of any given organic semiconductor may vary widely depending on purity, since any impurities present within a sample can lead not only to disruption of packing within the solid, but are also able to act as charge carriers or traps.[15] Additionally, different methods of device fabrication can lead to different crystal packing structures and grain size; therefore, the overall device structure, the choice of insulating dielectric and the nature of the source/drain contacts all have an effect on performance. Finally the testing method and conditions (temperature, pressure and whether or not the testing is performed under an inert atmosphere) may also impact upon the end performance observed. A clear example is the wide range of reported values in the literature for devices based on pentacene, with mobilities ranging from 2×10^{-3} cm^2 Vs^{-1}, reported for the first OFET based on pentacene,[16] all the way up to 40 cm^2 Vs^{-1} reported by Palstra et

al. for pentacene single crystal devices using 6,13-pentacenequinone as the gate dielectric.[17]

One other factor that must be considered is the stability of the organic semiconductor under ambient conditions. The stability is largely determined by the HOMO and LUMO energies of the semiconductor, along with the device structure. Many common organic semiconductors are relatively fragile and have limited stability in air, this is especially pronounced with *n*-type organic semiconductors in which the radical anions generated during device operation can readily react with oxygen, water, and hydroxyl groups on the dielectric surface.[7,18] Designing organic semiconductors with lower energy HOMO and LUMO levels can greatly improve air stability, leading to devices that can be operated under ambient conditions.[19]

1.1.2 Device Structure

Charge transport occurs adjacent to the dielectric in the first few layers of the semiconducting material,[20,21] this means that the nature of the interface between the dielectric and the semiconductor can have a dramatic effect on performance.[22,23] The choice of dielectric layer influences how the organic semiconductor is orientated within the device, as well as determining the growth of crystallites and the packing morphology within the film.[24,25] The roughness of the dielectric has been shown to affect mobility, with a smoother dielectric layer having a positive impact on mobility.[26] The most commonly used dielectric in the literature is SiO_2, which is readily thermally grown on the surface of silicon wafers. Often the surface of the inorganic dielectric is treated with an additional self-assembling layer; such treatments involve the use of alkane trichlorosilanes, HMDS, or substituted phosphonic acids.[25] The positive effect often observed when an additional surface treatment is carried out is thought to arise due to a combination of effects, including passivation of trapping sites on the surface, effects on crystallite growth and interconnectivity between crystallites due to changes in the crystallinity and roughness of the surface,[23,25,27] and alteration of the semiconductor alignment along the surface due to modulation of the surface polarity. Inorganic dielectrics, other than SiO_2, that have been used include HfO_2, Ta_2O_5, Al_2O_3, Y_2O_3, CeO_2

and TiO_2. Some of the most promising dielectrics are polymeric, and a range of different polymer dielectrics have also been used, allowing for the production of all organic transistors.[22]

Similarly the contact/semiconductor interface affects the initial injection of charge into the semiconducting channel. For *p*-type semiconductors high work function metals such as gold are most often used, the metal is normally chosen such that work function of the metal and the HOMO energy of the semiconductor are closely matched to ensure efficient charge injection, although for optimal performance other factors need to be considered such as the method of fabrication (vacuum conditions during metal deposition) and the energy difference between the work function at the surface of the metal in comparison to the SOMO energy of the semiconductor.[28] A large amount of work has been devoted to improving carrier injection through modification of the contacts, either involving the introduction of intermediate metal oxide layers[29,30] or chemical modification of the contact metal.[31]

The overall device structures also play an important role in determining performance. Devices are arranged in four common geometries; bottom-gate/top-contact, top-gate/bottom-contact, bottom-gate/bottom-contact and top-gate/top-contact. It has been observed that the bottom-gate/top-contact and top-gate/bottom-contact devices generally perform better than the other devices geometries. This is thought to result from a larger area of contact between the source/drain contacts and the organic semiconductor, and more favourable injection pathways, which cumulatively lead to a lower contact resistance.[31]

1.1.3 Crystal packing motifs

The manner in which individual molecules pack together is an important factor in determining the electrical properties of the bulk material as this impacts greatly on both the transfer integral (*t*) and the reorganizational energy (λ). Close, regular packing between molecules is required for efficient charge transport. Small molecule organic semiconductors are generally planar aromatic systems, which adopt one of several

common packing motifs, which exist more as part of a continuum rather than discrete unrelated packing structures.[32] The most common packing motif is the herringbone arrangement in which intermolecular electron repulsion leads to structures in which edge-to-face π-π stacking interactions dominate, giving two-dimensional electronic interactions (Figure 2, (a)). Less common are co-planar packing structures in which face-to-face π-π stacking interactions dominate (Figure 2, (b) and (c)). These structures exist with various degrees of displacement along the main axes of the molecule leading to 2-D π-stacking, in which two-dimensional electronic interactions are possible via interactions between adjacent stacks.[32] In face-to-face stacked structures the interactions between individual molecules are in general stronger, leading to better electronic coupling. Several organic semiconductors have been rationally designed to exploit this.[33-36]

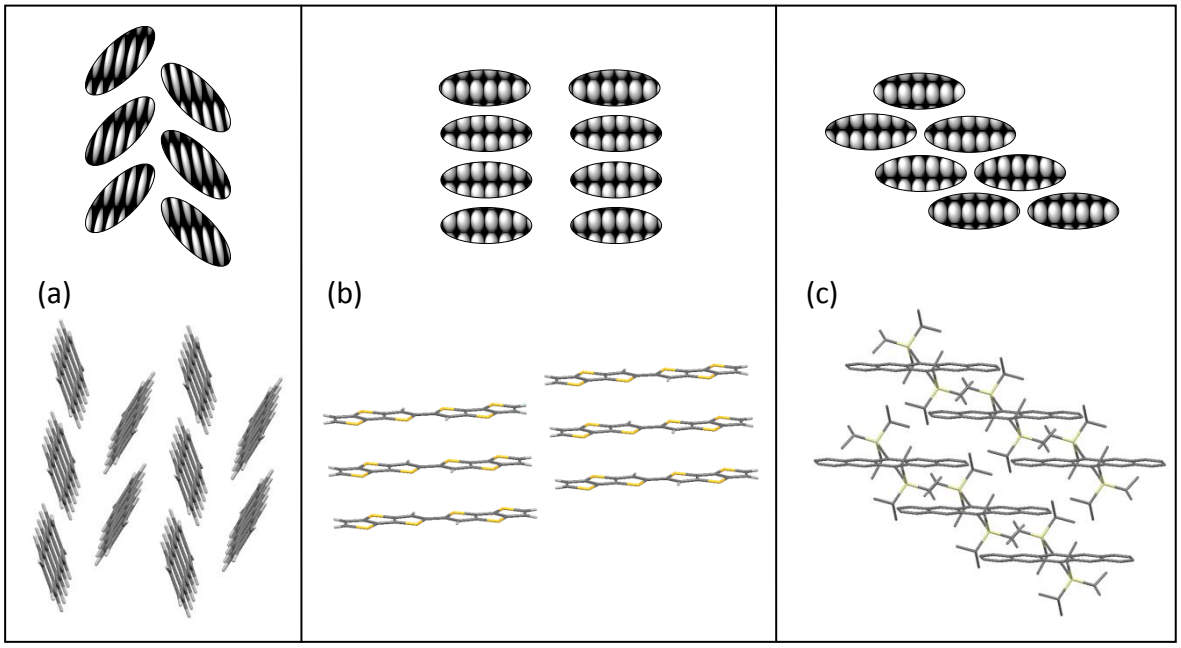
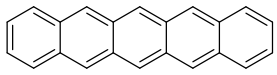


Figure 2 (a) Herring-bone packing [edge-to-face stacking dominates][37] (b) Co-planar π-π packing[38] (c) Displaced co-planar π-π packing[39]

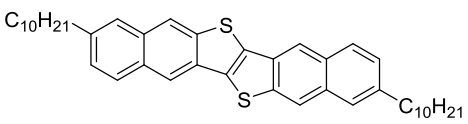
In addition to the overall packing motif adopted by an organic semiconductor, the alignment of the molecules within the device is also very important.[40] The best performing devices are obtained when molecules lie with the highest π-orbital overlap parallel with the direction of charge transport.[41,42]

1.1.4 Device fabrication methods and current state-of-the-art organic semiconductors

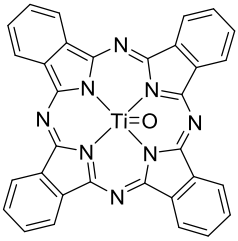
There are a wide variety of different methods for the deposition of organic semiconductors during device fabrication. Solution processing techniques involve dissolution of the organic semiconductor, followed by deposition of this solution onto the substrate by a range of methods (drop-casting,[43] inkjet printing,[44] spin-coating,[45] dip-coating,[46] Langmuir-Blodgett techniques,[47] zone-casting,[48] solution-shearing,[49] or spray-coating).[50,51] Solution processing techniques are advantageous in that they open the way for very low-cost large area device fabrication.[52] The highest mobility to date for a solution processed OFET was reported by Ong et al., who have shown a mobility of 10.9 cm^2 Vs^{-1} could be obtained using the polymer **5** (Figure 3).[53] Vacuum evaporation meanwhile provides generally better performance and is the most widely used deposition method,[51,54] with reported mobilities of up to 7.9 cm^2 Vs^{-1}, reported for **2**,[53] and 10 cm^2 Vs^{-1} reported for **3**.[55] The highest mobilities observed to date are based on single crystal devices; single crystal devices based on pentacene **1** and rubrene **4** have been shown to exhibit mobilities between 15-40 cm^2 Vs^{-1}.[17] However, single crystal based devices are purely of research interest and are not applicable to large scale manufacturing as delicate manipulation by hand is often required during device construction.



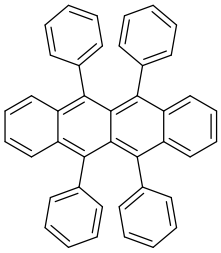
1 - 40 $cm^2 Vs^{-1}$ - Single crystal



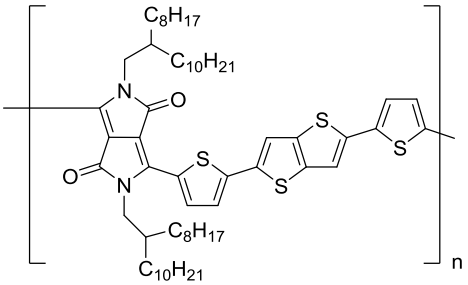
2 - 7.9 $cm^2 Vs^{-1}$ - Vacuum evaporation



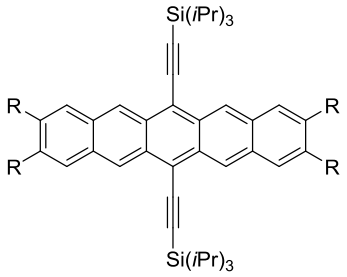
3 - 10 $cm^2 Vs^{-1}$ - Vacuum evaporation



4 - 40 $cm^2 Vs^{-1}$ - Single crystal

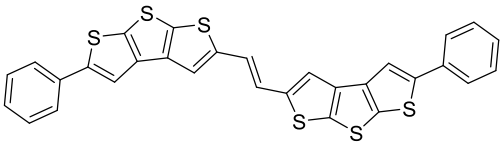


5 - 10.6 $cm^2 Vs^{-1}$ - Solution processed

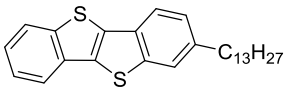


6 - R=H - 1.8 $cm^2 Vs^{-1}$

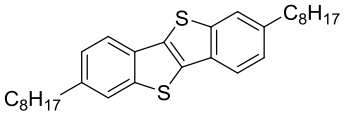
7 - R=Et - 3.92 $cm^2 Vs^{-1}$ - Solution processed



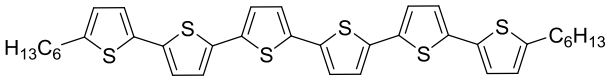
8 - 2.0 $cm^2 Vs^{-1}$ - Vacuum evaporation



9 - 17.2 $cm^2 Vs^{-1}$ - Vacuum evaporation



10 - 16.4 $cm^2 Vs^{-1}$ - Vacuum evaporation



11 - 1.1 $cm^2 Vs^{-1}$ - Solution processed

Figure 3 A selection of the highest performing materials in OFET devices.

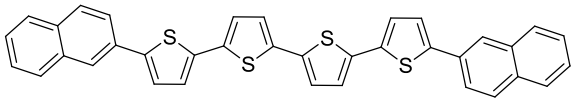
The best performing, and most well studied materials are acenes, in particular pentacene and its' derivatives. Whilst offering very high performance, pentacene itself is poorly soluble and suffers from low stability,[56] with the higher order acenes (hexacene and heptacene) possessing increasingly worse stability and solubility.[57,58] Hence, a variety of alternative materials have been synthesised and studied. One of the most successful strategies employed to improve stability and solubility has involved the substitution of

heteroatoms (primarily sulfur) into acenes, in order to lower the HOMO level and/or negate the instability due to specific reactive positions.[59-62] Blocking of the central reactive centre in pentacene by the incorporation of silylethynyl groups at the 6- and 13-positions (**6** and **7**) has also proved a successful way to improve both stability and solubility whilst retaining high charge mobility.[35,56,63] The addition of the silylethynyl groups at the 6- and -13 positions causes the compounds to adopt a face-to-face π-π packing motif, which is known to lead to good electronic coupling and charge mobility.

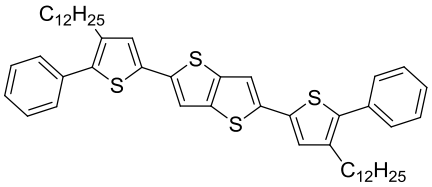
Mobilities above 1 $cm^2 Vs^{-1}$ have also been reported for phthalocyanines (such as **3**), the high mobility is thought to be a consequence of the very tight face-to-face π-π stacking geometries observed.[64-66] Oligomers displaying mobilities above 1 $cm^2 Vs^{-1}$ (such as **8** and **11** are much rarer with only a few examples reported in the literature.[41,67-73]

1.1.5 End-capped oligothiophene-based devices

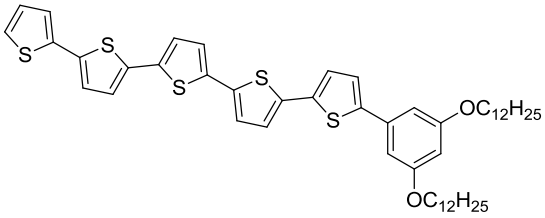
Oligothiophenes are amongst some of the most well studied organic semiconductors.[73,74] Acene end-capped oligothiophenes have been shown to be promising organic semiconductors, with the acene end-caps extending the conjugation length and improving stability through blocking of the reactive 2- and 5-positions.[68,75-85] Field effect mobilities of 6.2 $cm^2 Vs^{-1}$ have been reported for devices based on single crystals of **14**,[68] whilst mobilities and I_{on}/I_{off} values up to 0.40 $cm^2 Vs^{-1}$ and 1×10^5 have been reported for devices fabricated from **12** using vacuum evaporation (Figure 4).[83] Meanwhile devices manufactured by solution processing of **13** exhibited values an order of magnitude lower ($\mu = 3.1 \times 10^{-2}$ $cm^2 Vs^{-1}$ and $I_{on}/I_{off} = 4.5 \times 10^4$).[75]



12 - 0.40 $cm^2 Vs^{-1}$ - Vacuum evaporation



13 - 3.1×10^{-2} $cm^2 Vs^{-1}$ - Solution processed



14 - 6.2 $cm^2 Vs^{-1}$ - Single crystal

Figure 4 Charge mobilities observed for end-capped oligothiophene-based devices.

1.2 Summary

The field of organic electronics has expanded rapidly in the last ten years, with a large amount of research input from a variety of different fields focussed on the synthesis and development of new materials, the optimisation of device structure and fabrication, and on the underlying theories of device operation. This has led to the realisation of mobilities of up to 40 $cm^2 Vs^{-1}$ in single crystal based devices and up to 10.6 $cm^2 Vs^{-1}$ from solution processed devices. The current challenges lie in understanding how chemical structure relates to packing and ultimately device performance, to a level of detail such that the next generation of materials can be rationally designed to maximise device performance. Significant challenges also lie in the optimisation of device structure and fabrication, particularly in relation to the various interfaces present within devices which have been shown to have a large impact on performance.

2 Synthesis of benzo[*b*]carbazole end-capped oligothiophenes

2.1 Introduction

2.1.1 Phase tagging strategies

In the synthesis of libraries of organic compounds it is generally recognised that the main bottleneck in the whole process is the isolation and purification of the reaction products. Traditional techniques such as basic liquid-liquid extractions and flash column chromatography are both labour intensive and time consuming. One way of circumventing these problems is the use of phase tags which allow the compound of interest to be easily separated from the other components of a reaction mixture.

2.1.1.1 Solid-phase synthesis

Solid-phase synthesis using insoluble polymer supports or tags is one such approach, allowing for fast isolation of intermediates from the reaction solvent and excess reagents. This technique, which was originally designed for use in the field of peptide synthesis,[86] has since been extended to the synthesis of a wide range of targets.[86-88]

The choice of linker for attaching the organic substrate to the polymer support is an important consideration in solid-phase synthesis.[89,90] Sulfur-based linker systems are popular as they are stable to a wide range of reaction conditions, have variable oxidation states and are able to mediate chemistry α to the sulfur atom.[91,92]

However, solid phase synthesis suffers from several disadvantages:

- Exploiting a solid support requires an extra synthetic step at the beginning of the synthesis to incorporate the support and also an extra step at the end of the synthesis to release the products, thus increasing the length of the overall synthetic sequence.

- Reactions cannot be monitored by common methods (such as TLC, HPLC, IR and NMR), without cleavage of intermediates from the solid support.
- Reactions are heterogeneous, so large excesses of reagents and long reaction times are often required to drive reactions to completion.
- Solution-phase reaction procedures commonly require extensive optimisation for application in solid phase synthesis.
- Further purification by conventional techniques such as recrystallisation, chromatography and distillation cannot be performed without cleavage from the support.

2.1.1.2 Fluorous synthesis

Many of the problems listed above relate to the insolubility of the solid support; with this in mind, soluble phase tags have been developed that maintain the best features of solid phase synthesis whilst circumventing some of the problems that insolubility presents.[93] One of the most important classes of soluble phase tags is that based on perfluoroalkyl chains, the use of which was introduced by Horvath et al. in 1994.[94] Since this original paper the field has experienced rapid growth, with many diverse applications of fluorous chemistry published throughout the literature.[95-97]

Fluorous synthesis has many benefits over solid-phase synthesis, mostly due to the improved solubility of products and intermediates in common organic solvents:

- Reactions can be monitored by conventional methods (such as TLC, IR, HPLC and NMR) and intermediates can be characterised without cleavage of the tag.
- Reactions can be homogeneous and often do not require a large excess of reagents to drive them to completion.
- Reaction times are shorter due to more favourable solution-phase kinetics.[98]
- Perfluoroalkyl chains are chemically stable and have little effect on the reactivity of the attached molecule as a $(CH_2)_n$ spacer is typically used.

- Tagged products can be purified by both fluorous purification and conventional techniques such as chromatography, distillation and recrystallisation without cleavage of the tag.

Research in the field of fluorous chemistry can be split into two classes: heavy and light fluorous synthesis. In early work, separation of fluorous compounds focused on the use of liquid-liquid (biphasic and triphasic) extractions with fluorous solvents. This technique exploits the temperature variable miscibility of fluorous solvents with organic solvents, allowing reactions to be carried out in monophasic systems when heated, while allowing separation into two phases upon cooling. Efficient extraction by this method requires the use of molecules with high fluorine content, typically >60% w/w fluorine, which requires the attachment of multiple perfluoroalkyl chains and often leads to issues with solubility in normal organic solvents.

Most recent work has instead involved the use of fluorous solid-phase extraction (FSPE) (Figure 5).[99] The introduction of this technique dramatically improved the practicality of fluorous synthesis, importantly allowing for the efficient isolation of compounds with much lower fluorine content, typically <40% w/w fluorine, and circumventing the need for environmentally persistent fluorous solvents during the extraction procedure.

FSPE relies on the use of commercially available fluorous reverse-phase silica gel (typically $C_8F_{17}CH_2CH_2Si$- / Fluoro*Flash*® silica). The crude reaction mixture is loaded onto the column and eluted with a fluorophobic solvent (e.g. 80% MeCN/H_2O or 80% MeOH/H_2O) to remove any non-fluorinated materials.[100] Perfluorinated alkyl chains are both lipophobic and hydrophobic, and elution with a fluorophobic solvent is thought to cause aggregation of the perfluoroalkyl chains, leading to the retention of any fluorous materials. The column is then eluted with a fluorophilic solvent (e.g. MeCN, MeOH or THF) to obtain the tagged material (Figure 5). The aggregation of perfluoroalkyl chains is thought to arise from a solvophobic effect; the aggregation of fluorous chains results in the expulsion of ordered solvent molecules from the surface of each chain resulting in an increase in entropy.

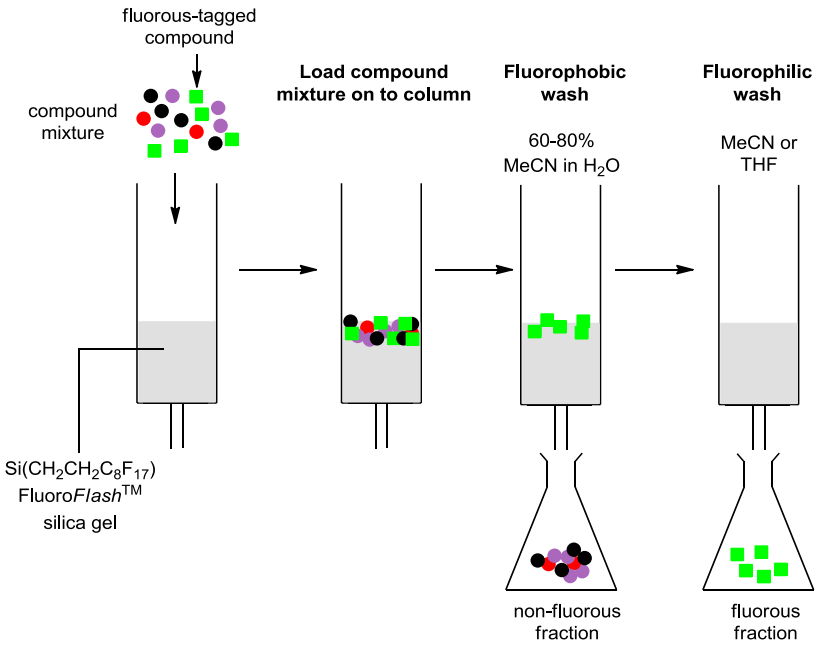


Figure 5 Separation of fluorous and non-fluorous compounds using FSPE.

Fluorous synthesis can be divided into two distinct classes, in a similar manner to solid-phase synthesis:

- Reactions in which fluorous catalysts, reagents, or scavengers are used.[101-104]
- Reactions in which substrates are covalently attached to a fluorous tag to aid isolation in multiple stages of a synthesis.[95,105]

When the substrates are covalently linked to the fluorous tag, the linker can be utilised in three different ways:[95]

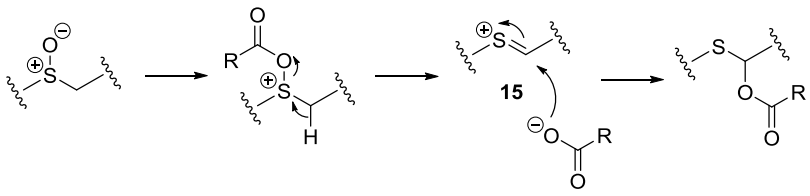
- The linker can act as a simple protecting group, where cleavage of the tag later in the synthesis reveals the original functional group. A wide range of fluorous variants of commonly used protecting groups have been employed in this manner (examples include fluorous variants of Boc,[106] TIPS,[107] MOM,[108] and THP,[109] amongst many others).
- The linker can also activate a functional group towards certain chemistry later in the route, allowing for conversion of the original functional group to another when it is later cleaved. An example of this type would be the conversion of

phenols to fluorous sulfonates, allowing later conversion to different functional groups via cross coupling.[110,111]

- Finally, a variant on the above exists where the linker requires activation before it can be cleaved.[112]

2.1.2 The Pummerer reaction

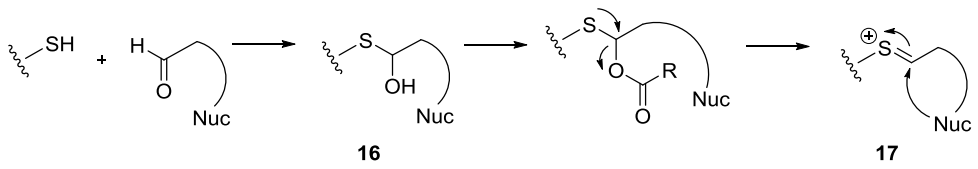
The Pummerer rearrangement[113] and associated Pummerer cyclisations and Pummerer-type reactions are well known as valuable synthetic tools, especially in the construction of carbocycles and heterocycles.[114-116] The basic Pummerer rearrangement involves the activation of sulfoxides by acetylation of the sulfoxide oxygen, followed by elimination, leading to the generation of a thionium electrophile **15** (Scheme 1). In the classical Pummerer rearrangement the thionium ion is then trapped by the acetate counterion; however, in practice the intermediate thionium ion can be trapped by a range of external or internal nucleophiles to generate a more diverse range of products. Where internal nucleophiles are utilised, Pummerer cyclisation reactions are observed.



Scheme 1

2.1.3 A new connective-Pummerer reaction

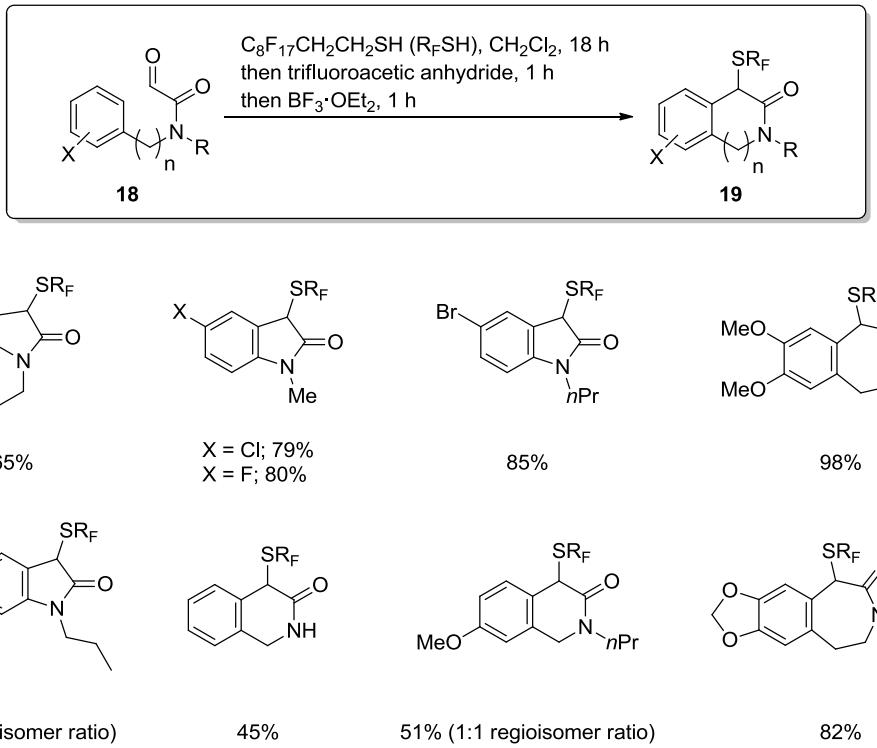
Within the Procter group a new approach for the generation of the key thionium ion intermediate has been developed.[116,117] The new connective-Pummerer reaction accesses the thionium ion intermediate **17** by bringing together aldehydes and thiols to generate hemithioacteal intermediates **16** which can then be activated in situ to generate the thionium ion (Scheme 2).



Scheme 2

Within the Procter group a tagging strategy was developed, using the connective-Pummerer cyclisation in conjunction with a soluble light fluorous thiol, in which the introduction of the fluorous phase tag triggers the key cyclisation event. The presence of the phase-tag aids downstream purification whilst its incorporation requires no additional synthetic steps.[117]

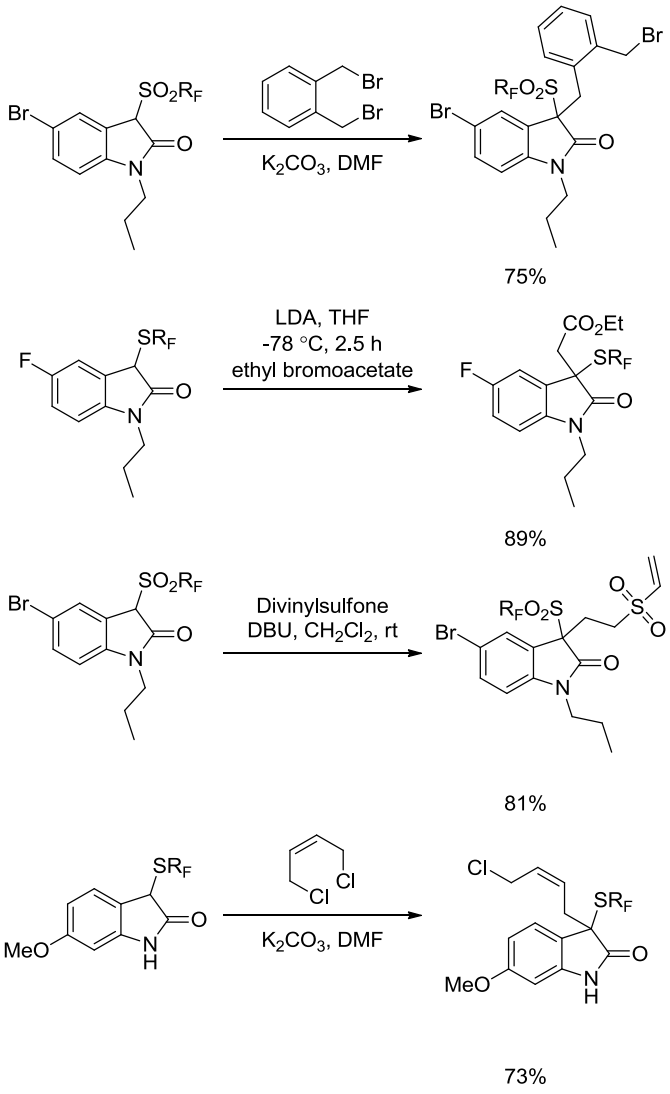
It has been demonstrated within the Procter group that this fluorous approach can be used to access a wide variety of oxindoles and other heterocyclic systems (Scheme 3).[117-123] In the following examples commercially available 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (R_FSH) is reacted with generic glyoxamide **18** to generate the corresponding hemithioacetal intermediate which is then acetylated and activated with $BF_3{\cdot}OEt_2$ to generate the key thionium intermediate. The aromatic ring then attacks the thionium ion, and after rearomatisation the desired cyclised product **19** is obtained. An important part of this procedure is the use of glyoxamide starting materials, which can be efficiently synthesised in excellent overall yields from the parent amines, often with no need for purification.[124]



Scheme 3

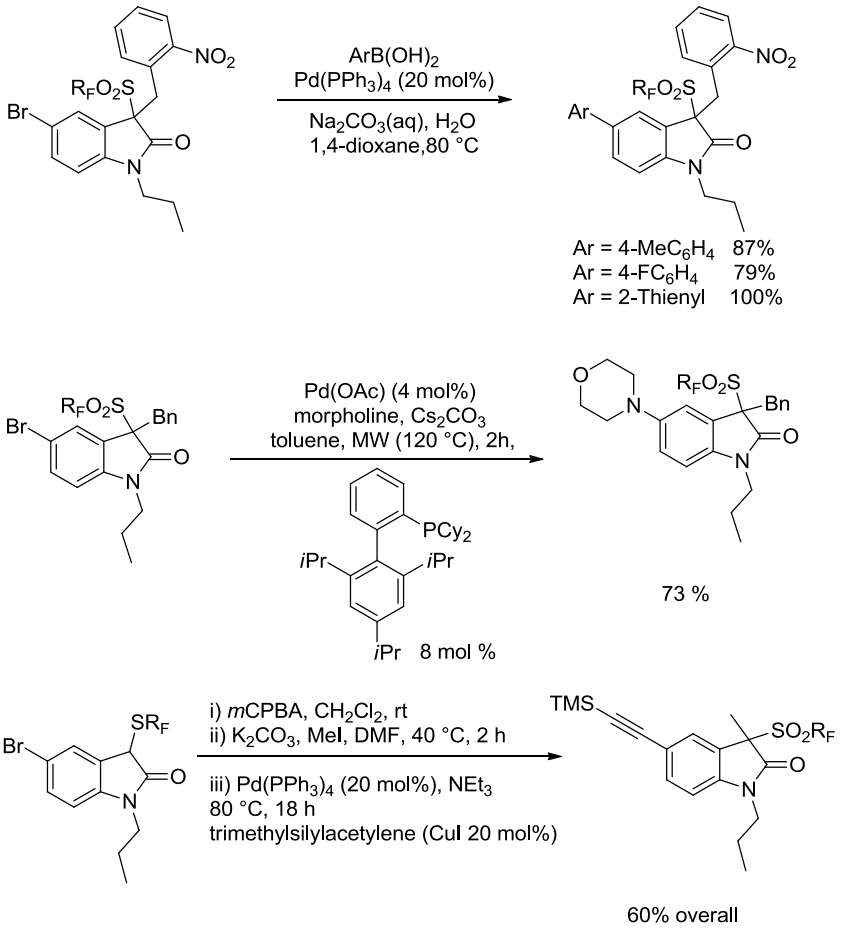
2.1.4 Manipulation of oxindole scaffolds-Introduction of diversity

The Procter group has shown that the fluorous-tagged heterocyclic intermediates could be further modified in a variety of ways. The sulfur linkage, at either the sulfide or sulfone oxidation level, can be used to facilitate alkylation or acylation α to sulfur using a range of electrophiles in good yields (Scheme 4).[117-121,123]



Scheme 4

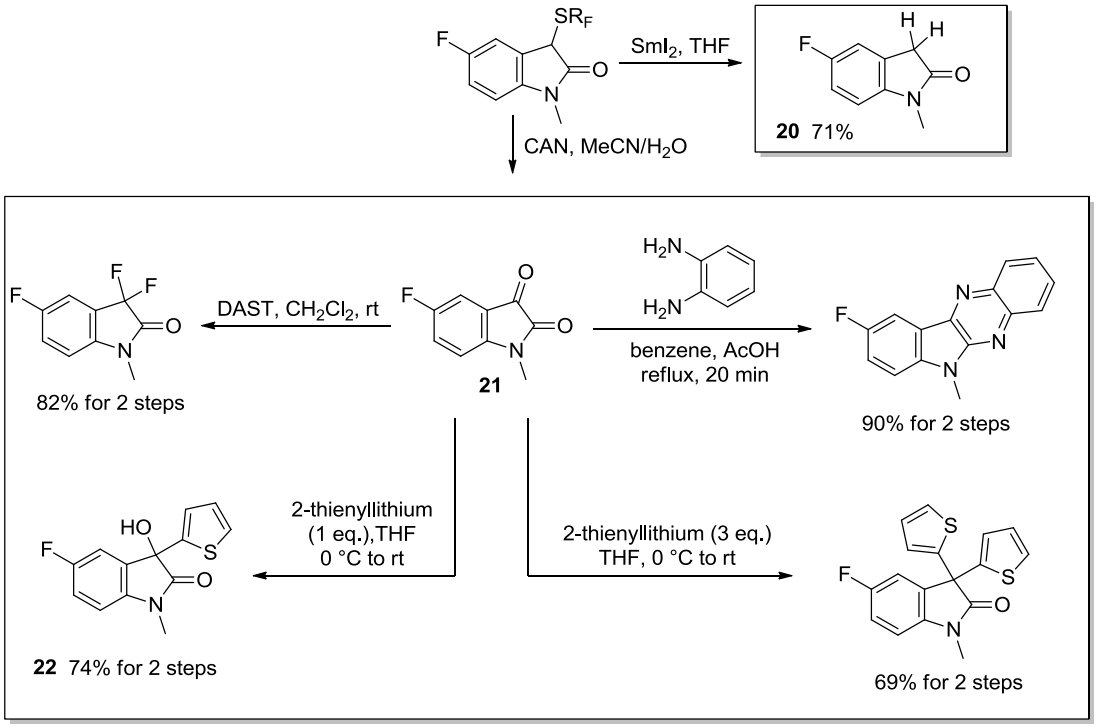
The group also showed that the presence of a bromine atom in the aromatic starting material could be exploited for further elaboration through palladium-catalysed coupling reactions (for example Sonogashira, Suzuki-Miyaura, and Buchwald-Hartwig reactions) (Scheme 5).[125]



Scheme 5

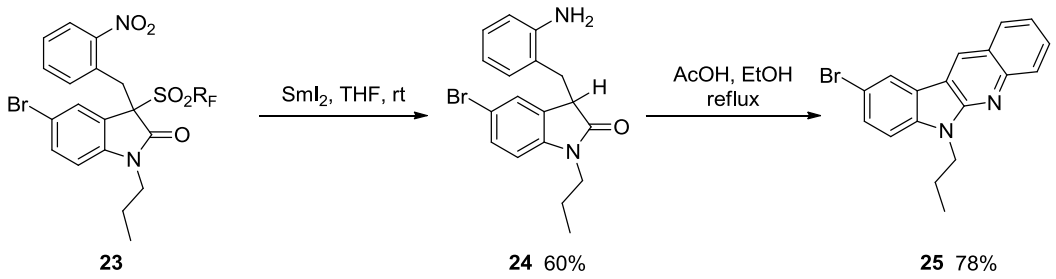
Both oxidative and reductive methods for the removal of the phase tag have been developed within the Procter group. Reduction with SmI_2 affords oxindole **20**, or alternatively oxidation with CAN gives isatin **21**, leaving a synthetically useful carbonyl group in place of the sulfur linker (Scheme 6).

The chemistry of isatins such as **21** has been widely studied previously.[126-130] The Procter group used a selection of this chemistry in their own work to demonstrate the range of heterocycles that can be accessed via oxidative tag cleavage (Scheme 6).[121] It is worth drawing attention in particular to compound **22** which inspired a side project described later in this thesis, aimed towards the synthesis of thiophene-flanked benzodipyrrolidone (**BPT**) based monomers.



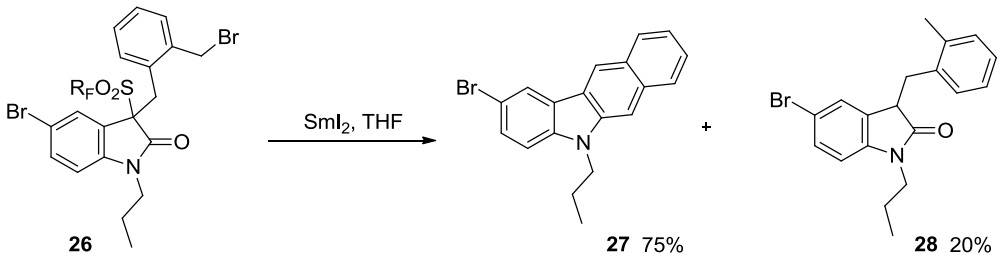
Scheme 6

Removal of phase tags often requires an extra step of little synthetic value. The Procter group was particularly interested in obtaining a greater synthetic return from the tag cleavage step, investigating whether the reagent that was used for reductive tag cleavage, SmI_2, could trigger further chemistry in the same step. Initial preliminary work in this area was carried out by Dr Karen James who showed that SmI_2 could be used to afford intermediate **24** in a single step from **23** by reductive tag cleavage and reduction of the nitro group. The amine could then be cyclised in the presence of acetic acid to yield **25** (Scheme 7). This methodology was later utilised in the synthesis of the natural product neocryptolepine.[118]



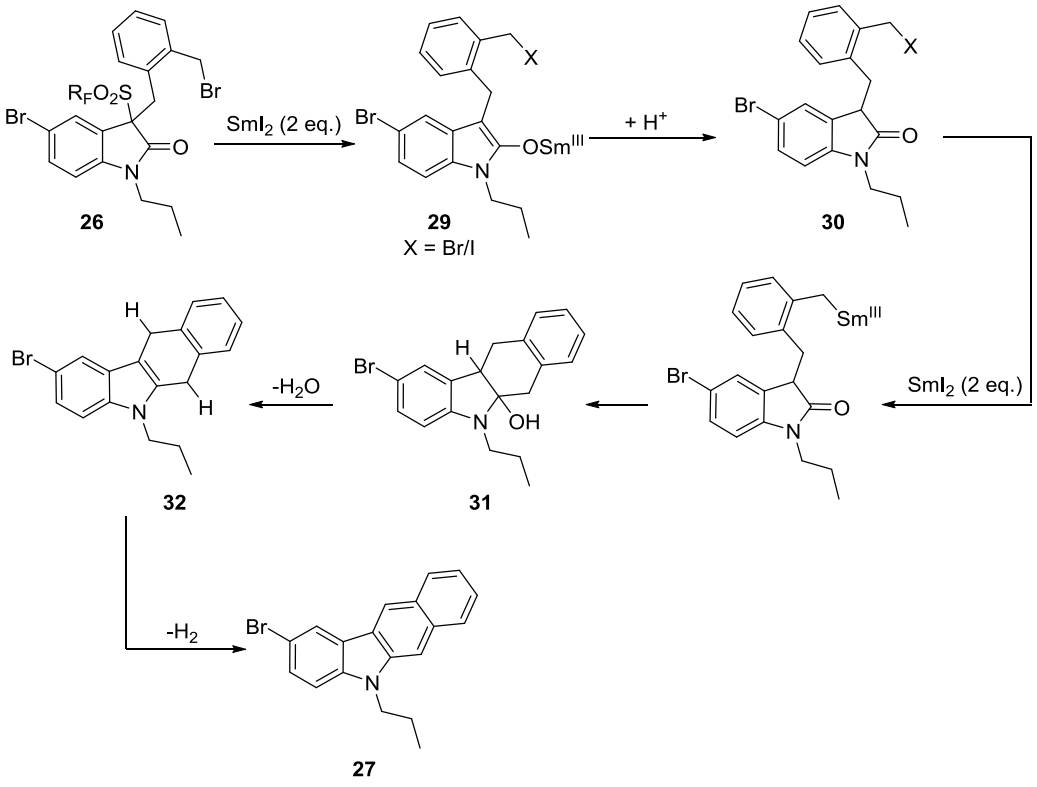
Scheme 7

More interestingly, it was found that if the alkylated intermediate **26** was added dropwise to 4 eq. of SmI_2 the cyclised benzo[*b*]carbazole product **27** was obtained as the major product, alongside a smaller quantity of the non-cyclised product **28** (Scheme 8).[121]



Scheme 8

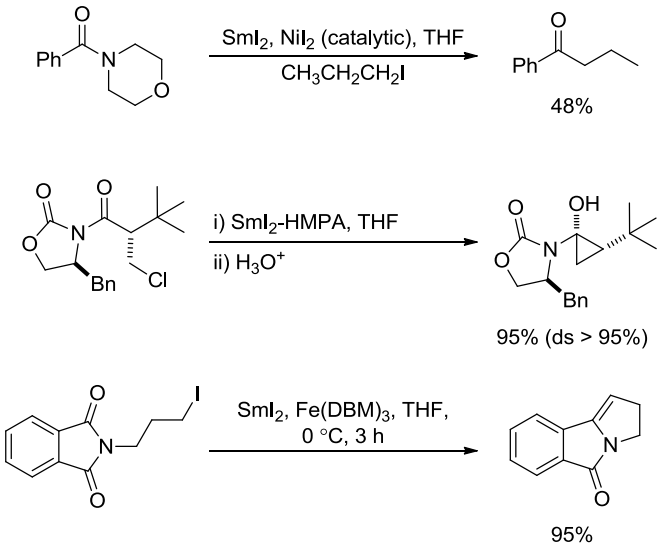
The formation of the benzo[*b*]carbazole product **27** is thought to proceed via initial cleavage of the tag to generate samarium-enolate **29**,[131] which is then protonated to regenerate the carbonyl group giving compound **30**. This then undergoes a samarium-mediated Barbier addition to the amide to give **31**,[132] followed by dehydration to give **32**, and aromatisation to yield **27** (Scheme 9).



Scheme 9

2.1.5 SmI_2-mediated Barbier reactions

The above benzo[*b*]carbazole synthesis represents a rare example of a SmI_2-mediated Barbier reaction involving addition into an amide. The coupling of organic halides and aldehydes, ketones, and esters mediated by SmI_2 is well studied, with a vast array of examples in the literature;[132-134] however, examples involving amides and imides are much more scarce (Scheme 10).[135-141]



Scheme 10

The reactions can be performed with the carbonyl and alkyl halide already present (Barbier conditions), or via formation of the organosamarium intermediate prior to addition of the carbonyl (Grignard conditions).[132] Three different mechanisms are possible for SmI_2-mediated Barbier reactions (Figure 6); most evidence points towards formation of an organosamarium intermediate which then adds into the carbonyl (Figure 6, Pathway 1),[142-144] although current evidence is not conclusive and it is likely that the exact mechanism is dependent on the conditions and substrate.[145] Assuming the reaction proceeds via pathway 1, for the reaction to be successful the rate of reduction of the intermediate radical must be faster than any competing cyclisation pathways, or radical abstraction from solvent or substrate.

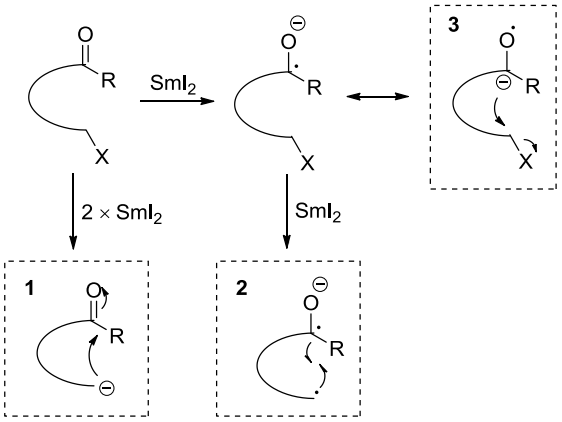


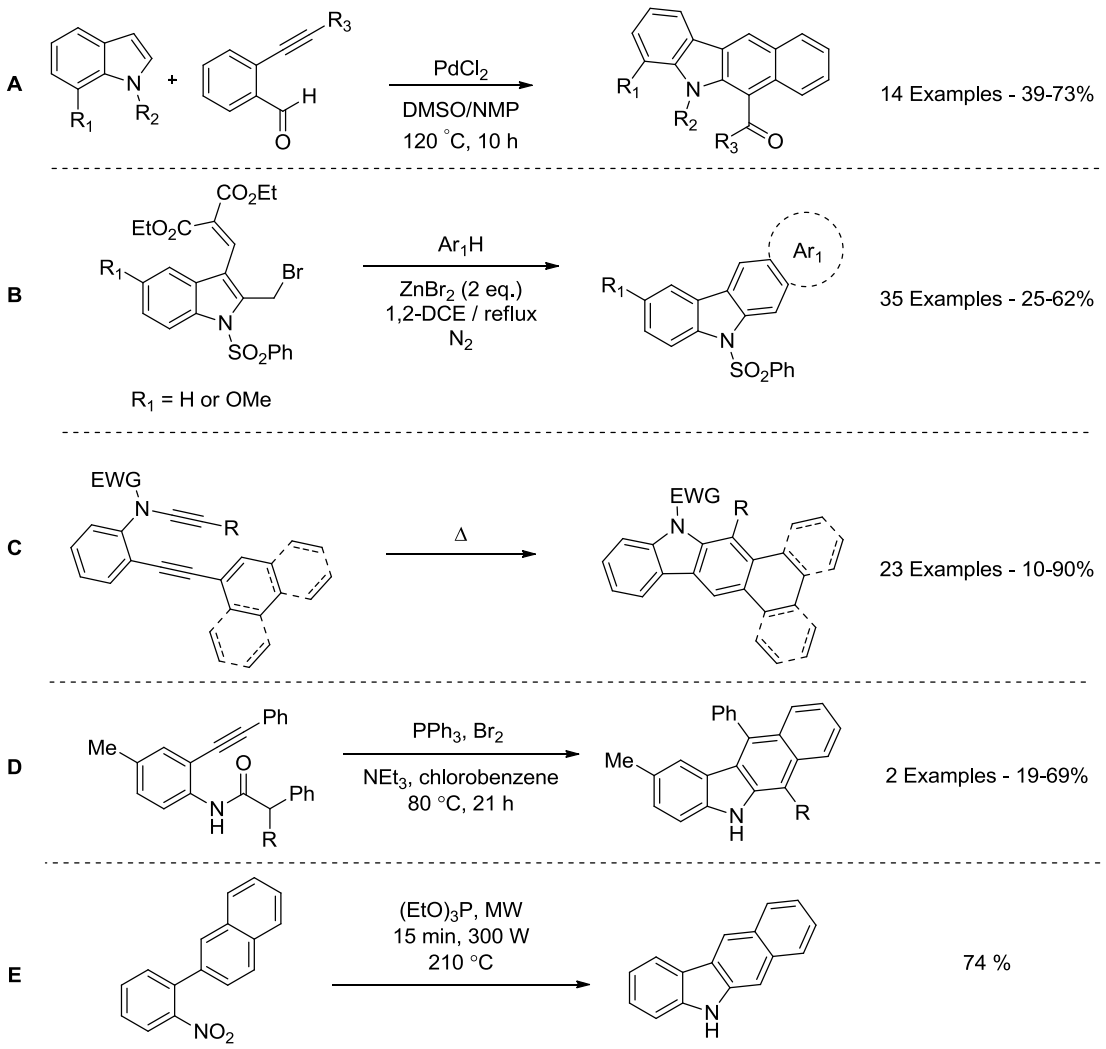
Figure 6 Possible mechanisms (1-3) of SmI_2-mediated Barbier reactions. [134]

The addition of additives (HMPA,[146] NiI_2,[147] H_2O,[148,149] alcohols,[150] amines,[151] LiCl and LiBr, [152] and $Fe(DBM)_3$) is known to alter both the reaction rates and mechanistic pathways of SmI_2-mediated processes. A variety of these additives have been used to promote SmI_2-mediated Barbier reactions. HMPA is thought to influence reactions in two main ways; coordination of HMPA to Sm(II) results in an increase in the reagent's reduction potential, with the HMPA ligands providing additional steric bulk around the reactive site helping to stabilise reactive intermediates.[146,153,154] The addition of inorganic salts (namely NiI_2, $FeCl_3$,[155] and $Fe(DBM)_3$) has proved beneficial. The most commonly used, NiI_2,[147] is thought to be reduced by Sm(II) to Ni(0) in situ, with transmetalation of organosamarium intermediates to nickel occurring during the reaction.[148,156,157] Irradiation with 560-700 nm wavelength light has also been used to facilitate SmI_2-mediated Barbier reactions, [155] the electron transfer in these cases is thought to occur from an excited state of SmI_2.[158,159]

2.1.6 Literature synthesis of benzo[*b*]carbazoles

The synthesis of carbazoles and related motifs has long attracted interest due to their presence in a range of biologically active compounds,[160] and more recently due to their use in organic electronics.[161-168] Despite this, no general methods exist for the synthesis of benzo[*b*]carbazoles, instead a plethora of different methods are found in the literature; Fischer indolisations,[169] Cadogen cyclisations,[170] radical cyclisations,[171-173] inverse electron-demand Diels-Alder reactions,[174] benzyne reactions with a variety of functionalised indoles,[175-178] and intramolecular dehydro Diels-Alder reactions,[179] amongst a wide range of other transformations,[180-184] have all been used in the

preparation of benzo[*b*]carbazoles (Scheme 11). In most cases these studies are limited to one or two examples aimed towards the synthesis of a specific target, whilst more general studies of substrate scope are rarer (Scheme 11, A-C).[179,180,184] In many cases the reaction conditions are harsh and/or the reaction necessitates the use of certain functional groups (Scheme 11, A, C, D), which ultimately end up attached to the core structure, and which can not be removed and are not necessarily desirable.



Scheme 11

2.2 Investigation of the mechanism of the SmI_2-mediated cleavage-cyclisation sequence

Initial studies began by focusing on the synthesis of benzo[*b*]carbazole structures, with the aim of developing our understanding of the Pummerer cyclisation and SmI_2-mediated cleavage–cyclisation steps and then applying this methodology to the two-directional synthesis of dibenzoindolo-[3,2-*b*]carbazole (**DBIC**) materials. It was intended that this process would also generate a series of benzo[*b*]carbazole monomers, which would be used to generate oligomers in conjunction with suitably functionalised oligothiophenes, using standard palladium catalysed C–C bond forming procedures (Figure 7).

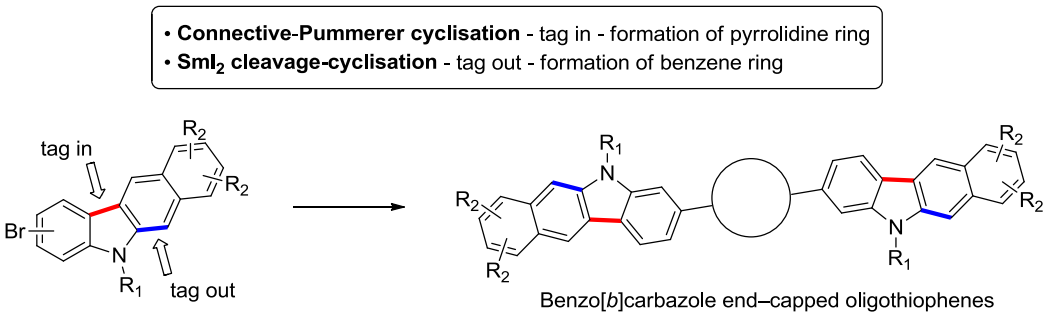
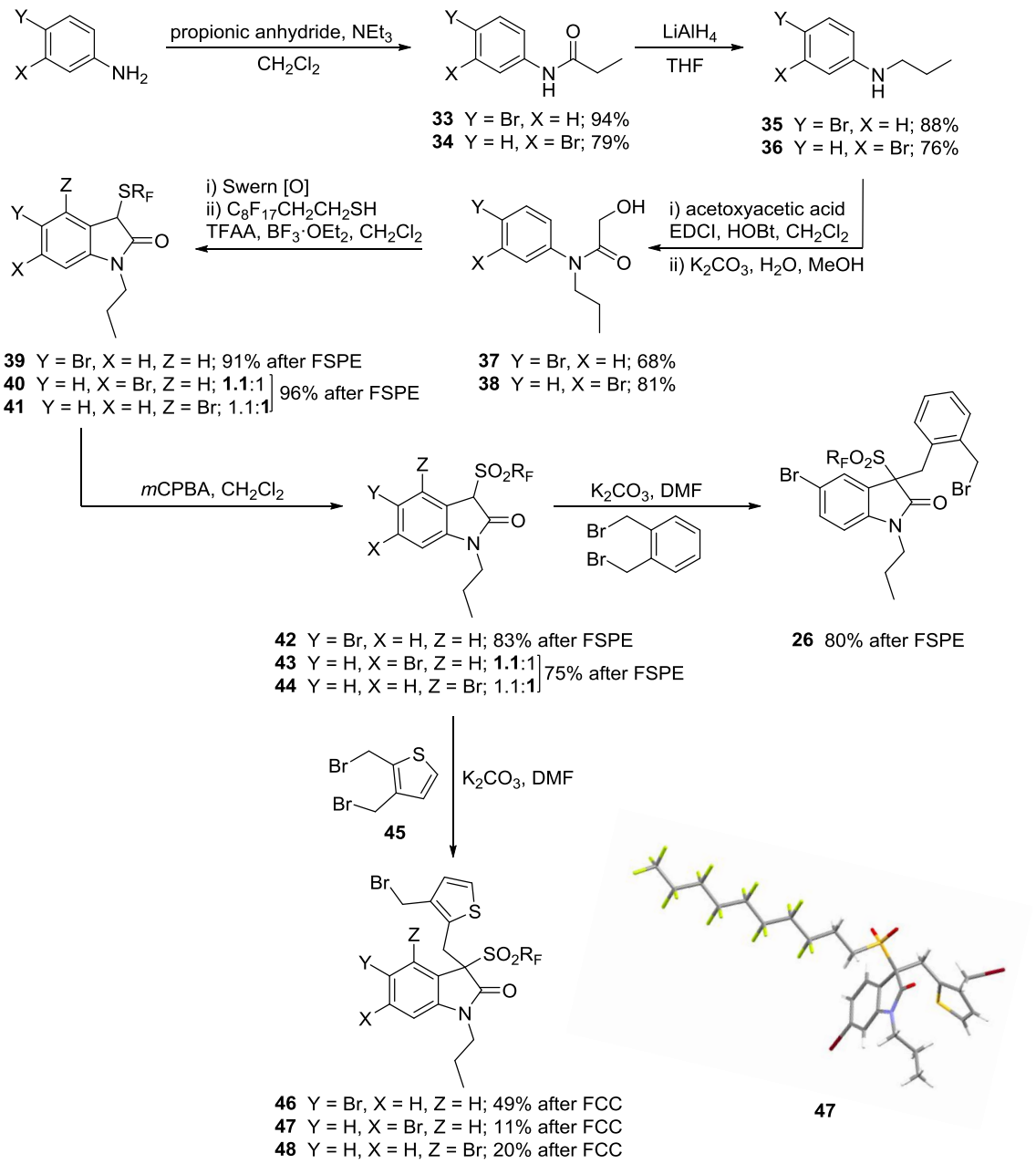


Figure 7 Proposed method to access benzo[*b*]carbazole end-capped oligothiophenes.

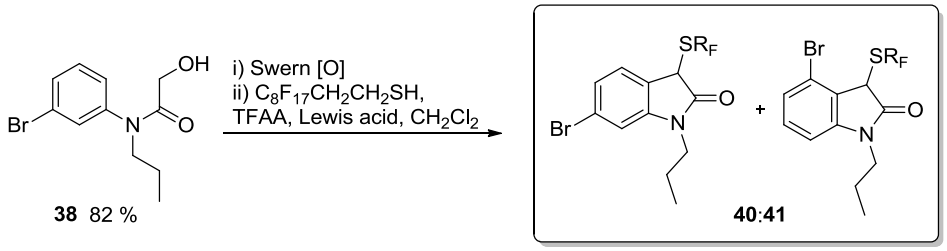
2.2.1 Preparation of substrates for investigation of SmI_2-mediated cleavage–cyclisation cascade

Work began by first synthesising substrates **26**, and **46**, **47**, and **48** in order to study the SmI_2 cleavage-cyclisation reaction. Firstly hydroxyamides **37** and **38** were synthesised in high overall yield from *p*-bromoaniline and *m*-bromoaniline in five steps via amide formation and $LiAlH_4$ reduction, followed by a second amide coupling step and deprotection (Scheme 12). Applying the standard connective-Pummerer cyclisation conditions developed within the Procter group[185] gave the cyclised product **39** in 91% yield after purification by FSPE. Unfortunately the regioselectivity of the Pummerer reaction in the case of substrate **38** was very low [1.1:1; **40**:**41**].



Scheme 12

A brief screen of alternative Lewis acids was then carried out to ascertain whether the regioselectivity could be improved, but in all cases no change in the regioselectivity of the reaction was observed (Table 1). $BF_3{\cdot}OEt_2$ gave the highest yield and the shortest reaction time. It was also found that when no Lewis acid was added the cyclisation did not proceed at all, in contrast to reactions involving glyoxamide substrates with electron donating groups (such as those containing methoxy substituents) on the aromatic ring.[123]



Scheme 13

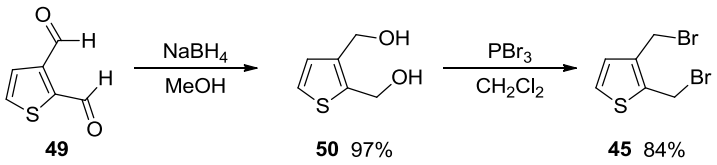
Lewis acid (eq.)	Ratio of regioisomers (**40**:**41**)[a]	Yield / %	Reaction time / hrs after LA addition
None	*No cyclisation observed*	0	24
$BF_3{\cdot}OEt_2$ (2.0)	1.1:1	96	2.5
$Sc(OTf)_3$ (0.2)	1.1:1	81	2.5
$ZnCl_2$ (1.0)	1.1:1	77	17.5

Table 1 Investigation of alternative Lewis acids; [a] Ratio observed by ^{1}H NMR after FSPE.

The fluorous-tagged oxindoles were then oxidised to the sulfone oxidation level using *m*CPBA in good yield following purification by FSPE. The oxindole **42** was then alkylated with 1,2-*bis*(bromomethyl)benzene, or 2,3-*bis*(bromomethyl)thiophene. The alkylation of **42** with 1,2-*bis*(bromomethyl)benzene proceeded to give the desired product **26** in 80% yield following purification by FPSE. The alkylation of **42** with 2,3-*bis*(bromomethyl)thiophene proceeded in good selectivity (~5:1-crude ^{1}H NMR ratio after FSPE) in favour of alkylation of the thiophene at the 2-position. Careful chromatography afforded the desired isomer in 49% yield. The mixture of oxindoles **43** and **44** was also alkylated with 2,3-*bis*(bromomethyl)thiophene to give a mixture of isomers, from which the desired product **47** was isolated in just 10% yield. A single crystal of compound **47** was obtained, from which the regioselectivity of the alkylation with 2,3-*bis*(bromomethyl)thiophene was confirmed by X-ray crystallography (Scheme 12 and Appendix A).

The alkylating agent 2,3-*bis*(bromomethyl)thiophene **45** was itself synthesised in high overall yield from 2,3-thiophenedicarboxaldehyde **49** in two steps via $NaBH_4$ reduction and bromination with PBr_3 (Scheme 14).[186] The final product 2,3-

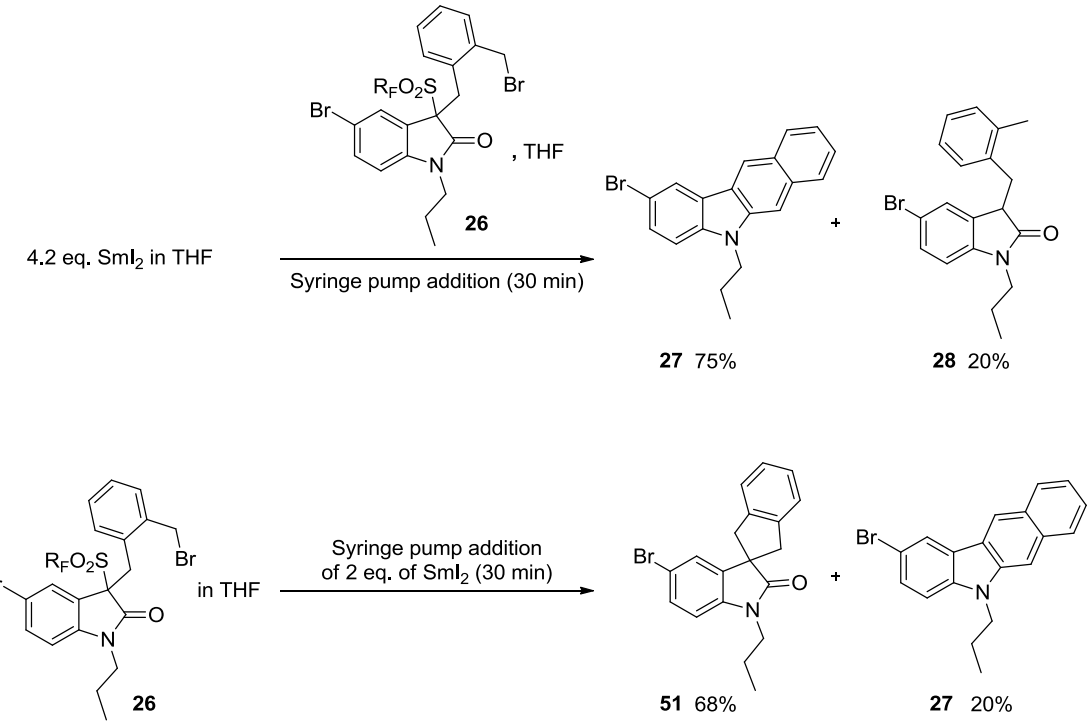
bis(bromomethyl)thiophene **45** was found to readily degrade to form a black insoluble material if left under ambient conditions but could be kept for several months if stored under an inert atmosphere at 0 °C.



Scheme 14

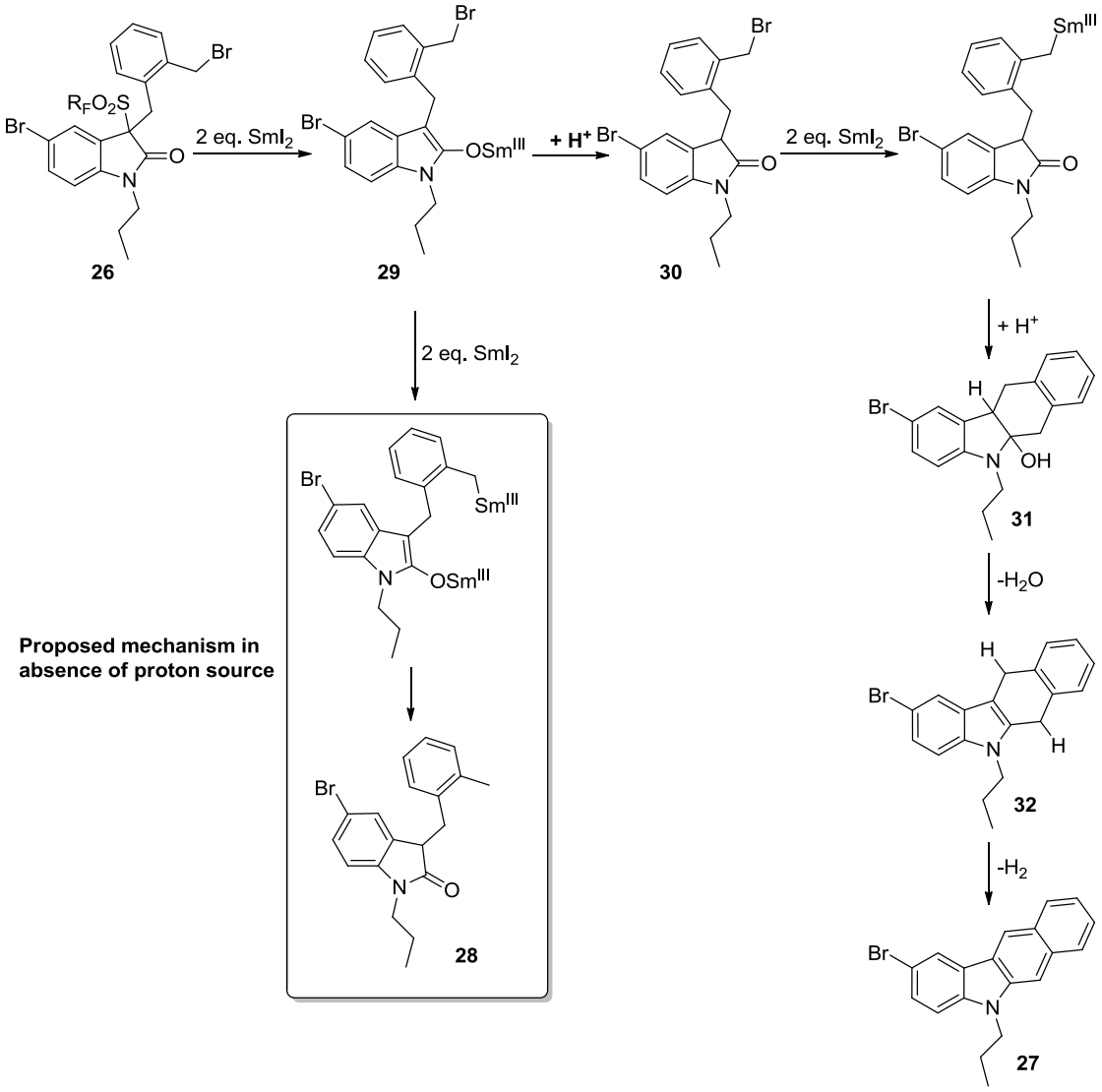
2.2.2 Optimisation of the SmI_2-mediated cleavage–cyclisation reaction

As discussed it was found earlier within the Procter group that slow addition of **26** to 4.2 eq. of SmI_2 proceeded to give the annulated product **27** in good yield (Scheme 8). Conversely, slow addition of 2.2 equivalents of SmI_2 to **26** was found to give the spirocyclised product **51** as the major product (Scheme 8).[121]



Scheme 8

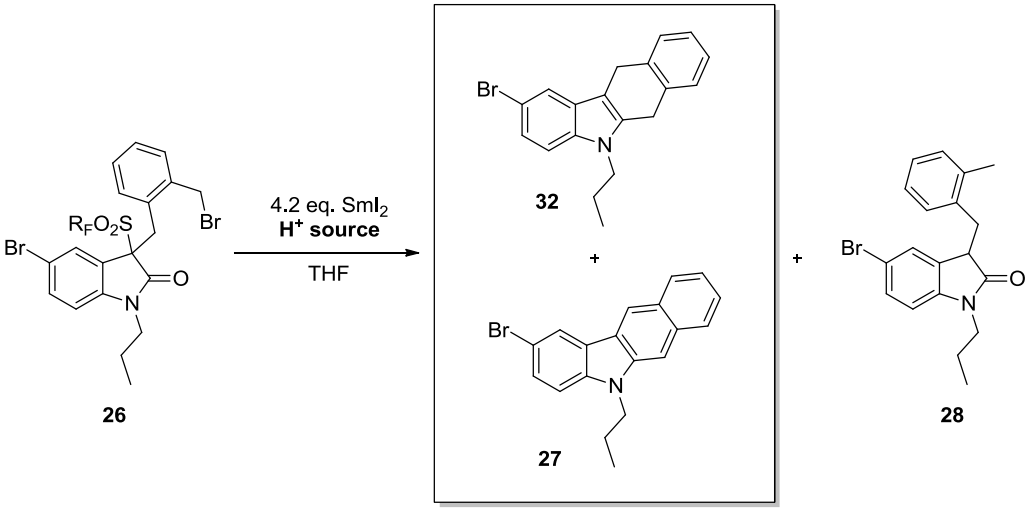
Attempts to repeat this earlier work resulted in complete conversion to the non-cyclised product **28**, with only trace amounts of the desired cyclisation products **27** and **32** observed (Table 2, Entry 1).



Scheme 15

It had previously been proposed that the mechanism for the reaction proceeds via initial reductive cleavage of the fluorous tag to generate Sm(III)-enolate **29**, which is then protonated to regenerate the oxindole carbonyl. It is postulated that this is then followed by generation of a benzylic Sm(III) species which attacks the oxindole carbonyl to generate a cyclised intermediate **31**, which then undergoes dehydration and aromatisation to afford the final benzo[*b*]carbazole product **27**. In this proposed mechanism it was not clear where the proton required for protonation of the Sm(III)-

enolate originates from; H_2O is generated via dehydration of the intermediate **31**, and it was thought that the reaction may possibly proceed due to the presence of trace amounts of water in the reaction mixture. Based on this proposed mechanism it was considered that an additional proton source may be required to protonate the Sm(III)-enolate intermediate efficiently (Scheme 15).



Entry	H^+ Source	Eq. of H^+	[a]Order of Addition	Addition time / min	[b]Ratio **32** + **27**:**28**
1	None	-	1	20	1: > 15
2	Trifluoroethanol	1.0	1	20	1 : 0.9
3	**Trifluoroethanol**	**1.0**	**2**	**20**	**1 : 0.1**
4	*t*BuOH	1.0	1	20	1 : 3.8
5	MeOH	1.0	2	20	1 : 1.0
6	H_2O	1.0	2	20	1 : 0.2
7	Trifluoroethanol	2.0	2	20	1 : 0.3
8	Trifluoroethanol	1.0	2	1	1 : 0.1
9	Trifluoroethanol[c]	1.0	2	20	1 : 0.2

Table 2 Investigation of conditions for the SmI_2-mediated cleavage-cyclisation reaction; [a] 1 = Substrate and trifluoroethanol into SmI_2, 2 = SmI_2 into substrate and trifluoroethanol; [b] Ratios of cyclised products **27** and **32** to non cyclised product **28** measured by ^1H NMR of crude; [c] 0.1 mM instead of 0.02 mM solution of **26**.

A brief screen of conditions revealed that performing the reaction under the standard conditions, but with the addition of 1.0 eq. of trifluoroethanol (TFE) as a proton source led to increased formation of the desired cyclised product **32**, which had cyclised and

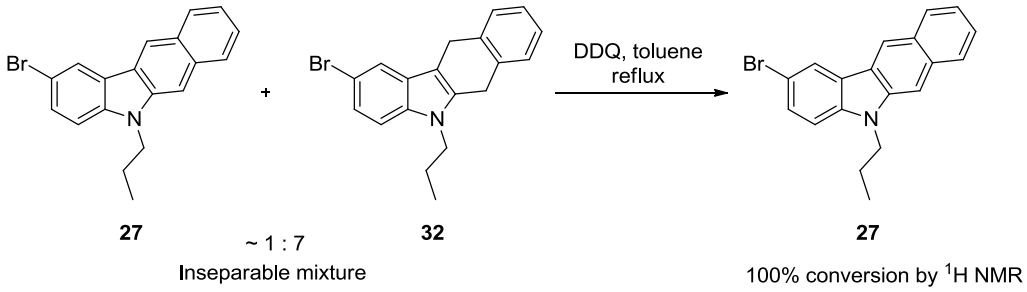
dehydrated, but which had not undergone the final aromatisation step (Table 2, Entry 2). Alongside this compound a trace amount of the aromatised product **27** was observed, along with the non-cyclised impurity **28** (Table 2).

Reversing the order of addition, such that the SmI_2 solution was added to the mixture of trifluoroethanol and substrate resulted in an improved ratio of cyclised to non-cyclised products (Table 2, Entry 3). We also investigated the effect of changing the nature of the proton source; it was found that less acidic proton sources, MeOH and *t*BuOH, gave lower levels of conversion to the cyclised products **27** and **32** (Table 2, Entries 3 and 5). Using H_2O as the proton source gave slightly lower conversion than trifluoroethanol; it is therefore probable that in the initial report detailing this transformation residual water was present in the starting material, sufficient enough to allow the cleavage–cyclisation sequence to proceed (Table 2, Entry 6).

Using a higher number of equivalents of trifluoroethanol gave a slightly lower level of conversion to the desired cyclised product (Table 2, Entry 7). This result gives some support to our proposed mechanism, suggesting that an excess of proton source may interfere with the cyclisation step through quenching of the benzylic organosamarium intermediate. Increasing the rate of addition had a negligible effect on the ratio of cyclised to non-cyclised compounds (Table 2, Entry 8), whereas carrying out the reaction at a higher starting concentration of **26** had a slight negative effect (Table 2, Entry 9).

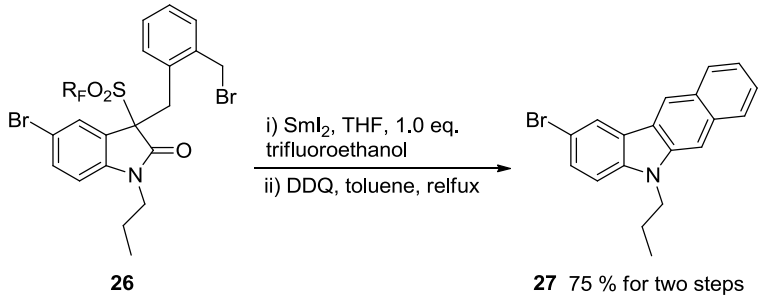
In all cases the majority of the cyclised material was found in the non-aromatised lower oxidation state **32**, with only traces of the fully aromatised product **27** visible by ^{1}H NMR. Attempts to alter the ratio of the aromatised product to non-aromatised intermediate by simply stirring the reaction mixture for prolonged periods of time before and after quenching the SmI_2 with air was tested; however, this failed to affect the ratio of aromatised product to non-aromatised intermediate.

It was then found that aromatisation of intermediate **32** could be brought about cleanly by heating with 1 eq. of DDQ at reflux in toluene (Scheme 16).[178] A control experiment demonstrated that the addition of DDQ was essential.



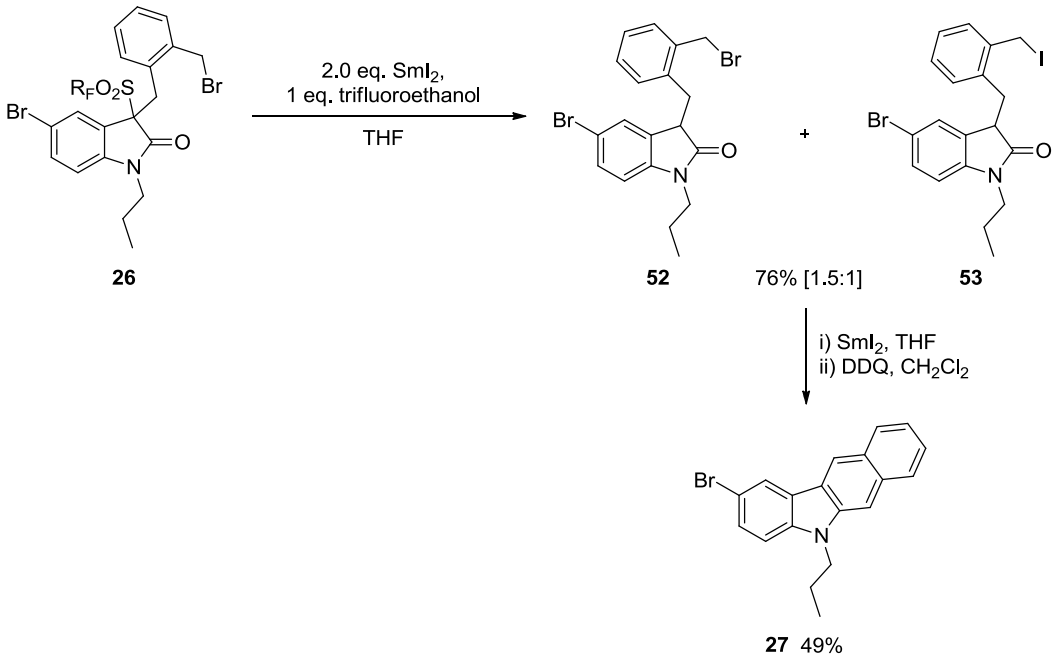
Scheme 16

Although the DDQ oxidation step increases the overall number of steps, it has been shown that both the initial SmI_2 cleavage-cyclisation and DDQ reaction can be carried out efficiently without any purification between the two steps in good overall yield (Scheme 17).



Scheme 17

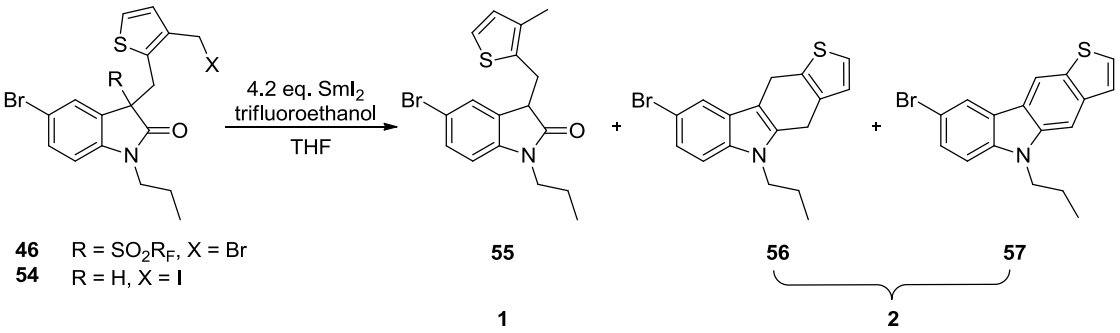
In order to validate the proposed mechanism, the starting material **26** was treated with 2.0 equivalents of SmI_2 in the presence of one equivalent of trifluoroethanol. A mixture of compounds **52** and **53** was obtained in 75% yield (1.5:1 ratio [**52**:**53**]), with the benzylic iodide presumably forming via a Finkelstein reaction.[132,155] It appeared that complete cleavage of the fluorous tag had occurred and the resulting enolate had then been protonated; supporting the proposed mechanism, in which cleavage of the fluorous tag occurs first. It was then demonstrated that this intermediate could be converted through to the fully aromatised product **27** in 49% yield by treatment with 2.1 eq. of SmI_2 in THF, followed by oxidation with DDQ (Scheme 18).



Scheme 18

With a better understanding of the SmI_2-mediated cleavage–cyclisation cascade, the improved conditions were then applied to compound **46**. Unfortunately, all attempts to access the annulated product resulted predominately in the formation of the non-cyclised compound **55,** with only trace amounts of the desired cyclised products **56** and **57** observed (Scheme 19 and Table 3).

Altering several parameters, such as order of addition, rate of addition, and number of equivalents of trifluoroethanol, failed to have any significant effect on the product distribution (Table 3), with the major product always being the non-cyclised compound **55**.

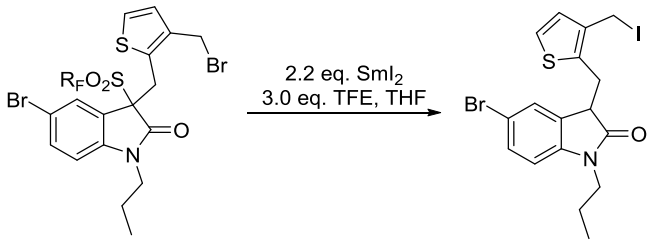


Scheme 19

Entry	Starting material	TFE / eq.	[a]Order of Addition / Conditions	Temp / °C	[b]Ratio **55**:**56** + **57**
1	**46**	1.0	B	20	1:0.1
2	**46**	1.0	B	20	1:<0.1
3	**46**	1.0	A	20	1:0.1
4	**46**	0.5	B	20	1:0.1
5	**46**	0	B	20	1:0.2
6	**46**	1.0	B	0	1:0.2
7	**46**	1.0	A	20	1:0.1
8	**54**	0	B	20	1:<0.1
9	**54**	0	C	20	1:0.7
10	**46**	1.0	C	20	1:<0.1

Table 3 Investigation of conditions for the SmI_2-mediated cleavage-cyclisation reaction; [a] A = Substrate and trifluoroethanol into SmI_2, B = SmI_2 into substrate and trifluoroethanol, C = Substrate and trifluoroethanol added into SmI_2 premixed with 2 mol% NiI_2; [b] Ratios of cyclised products **56** and **57** to non cyclised product **55** measured by ^{1}H NMR of crude.

From these results it was not clear whether the fluorous tag cleavage step or the cyclisation step was causing the problem leading to the undesired non-cyclised product **55**. Using just 2.2 equivalents of SmI_2 in the presence of excess trifluoroethanol it was shown that the tag cleavage step proceeded as expected to give compound **54**, albeit this time with iodine completely substituted for bromine (Scheme 20). The low yield of the de-tagged intermediate is thought to be due to the instability of the iodide during purification, rather than poor conversion as indicated by the crude ^{1}H NMR before purification.



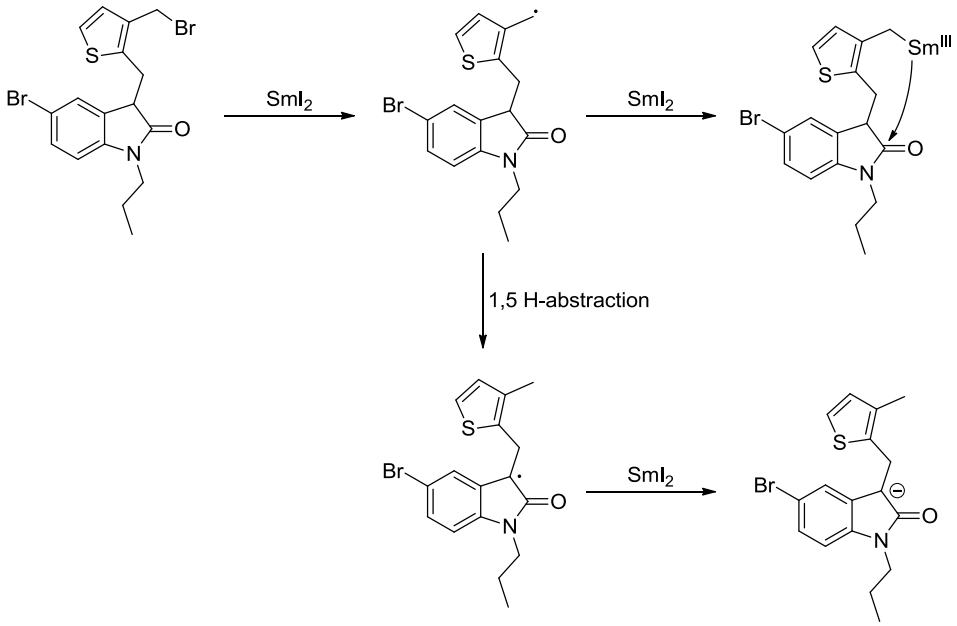
46 **54** 40%

Scheme 20

We then attempted to take this intermediate **54** onwards to give the cyclised product by reacting with 2.2 equivalents of SmI_2; however, this simply led to formation of the over-reduction product **55**, indicating that the formation of the Sm(III)-thienly methyl species and attack at the oxindole carbonyl was not proceeding as desired and was leading instead to the observed unwanted product (Table 3, Entry 8).

It is well known in the literature that the addition of NiI_2 can be used to promote SmI_2-mediated Barbier reactions.[187] Promisingly, when the de-tagged intermediate **54** was treated with SmI_2 and a catalytic amount of NiI_2, an increase in the ratio of the cyclised to non cyclised products was observed (Table 3, Entry 9), albeit the non-cyclised impurity still was the major product. Unfortunately when the analogous one-pot cleavage-cyclisation reaction was attempted in the presence of catalytic NiI_2, no significant improvement was observed (Table 3, Entry 10).

It seems likely that the different product distribution obtained upon treatment with SmI_2 for substrate **46** relative to **26** could be due to the differing stability of the benzylic and thienyl methyl radicals; with the thienylic radical the rate of reduction of the intermediate radical may be slower than competing radical processes (1,5-hydrogen atom abstraction from the indole 3-position or hydrogen atom abstraction from THF), which limits conversion to the thienylic Sm(III) species and thus to the desired cyclisation products (Scheme 21).



Scheme 21

2.3 Synthesis of benzo[*b*]carbazole end-capped oligothiophenes

Initial work had focussed on the synthesis of benzo[*b*]carbazoles with functionality at the 5-position, due to the ease of synthesis of the substrates needed for investigation of the SmI_2-mediated cleavage-cyclisation reaction.

In order to generate a library of linear oligothiophenes it was necessary to generate benzo[*b*]carbazoles with functionality at the 3-position (Figure 9). Since 3-bromoaniline derived substrates were found to give poor selectivity in the connective-Pummerer cyclisation an alternative strategy was required.

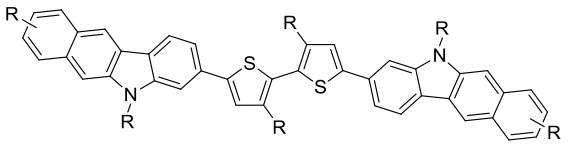


Figure 9 General structure of the target compounds

2.3.1 Option 1-Performing cross coupling prior to connective-Pummerer reaction

Firstly, the possibility of performing Stille cross couplings prior to the connective-Pummerer cyclisation was investigated, in order to establish if the thiophene substituent could be used to direct the connective-Pummerer cyclisation (Figure 10).

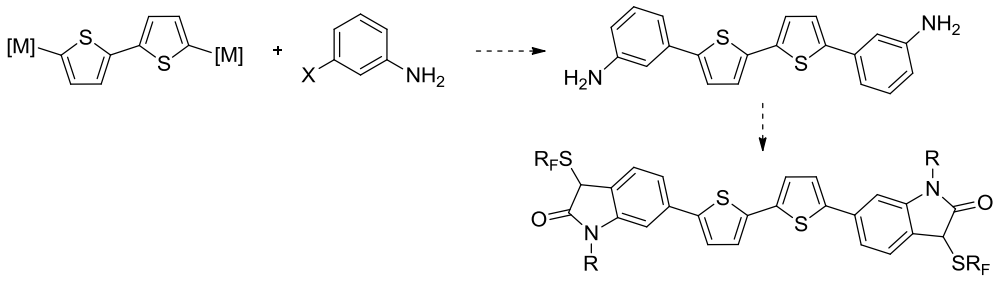
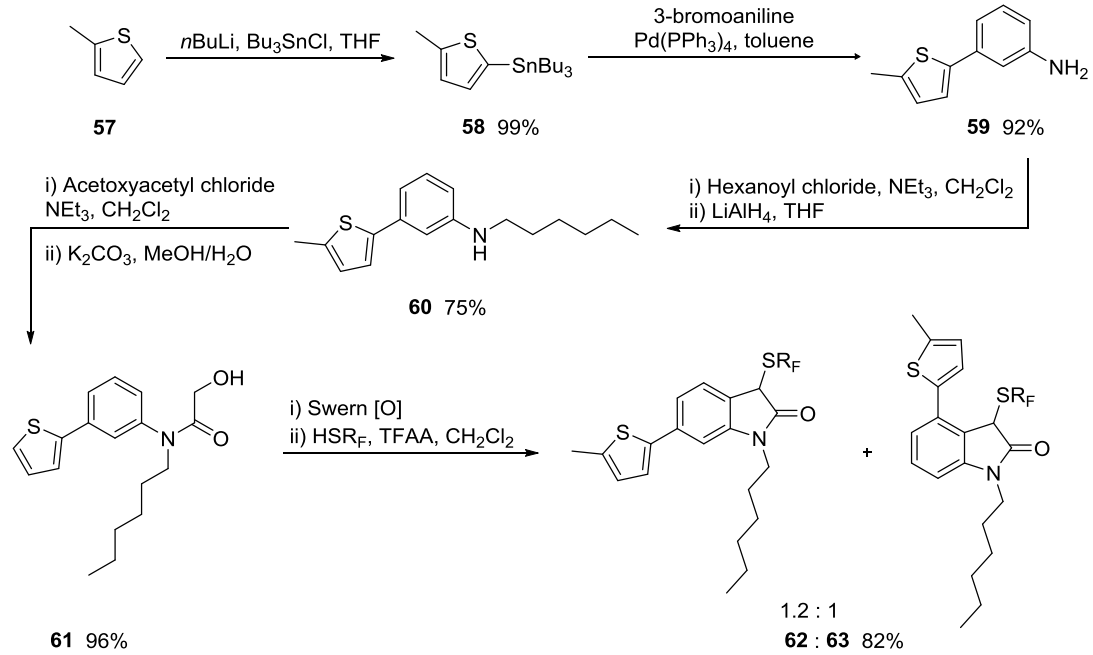


Figure 10 Proposed method of altering the regioselectivity of the Pummerer cyclisation by performing cross coupling prior to the connective-Pummerer reaction.

To investigate the influence of the thiophene linker on the connective-Pummerer cyclisation, 2-methylthiophene was chosen as a model group. Stille cross coupling of **58** with *m*-bromoaniline gave **59** in excellent yield, this was then progressed to give **61** in good overall yield using acetoxyacetyl chloride (Scheme 22). It was found that the connective-Pummerer cyclisation in this instance proceeded without the addition of a Lewis acid, using similar conditions to those developed separately within the Procter group for the cyclisation of electron-rich systems, such as those containing methoxy substituents.[123] Unfortunately, it was found that the thiophene substituent afforded only a slight increase in the regioselectivity of the cyclisation (**62**:**63**, 1.2 : 1 by ^{1}H NMR); therefore, this strategy was not investigated further.



Scheme 22

2.3.2 Option 2-Control of regioselectivity using a protected hydroxyl group

A different strategy utilising a protected hydroxyl group was then investigated. It has been shown previously in the Procter group that a methoxy substituent in the 3-position of aniline derived glyoxamides gives good regioselectivity in the connective-Pummerer cyclisation to deliver oxindoles (typically 5:1 in favour of the desired regioisomer).[123] It was therefore proposed that a protected hydroxyl group such as a PMB or benzyl ether could potentially give similar regioselectivity to that obtained with a methoxy group, whilst allowing for facile coupling through this position later in the synthesis via deprotection and conversion to the corresponding tosylate. With respect to the deprotection step, the employment of a PMB ether was preferred due to the good literature precedent for deprotection of PMB ethers using DDQ,[188] as this would potentially allow us to negate a separate deprotection step by performing deprotection during the DDQ mediated final aromatisation step of our synthesis (Figure 11).

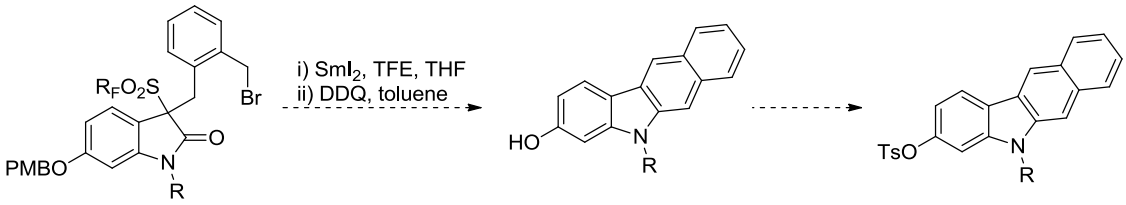
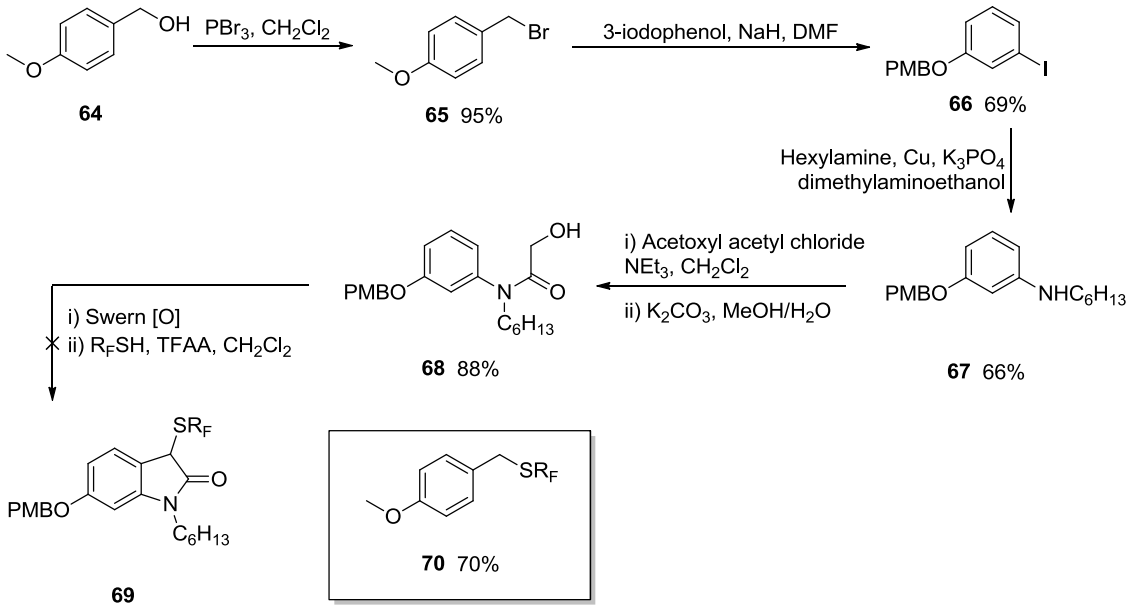


Figure 11 Proposed method of improving the regioselectivity of the Pummerer cyclisation by using a protecting group strategy.

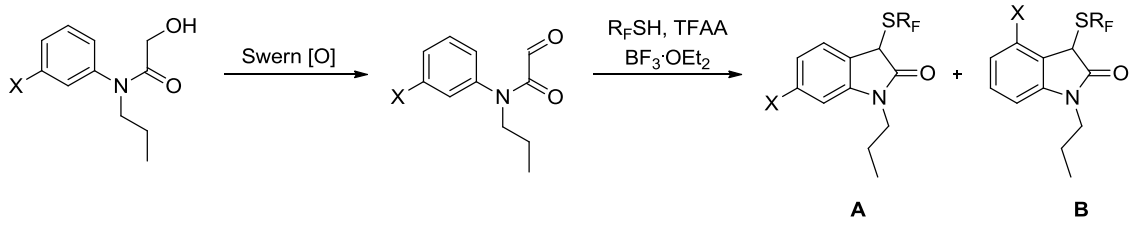
The PMB protected intermediate **67** was synthesised via Ullmann coupling of **66** with *n*-hexylamine in good yield.[189] The intermediate **67** was then taken on to **68** using the previously developed conditions in good overall yield (Scheme 23). Unfortunately under the reaction conditions for the connective-Pummerer step the PMB ether was found to be labile;[190] irrespective of whether a Lewis acid was present or not, the reaction proceeded to give a complex mixture of products from which none of the desired product could be isolated. Compound **70** was isolated as the major product after the reaction, indicating the incompatibility of PMB ethers with our standard connective-Pummerer reaction conditions.



Scheme 23

2.3.3 Option 3-Control of regioselectivity using a Nonaflyloxy group

Separately in the Procter group, Dr Coote had shown the effect of a range of different halogens and pseudo halogens on the regioselectivity of the connective-Pummerer cyclisation (Table 4).[191]



X	Yield / % (2 steps)	Regioselectivity (**A**:**B**)[a]
F	77	13:1
Cl	78	1.5:1
Br	75	1.1:1
I	71	1:2
OTs	69	3:1
ONf	**68**	**4:1**

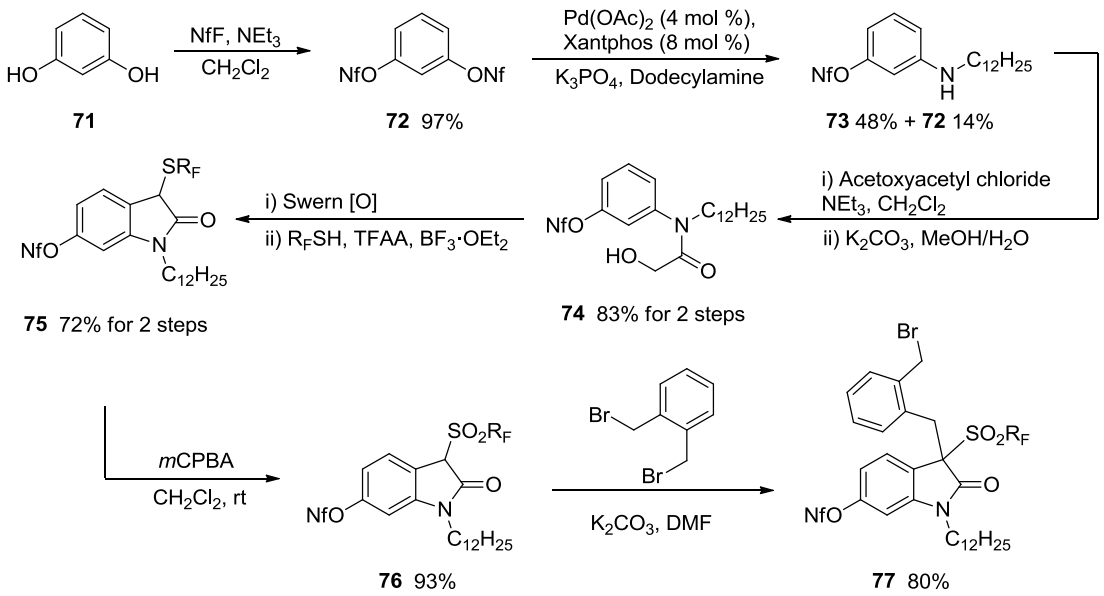
Table 4 The effect of a range of halogens and pseudo-halogens on the regioselectivity of the connective-Pummerer reaction ; [a] Determined by ^{1}H NMR.

The optimum regioselectivity was obtained when either a fluoro or nonaflyloxy substituent was used. Despite the best regioselectivity being observed with the fluoro substituent, the nonaflyloxy-substituted compound was selected as the best candidate for further investigation. The possibility to extend the use of FSPE throughout a larger portion of the route and the wider literature precedent for the final coupling reaction were the deciding factors behind this choice.[95]

2.3.4 Synthesis of nonaflyloxy substituted benzo[*b*]carbazoles

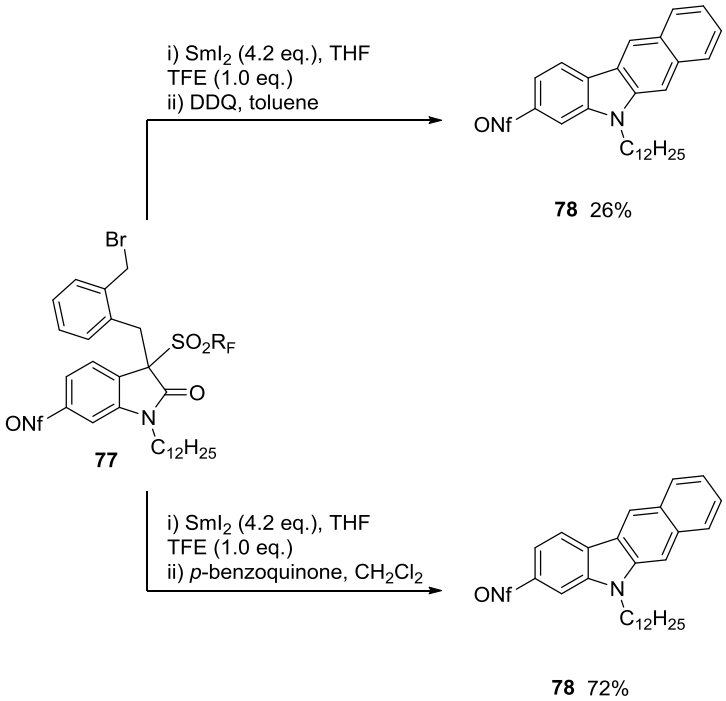
The synthesis of nonaflyloxy-substituted benzo[*b*]carbazoles began with the synthesis of **72** from resorcinol in excellent yield, followed by a palladium catalysed Buchwald-Hartwig amination which proceeded in 48% yield (62% brsm). The optimal reaction time was found to be ~24 h; longer reaction times gave similar yields of product but lower levels of recovered starting material.

The intermediate **73** was then taken onwards to **74** using the previously developed procedure in good overall yield (Scheme 24). The nonaflyloxy group proved to be unstable under the conditions used during the alcohol deprotection, thus reaction times had to be kept to a minimum. The optimal reaction time was found to be 40 min, beyond this the yield of product began to decrease, most probably due to cleavage of the nonaflyloxy-substituent. The Swern oxidation and connective-Pummerer cyclisation proceeded in good yield as expected to give a 4:1 mixture of regioisomers in favour of the desired regioisomer after purification by FSPE. Careful separation of the regioisomers on silica gel gave the desired isomer in 72% yield. The oxidation and alkylation steps proceeded in good yields to give **77** the substrate for the key SmI_2-mediated reaction. Again the reaction time had to be minimised during the alkylation step to avoid cleavage of the nonaflyl group under the basic reaction conditions utilised for the alkylation reaction, with reaction times of 2 hours giving the optimum yield.



Scheme 24

The substrate reacted as expected in the SmI_2-mediated cyclisation; the crude ^1H NMR indicated high conversion to the desired cyclised intermediate; however, treating the non-aromatised intermediate with DDQ in toluene resulted in an overall isolated yield of only 26% for the two steps.



Scheme 25

It was then found that switching to a milder oxidant, *p*-benzoquinone in CH_2Cl_2 gave an improved overall yield of 72% for the two steps (Scheme 25). An attempt to telescope

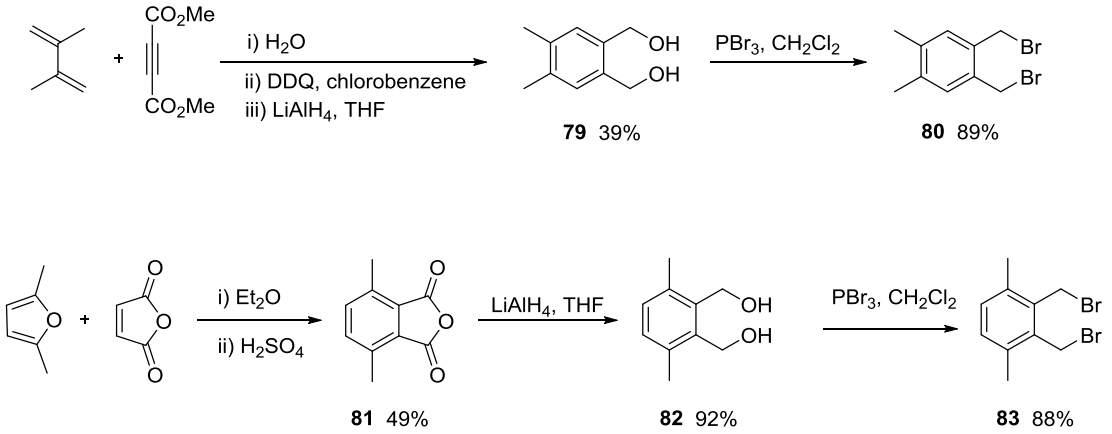
the cleavage–cyclisation and aromatisation steps by adding the *p*-benzoquinone immediately after quenching the SmI_2 proved to be unsuccessful, and it was apparent that a basic aqueous work-up and solvent swap into CH_2Cl_2 was necessary.

2.3.5 Investigation into the scope of the SmI_2-mediated cleavage-cyclisation reaction

In order to investigate the scope of the key SmI_2-mediated reaction, a range of different *ortho*-*bis*(bromomethyl) aromatic compounds were synthesised.

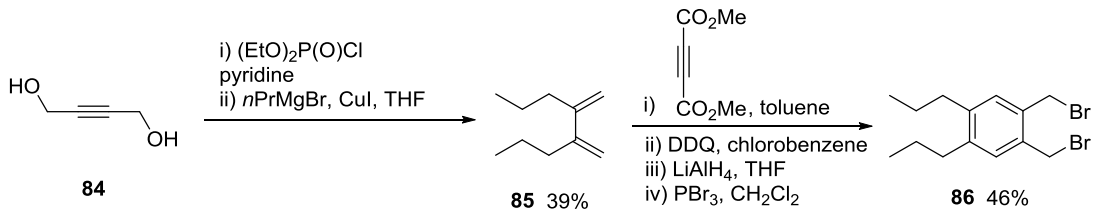
2.3.5.1 Synthesis of *bis*-bromomethylbenzene alkylating agents

The compounds, **80** and **83** were synthesised via initial [4+2] cycloadditions followed by aromatisation, reduction and substitution (Scheme 26).[192] The weakly electron donating methyl groups will alter the electronic properties of the final materials by raising the HOMO energy, and may also provide improved solubility. The two different substitution patterns may additionally alter the packing morphology of the final compounds.[193,194]



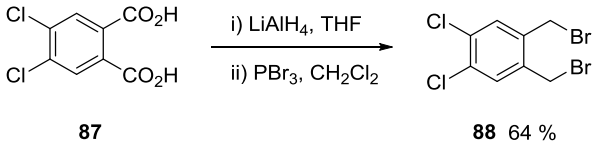
Scheme 26

An extended propyl substituted version of **80** was also synthesised via the same route (Scheme 27). The initial diene **85** was synthesised by Grignard addition to the diphosphate which was in turn synthesised by treatment of **84** with diethyl chlorophosphate in pyridine.



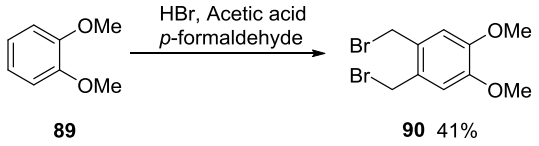
Scheme 27

The chlorinated alkylating agent **88** was also synthesised in two steps via reduction of diacid **87** and bromination in 64% overall yield (Scheme 28). The introduction of chloro-substituents onto acenes has previously been shown to be a valid strategy for achieving good *n*-type transport and ambipolar materials, as well as improving the performance of indolo[3,2-*b*]carbazoles through modification of crystal packing.[195-197]



Scheme 28

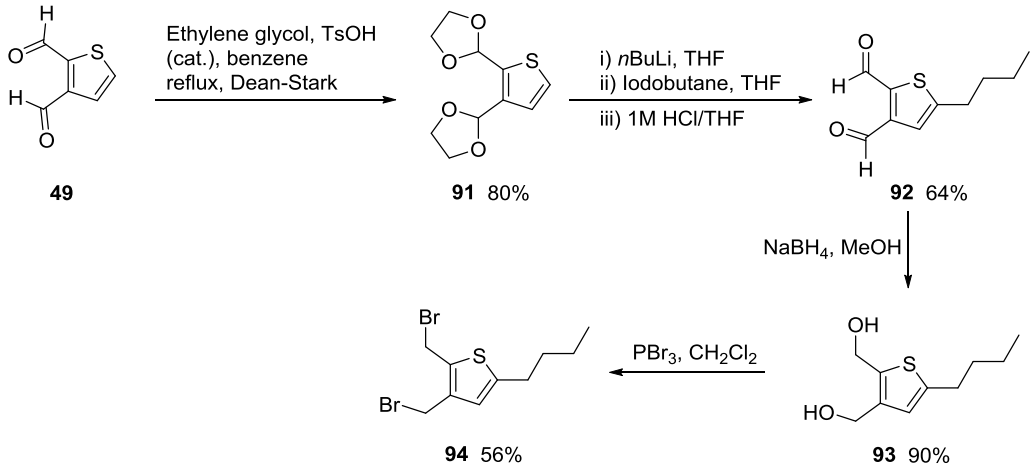
Compound **90** was synthesised in 41% yield via bromomethylation of **89** using paraformaldehyde and HBr in acetic acid (Scheme 29).[198] The addition of electron donating methoxy groups is expected to alter the electronic properties of the final materials by raising the HOMO energy.[56,199] Additionally the possible extension to longer, more solubilising alkoxy groups could affect stacking morphology and give an additional option for increasing the solubility of the final materials.



Scheme 29

The incorporation of a fused thiophene unit into the endcaps would be desirable.[200,201] Since earlier SmI_2-mediated reactions using thiophene containing substrates had been unsuccessful, a modified substrate was investigated possessing a short alkyl chain in order to protect the 2-position and provide another means of controlling solubility. The commercially available starting material **49** was protected and alkylated with iodobutane,

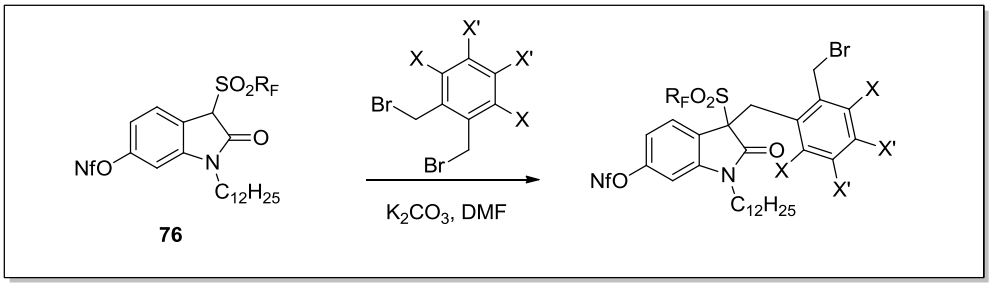
to give **92** in 51% yield after deprotection. The dialdehyde was then reduced to give diol **93**, and then brominated to yield the desired alkyating agent **94** (Scheme 30).[202]

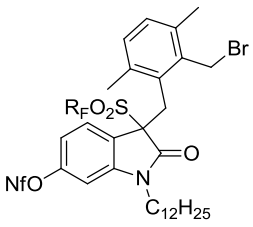


Scheme 30

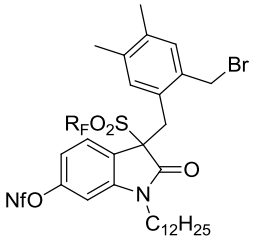
2.3.5.2 Alkylation of fluorous tagged-oxindoles

The alkylation of sulfone **76** with **80**, **83**, **86**, and **88** proceeded to give the desired products in good yields (Scheme 31). All the products were initially purified by FSPE and flash column chromatography on silica gel except for **97** which was obtained in high purity after FSPE only. Compounds **98** and **99** were obtained in low purity after FSPE and displayed poor stability on silica gel, therefore low yields of both products were obtained after purification by flash column chromatography. Unfortunately, the methoxy substituted compound **99** was found to be particularly unstable and attempts to purify this compound using silica gel resulted in complete decomposition.

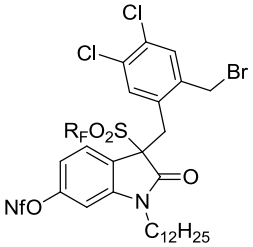




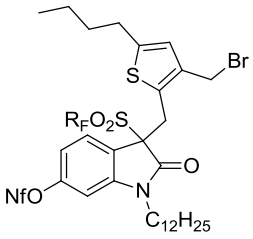
95 73% (FSPE and FCC)



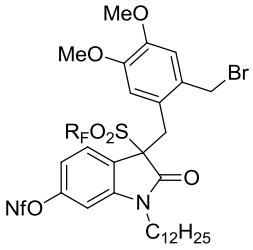
96 74% (FSPE + FCC)



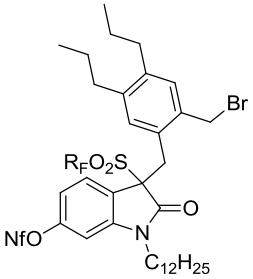
97 84% (FSPE)



98 15% (FSPE and FCC)



99 88% (FSPE), 0% (FCC)



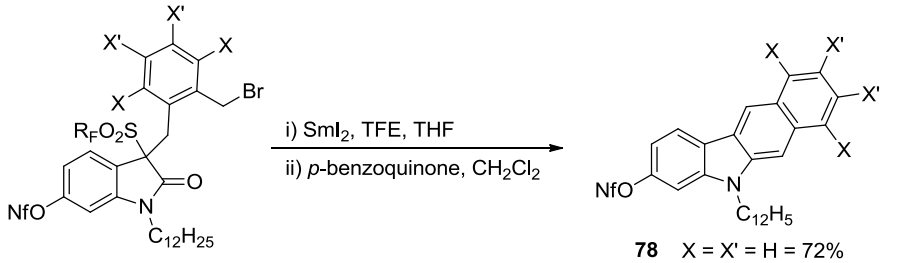
100 74% (FSPE + FCC)

Scheme 31

In the alkylation step, it was necessary to use an excess of the alkylating agent to prevent the formation of dimers. FSPE allows facile separation of this excess alkylating agent from the tagged product mixture and the alkylating agents could be recovered from the non-fluorous FSPE wash in 41-70% yield after an an aqueous work up and column chromatography on silica gel.

2.3.5.3 Investigation of SmI_2-mediated cleavage-cyclisation reaction

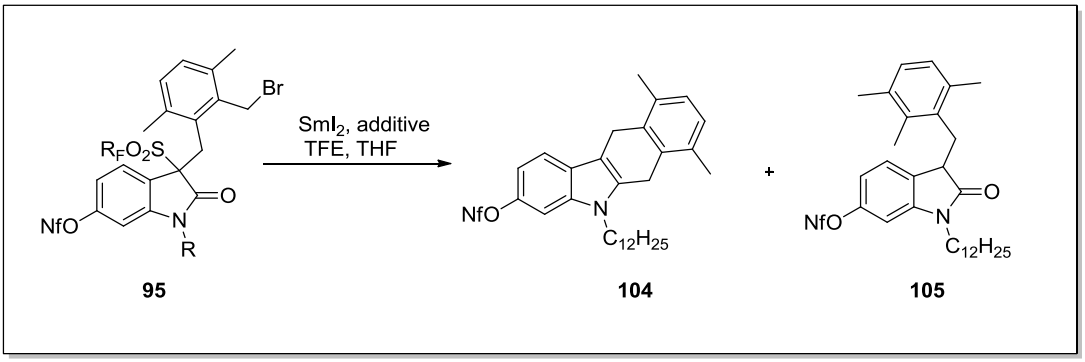
The alkylated intermediates were then subjected to the SmI_2-mediated cleavage-cyclisation reaction conditions. In the case where additional methyl or propyl substituents were incorporated into the final ring (**101**-**103**) the reactions proceeded to give the desired benzo[*b*]carbazoles in moderate to good yields (Scheme 32).



78 X = X' = H = 72%
101 X = CH_3, X' = H = 50%
102 X = H, X' = CH_3 = 79%
103 X = H, X' = C_3H_7 = 69%

Scheme 32

In the case of compound **101,** the reaction initially gave the desired product in just 29% yield. A brief screen of alternative conditions revealed that increasing the reaction temperature and speed of addition of SmI_2 led to an increase in the ratio of cyclised product to non-cyclised by-product observed in the crude ^{1}H NMR after the first SmI_2-mediated step, giving the product in an overall yield of 50% for two steps (Table 5).

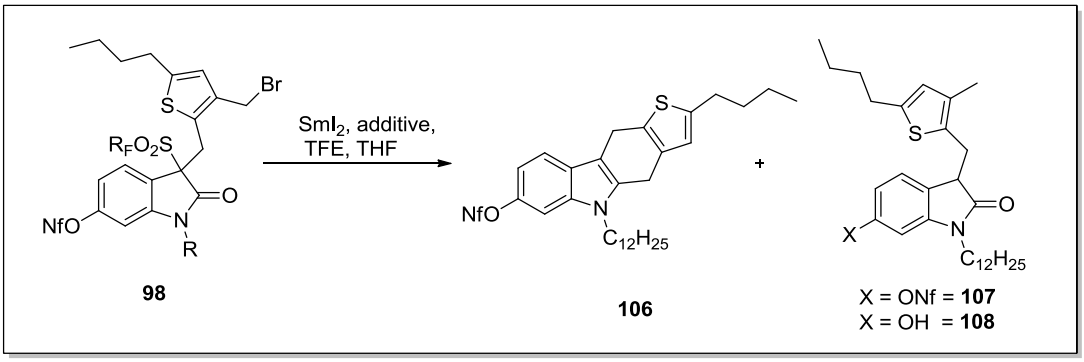


95 **104** **105**

Conditions	**104**:**105**[a]	**101** / %[b]
0 °C / 1 min	1:1.0	37
rt / 1 min	1:0.7	43
50 °C / 1 min	**1:0.6**	**50**
rt / 20 min	1:1.1	29

Table 5 Optimisation of conditions for the SmI_2-mediated cleavage-cyclisation reaction; [a] Ratio of **104**:**105** determined by ^{1}H NMR of crude; [b] Isolated yield of **101** after oxidation with *p*-benzoquinone.

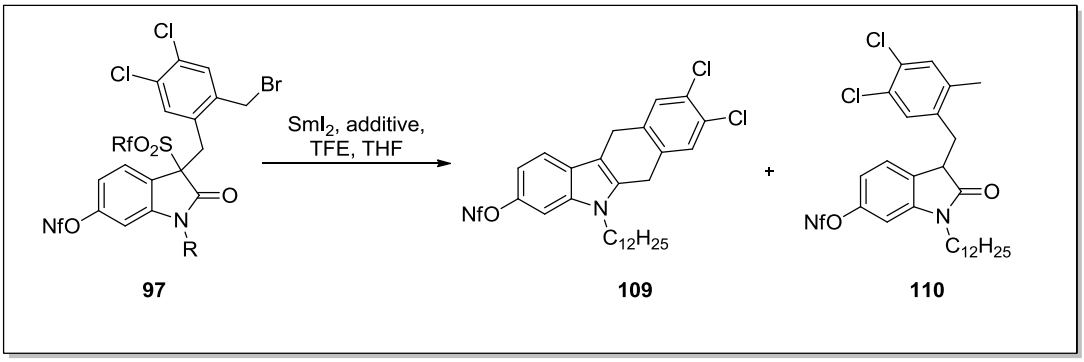
Unfortunately, with substrates **97** and **98**, only traces of the desired products were observed. Instead the non-cyclised by-product was observed as the major product, where cleavage of the fluorous tag and bromine had occurred without cyclisation.



Conditions	**106** / %[a]	**107** / %[a]	**108** / %[a]
No additive	-	69	-
LiCl (72 eq.)	-	35	23
LiBr (72 eq.)	-	-	63
NiI_2 (2 mol%)	**12**	**64**	**-**
HMPA (8.5 eq.)	-	44	-

Table 6 Investigation of the effects of additives on the SmI_2-mediated cleavage-cyclisation; [a] Isolated yield.

Alternative conditions for the cyclisation of substrate **98** were then investigated (Table 6). LiBr, LiCl, NiI_2 and HMPA were examined to see their effect on the reaction. The reactions again failed to give the cyclised product, with the additional additives having no significant beneficial effect. In the presence of LiCl and LiBr only non-cyclised products **107** and **108** were observed after column chromatography. Notably, with LiCl and LiBr, cleavage of the nonaflate group was also observed. In the presence of catalytic NiI_2, a small increase in the amount of the cyclised product **106** was observed.



97 109 110

Conditions	**109** / %[a]	**110** / %[a]
No additive	-	60
NiI_2 (3 mol%)	-	63
$Fe(DBM)_3$ (1 mol%)	-	60

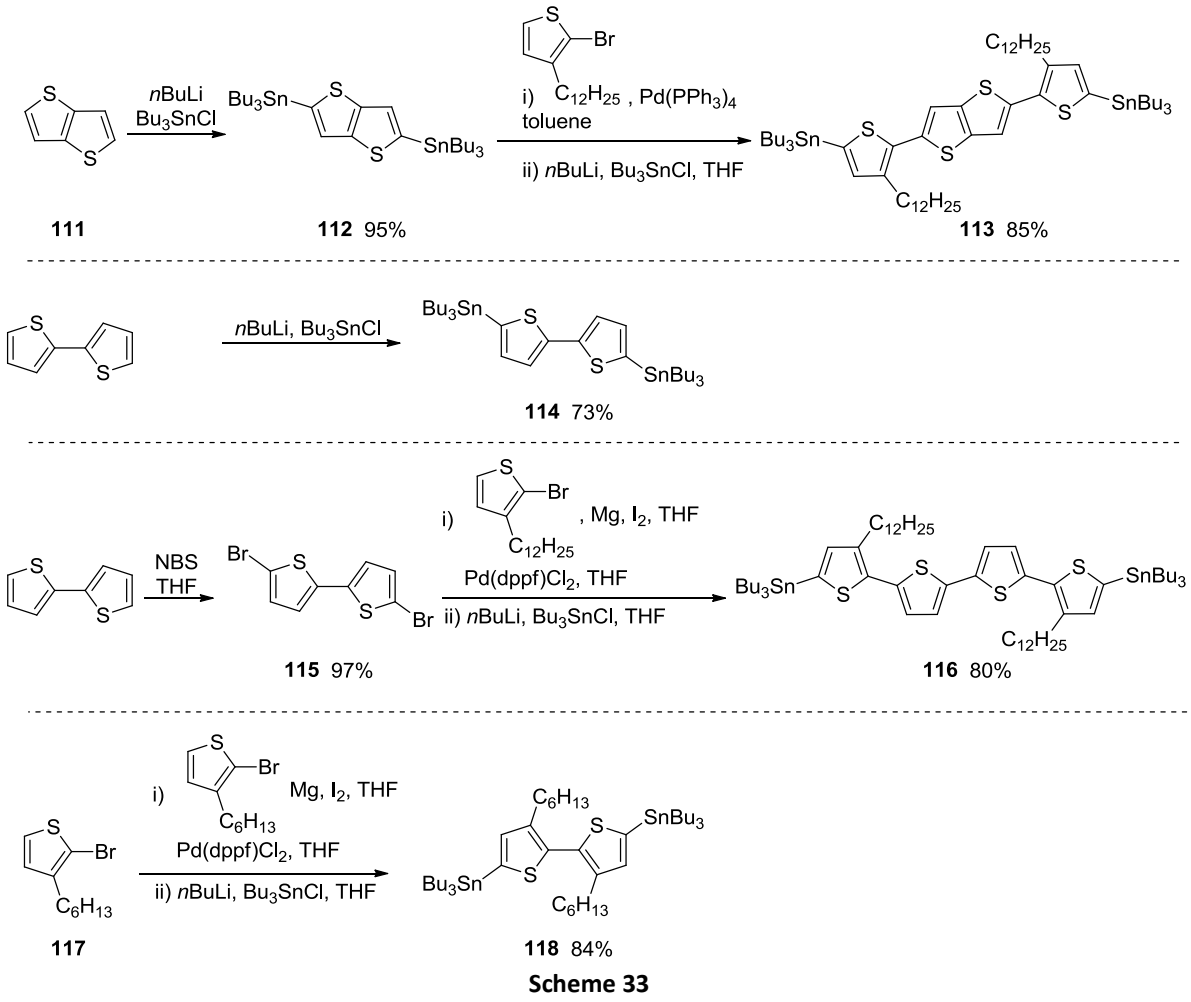
Table 7 Optimisation of conditions for the SmI_2-mediated cleavage-cyclisation reaction; [a] Isolated yield

Similarly with substrate **97**, the addition of NiI_2 and $Fe(DBM)_3$ failed to offer any improvement in conversion to the cyclised products (Table 7).

2.3.6 Synthesis of benzo[*b*]carbazole end-capped thiophenes

2.3.6.1 Synthesis of thiophene-based linkers

Next a range of oligothiophene linkers were synthesised with which to couple the nonaflyloxy-benzo[*b*]carbazoles. Five different linkers (Scheme 33) were synthesised, all using standard literature procedures,[75,203-212] differing in the number of thiophene units incorporated and in the degree of ring fusion of the central two rings. Solubilising alkyl chains were incorporated onto the longer linkers in order to improve solubility.



Scheme 33

2.3.6.2 Stille cross couplings to generate a library of end-capped oligothiophenes

The nonaflyloxy-functionalised benzo[*b*]carbazoles were then combined with the thiophene-based linkers using standard conditions for the Stille cross coupling of aryl sulfonates.[213,214] Heating the corresponding benzo[*b*]carbazole and stannane in the presence of $Pd(PPh_3)_4$ and LiCl in DMF pleasingly yielded a range of the desired end-capped oligothiophenes in 63-82% yield (Figure 12). The materials were isolated by precipitation from the reaction mixture by the addition of MeOH. The compounds were then purified by recrystallisation, except for **119**, **120**, and **121**, which were sufficiently soluble to allow for an initial purification step using flash column chromatography prior to recrystallisation.

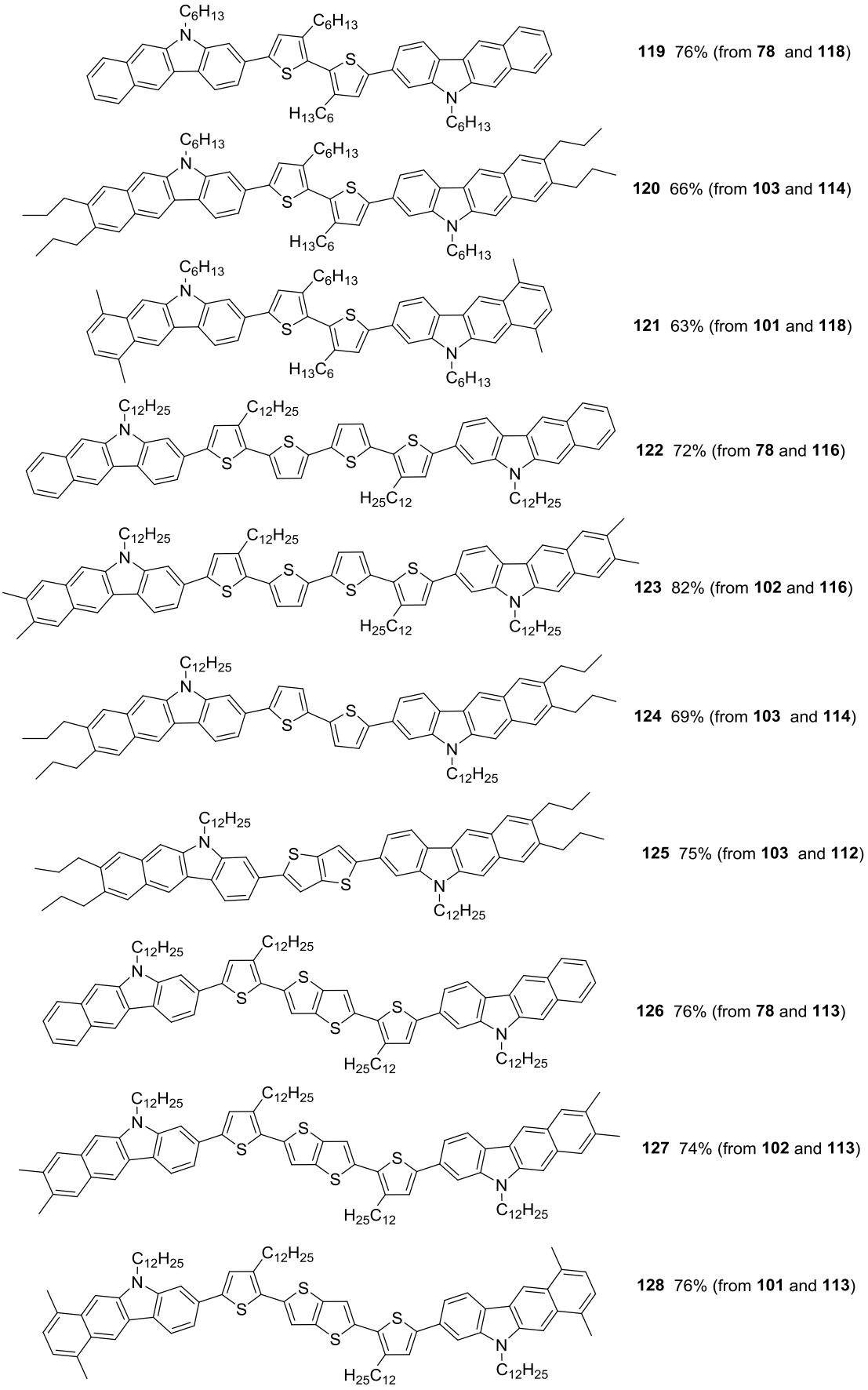


Figure 12 Synthesis of Benzo[*b*]carbazole end-capped oligothiophenes. Conditions: Benzo[*b*]carbazole (2 eq.), stannane (1 eq.), $Pd(PPh_3)_4$ (2 mol%), LiCl (1 eq.), DMF, 110 °C, 24 h.

2.4 Physical properties of benzo[*b*]carbazole end-capped oligothiophenes

2.4.1 Optical and electronic properties

The optical and electrochemical properties of the end-capped oligothiophenes were examined by UV-Vis absorption spectroscopy and cyclic voltammetry.

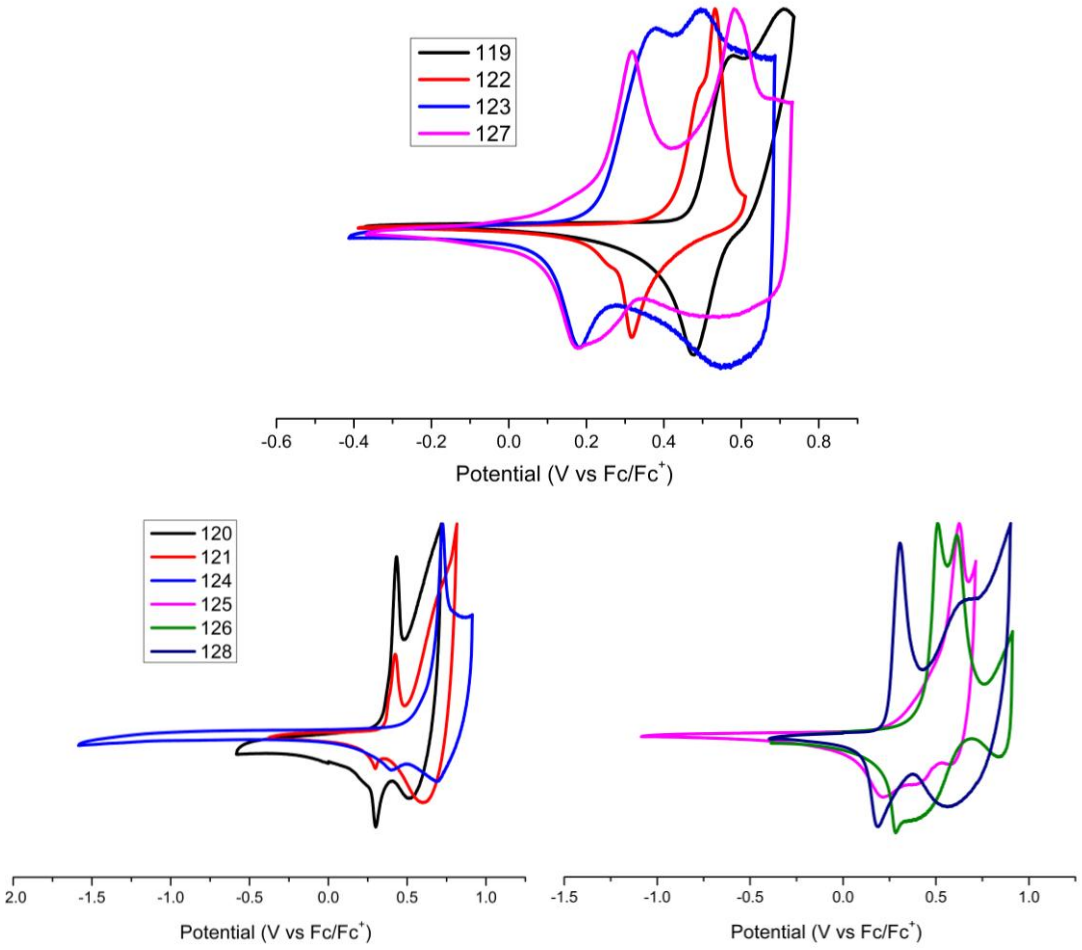


Figure 13 Cyclic voltammograms of compounds **119**-**128**. Cyclic voltammetry was performed using a scan speed of 100 mVs^{-1}, a supporting electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate in MeCN, a Pt wire counter electrode, an $Ag/AgNO_3$ reference electrode and a Pt foil working electrode upon which the compounds to be measured were spin coated from a 1% w/w solution of toluene to give a thin film.

Cyclic voltammetry was undertaken using spin coated thin films on platinum foil as the working electrode and $Ag/AgNO_3$ as the reference electrode in an MeCN solution containing 0.1 M $TBAPF_6$ as a supporting electrolyte. The redox behaviour was referenced against ferrocene (Fc) as an internal standard, and HOMO energy levels were

then calculated using the equation E_{HOMO} (eV) = -(5.1 + E_{Ox} - $E_{Fc/Fc+}$).[215] The estimated HOMO levels all lie in the range -5.3 to -5.6 eV, which suggests good stability under ambient conditions. The addition of alkyl substituents on the outermost rings has the effect of raising the HOMO energy level (Figure 13, **122** and **123**), as does extension of the thiophene-based linker (Figure 13, **119** and **122**), whilst the incorporation of fused rings in the linker has limited impact (Figure 13, **123** and **127**).

Solution UV-Vis spectra of the compounds are shown in Figure 14. As expected, a red shift is observed upon extension of the central oligothiophene linker (Figure 14, **119** and **122**), while the addition of alkyl substituents has neglible impact on the appearance of the spectra (Figure 14, **122** and **127**). Optical band gaps were calculated from the absorption onset (λ_{onset}), and LUMO energy levels were estimated using the equation E_{LUMO} (eV) = E_{HOMO} (eV) + E_g (eV). The low intensity peak observed for compound **123** is not thought to be significant (Fig 14).

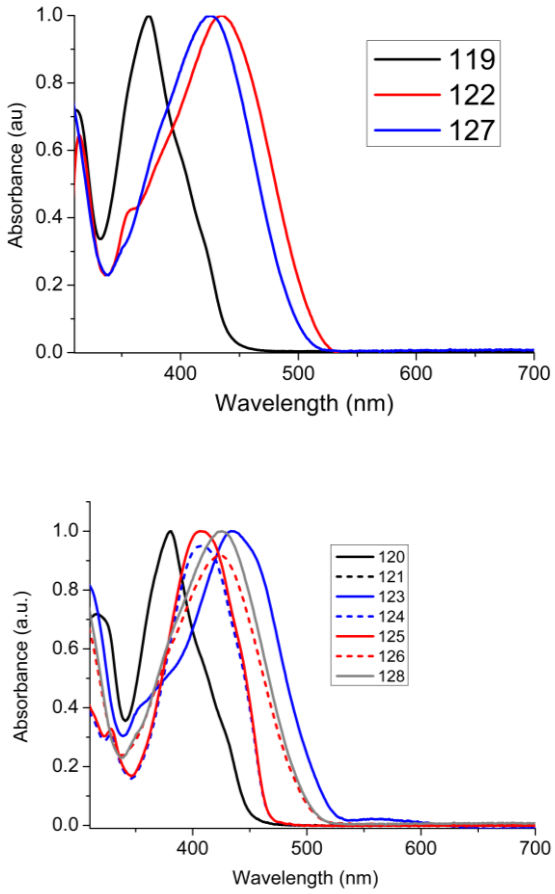


Figure 14 UV-Vis spectra of compound **119**-**128.**

The optical and electrochemical properties of **119**-**128** are collated in Table 8. Good agreement between the HOMO energies estimated experimentally from cyclic voltammetry and those estimated computationally by Dr Iain Grace was observed (Table 8).

Compound	HOMO / eV[a]	LUMO / eV[b]	HOMO calc[c]	LUMO calc[c]	λ_{onset} / nm[d]	E_g / eV[e]
119	-5.57	-2.76	-5.60	-1.29	442	2.81
120	-5.46	-2.70	-5.46	-1.18	450	2.76
121	-5.45	-2.69	-5.52	-1.25	450	2.76
122	-5.52	-3.12	-5.37	-1.53	517	2.40
123	-5.35	-2.96	-5.26	-1.91	518	2.39
124	-5.60	-3.06	-5.48	-1.26	489	2.54
125	-5.61	-2.94	-5.54	-1.14	465	2.67
126	-5.54	-3.05	-5.42	-1.43	498	2.49
127	-5.34	-2.86	-5.31	-1.43	499	2.48
128	-5.39	-2.91	-5.34	-1.48	500	2.48

Table 8 Optical and electrochemical properties of **119**-**128**; [a] Calculated using E_{HOMO} (eV) = -(5.1 + E_{Ox} - $E_{Fc/Fc+}$); [b] Calculated using E_{LUMO} (eV) = E_{HOMO} (eV) + E_g (eV); [c] Calculated using DFT, by Dr I. Grace [See SI of *Org Lett*, **2012**, 5744 for a discussion of the method used in the calculations]; d Obtained by UV-Vis spectroscopy of a dilute solution of the compound of interest in CH_2Cl_2; [e] Calculated from the absorption onset using $E=hc/\lambda_{onset}$.

2.4.2 Thermal properties

Thermogravimetric analysis indicated that all the materials possessed good thermal stability, with onsets of decomposition (T_{onset}) all occurring above 400 °C under an inert nitrogen atmosphere (Table 9).

Further analysis of the thermal properties of the oligomers was carried out by DSC (Figure 15). Compounds **119**, **122**, **123**, **125**, **126**, and **127** all showed single melting point transitions in the range 160–220 °C. Compounds **120** and **121** appeared to be amorphous and did not crystallise upon cooling after the initial heating and cooling cycle and no further endotherms or exotherms were observed on further cycling. Compound **124** showed polymorphic behaviour, displaying two endothermic transitions, a melting

transition at 211 °C and an additional transition at 186 °C. Compound **128** also showed polymorphic behaviour, exhibiting an initial cold crystallisation peak followed by two endothermic melting transitions separated by an exothermic crystallisation.

Compound	Decomposition T_{onset} / °C
119	455
120	436
121	437
122	467
123	437
124	484
125	469
126	443
127	444
128	443

Table 9 Thermogravimetric analysis of compounds **119**-**128**; Measured at a heating rate of 10 °C/min under a flow of N_2.

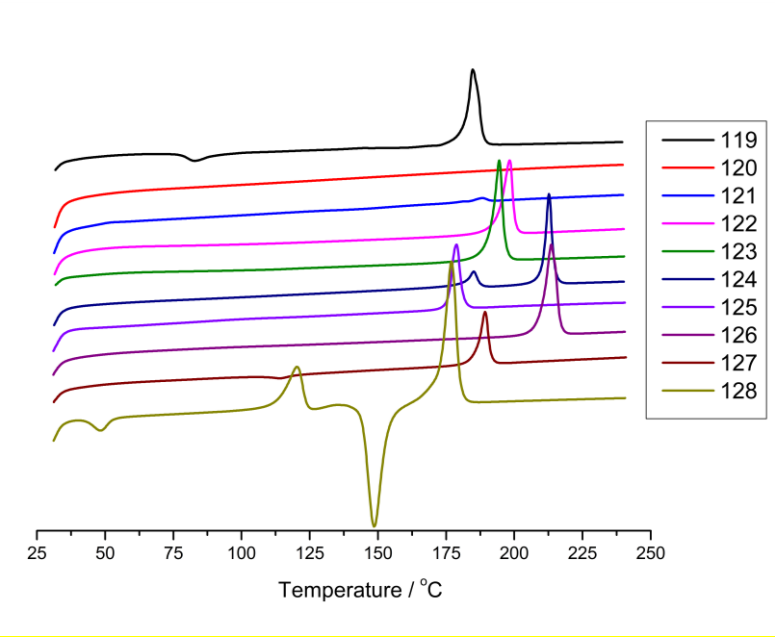


Figure 15 DSC traces of compounds **119**-**128** showing the seconding heating scan; Measured at a heating rate of 10 °C/min under a flow of N_2.

2.5 OFET Devices based on benzo[*b*]carbazole end-capped oligothiophenes

2.5.1 Investigation of device fabrication conditions

The fabrication of OFET devices by both drop casting and spin coating onto a selection of substrates with different dielectric layers (SiO_2 and OTS-SiO_2) was investigated. The effect of the processing solvent, spin speed and duration, substrate temperature, and annealing temperature were also investigated. Initial studies of device fabrication were carried out using compound **123** and the findings from this work were used to guide the fabrication of devices based on the other compounds in the set. All the devices were constructed in a top-contact geometry as this has been shown to generally yield higher performing devices.[31]

Firstly compound **123** was dissolved in a selection of suitable solvents (TCE, *o*-DCB, $CHCl_3$, and *o*-xylene) to give 0.5% w/w solutions. To obtain complete solutions it was necessary to heat the initially formed suspensions.

The first attempts to produce thin films from solution indicated that spin coating of the material produced much better quality continuous films. Drop casted films from $CHCl_3$ or *o*-DCB onto bare SiO_2 and OTS-SiO_2 at room temperature and with a heated substrate unfortunately gave discontinuous films from which no working devices could be obtained.

Spin coating from *o*-DCB and *o*-xylene onto bare SiO_2 and OTS-SiO_2 failed to give thin films with the solution not effectively wetting the substrate surface under a range of spin speeds. Switching to $CHCl_3$ allowed films to be obtained on OTS-SiO_2 using a room temperature substrate and on SiO_2 at a range of temperatures, whilst TCE solutions gave films on SiO_2 only. The charge mobility observed was found to be higher using $CHCl_3$ as the deposition solvent compared to TCE (Table 10, Entries 1 and 8).

The effect of heating the substrate immediately prior to the deposition was also investigated. The optimal temperature was found to be 65 °C, presumably because at

lower temperatures the OSC quickly precipitates out of solution upon contact with the lower temperature surface, and at higher temperatures faster loss of solvent via evaporation occurs which would also lead to the material rapidly precipitating (Table 10, Entries 7, 9, and 12).

	Solv. (temp. / °C)	Sub. temp.[a] / ° C	Dielec.	Spin sp. / rpm (dur. / min)	Anneal temp.[b] / °C	μ / $cm^2 Vs^{-1}$ [d]	I_{on}/I_{off}	V_T / V	Hyst. / V
1	TCE (65)	65	SiO_2	3000 (3)	100	1.33×10^{-2} ($\pm 3 \times 10^{-3}$)	5×10^4	-13	4
2	$CHCl_3$ (60)	100	SiO_2	2000 (2)	60	7.09×10^{-3} ($\pm 2 \times 10^{-4}$)	5×10^3	-2	1
3	$CHCl_3$ (60)	100	SiO_2	2000 (2)	100	1.13×10^{-2} ($\pm 2 \times 10^{-3}$)	6×10^3	-1	1
4	$CHCl_3$ (60)	100	SiO_2	2000 (2)	140	1.79×10^{-2} ($\pm 4 \times 10^{-3}$)	7×10^3	-6	2[e]
5	$CHCl_3$ (60)	100	SiO_2	2000 (2)	180		Film melted		
6	$CHCl_3$ (60)	100	SiO_2	4000 (2)	100	1.25×10^{-2} ($\pm 3 \times 10^{-3}$)	4×10^4	-3	1
7	$CHCl_3$ (60)	100	SiO_2	5000 (2)	100	1.54×10^{-2} ($\pm 3 \times 10^{-4}$)	7×10^3	-6	2
8	**$CHCl_3$ (60)**	**65**	**SiO_2**	**3000 (3)**	**100**	**2.26×10^{-2} ($\pm 3 \times 10^{-3}$)**	**2×10^3**	**-15**	**2**
9	$CHCl_3$ (60)	65	SiO_2	5000 (3)	100	2.56×10^{-2} ($\pm 3 \times 10^{-3}$)	8×10^3	-24	6[e]
10	$CHCl_3$ (60)	25	OTS	3000 (3)	100	2.05×10^{-2} ($\pm 1 \times 10^{-2}$)	1×10^4	-11	2[e]
11	$CHCl_3$ (60)	25	SiO_2	3000 (3)	100	6.68×10^{-3} ($\pm 1 \times 10^{-3}$)	2×10^3	-23	4
12	$CHCl_3$ (60)	25	SiO_2	5000 (3)	100	1.13×10^{-2} ($\pm 1 \times 10^{-3}$)	4×10^3	-18	3
13	$CHCl_3$ (60)[c]	25	SiO_2	3000 (3)	100	4.95×10^{-3} ($\pm 2 \times 10^{-4}$)	2×10^3	-14	3

Table 10 Optimisation of device fabrication conditions; Device fabrication and analysis performed under dry conditions under an atmosphere of N_2; All solutions used were 0.5% w/w of 123 concentration except where specifically noted; [a] Substrate heated at stated temperature in oven immediately prior to deposition of OSC solution; [b] Annealing performed for 1 h, followed by a slow cool at 10 °C per 10 min; [c] 1% w/w solution of OSC; [d] Values are based on the average of the three best performing devices assessed by mobility; [e] Devices functioning improperly-inconsistent device performance.

The effect of annealing temperature on device performance was also studied. An annealing temperature of 100 °C gave the optimal performance, with an annealing temperature of 140 °C giving inconsistent transfer characteristics and improperly functioning devices. Higher temperatures (>160 °C) were found to cause melting of the films (Table 10, Entry 5).

Using an OTS-SiO_2 dielectric layer gave inconsistent results with bad transfer characteristics making the extraction of accurate mobilities impossible (Table 10, Entry 10). Increasing the concentration of the solution of OSC from 0.5% w/w to 1% w/w was found to lead to lower performance as a result of faster precipitation of the material from solution upon contact with the substrate (Table 10, Entry 13).

The best performing devices displayed a mobility of 2.26×10^{-2} cm^2 Vs^{-1} (Table 10, Entry 8 and Figure 16) is similar to values observed for closely related solution processed acene end-capped oligothiophenes in the literature such as **13** (3.1×10^{-2} cm^2 Vs^{-1} [See Figure 4]).

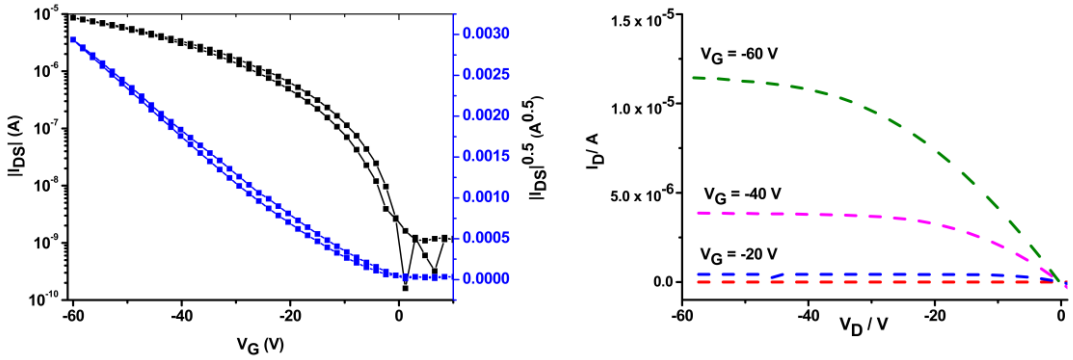
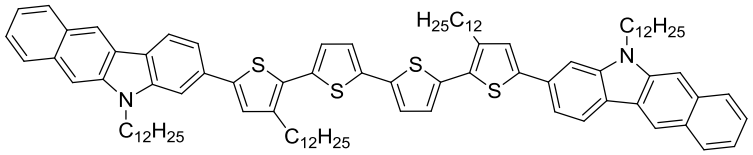


Figure 16 Transfer (left) and output (right) curves for compound **123** (Table 10, Entry 8).

2.5.2 Summary of device performance of benzo[*b*]carbazole end-capped oligothiophenes

Devices based on compound **122** were fabricated using a 0.4 % w/w solution in TCE (Table 11). The lower solubility of compound **122** in chloroform necessitated this change in solvent and concentration. Compound **122** exhibited similar performance to that displayed by **123**, and increasing the spin speed (from 3000 rpm to 5000 rpm) and annealing temperature (100 °C to 140 °C) was found to improve the performance.



122

Conditions	μ / cm^2 Vs^{-1}	I_{on}/I_{off}	V_T / V	Hysteresis / V	No. working devices
1	9.92×10^{-3} ($\pm 1 \times 10^{-3}$)	5×10^3	-17	3	6/9
	1.07×10^{-2} ($\pm 4 \times 10^{-4}$)	8×10^3	-17	3	
2	**1.30×10^{-2} ($\pm 3 \times 10^{-3}$)**	**9×10^3**	**-18**	**3**	**6/9**
	1.48×10^{-2} ($\pm 3 \times 10^{-3}$)	**1×10^4**	**-19**	**3**	
3	4.20×10^{-3} ($\pm 2 \times 10^{-3}$)	1×10^3	-17	6	5/9
	5.10×10^{-3} ($\pm 2 \times 10^{-3}$)	1×10^3	-16	5	
4	6.26×10^{-3} ($\pm 2.6 \times 10^{-3}$)	3×10^3	-18	5	4/9
	7.35×10^{-3} ($\pm 1.8 \times 10^{-3}$)	4×10^3	-18	6	

Table 11 Summary of the performance of devices based on **122**; 0.4% w/w **122** in trichloroethylene at 85 °C deposited onto a heated substrate (85 °C); Black (top) is average of all working devices, red (bottom) is average of best three devices (based on μ); Conditions: [1] 5000 rpm for 3 min, annealed at 100 °C for 1 h; [2] 5000 rpm for 3 min, annealed at 140 °C for 1 h;[3] 3000 rpm for 3 min, annealed at 100 °C for 1 h; [4] 3000 rpm for 3 min, annealed at 140 °C for 1 h.

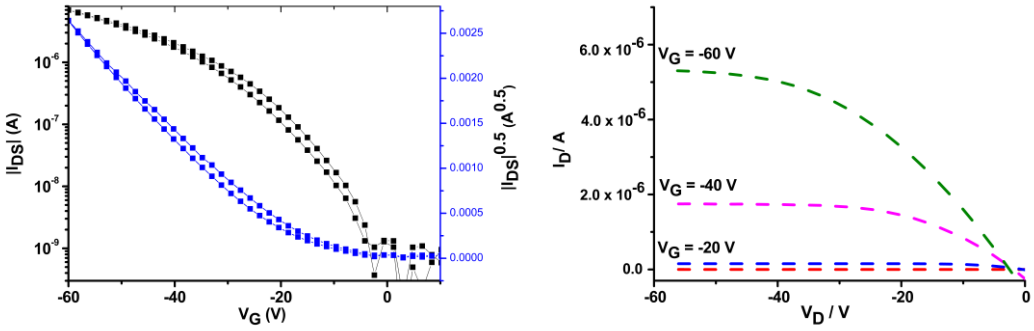
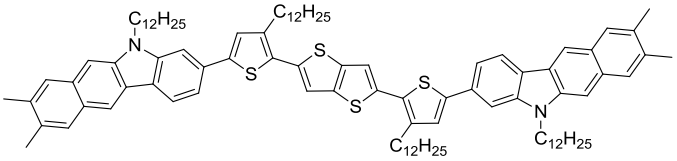


Figure 17 Transfer (left) and output (right) charactersistics for compound **122** (Table 11, Entry 2).

Compounds **126** and **127** with fused central rings in general displayed mobilities at least an order of magnitude lower than observed for **122** and **123**, which may potentially be related to the poorer solubility of these compounds leading to faster, less controlled precipitation of the materials during deposition (Tables 12 and 13). Compound **127** was deposited from a 0.4% w/w solution in toluene as a solution could not be obtained using either TCE or $CHCl_3$.



127

Conditions	μ / cm^2 Vs^{-1}	I_{on}/I_{off}	V_T / V	Hysteresis / V	No. working devices
1	1.40×10^{-3} ($\pm 3 \times 10^{-4}$)	1×10^3	-8	4	6/9
	1.60×10^{-3} ($\pm 3 \times 10^{-4}$)	2×10^3	-8	4	
2	7.86×10^{-4} ($\pm 5 \times 10^{-5}$)	4×10^3	-9	4	5/9
	8.14×10^{-4} ($\pm 6 \times 10^{-5}$)	3×10^3	-9	3	
3	**1.63×10^{-3} ($\pm 1 \times 10^{-4}$)**	**4×10^3**	**-9**	**4**	**8/9**
	1.76×10^{-3} ($\pm 2 \times 10^{-4}$)	**4×10^3**	**-10**	**4**	
4	6.76×10^{-4} ($\pm 9 \times 10^{-5}$)	4×10^3	-11	7	6/9
	7.43×10^{-4} ($\pm 6 \times 10^{-5}$)	6×10^3	-12	7	

Table 12 Summary of the performance of devices based on **127**; 0.4% w/w **127** in trichloroethylene at 50 °C deposited onto a heated substrate (50 °C); Black (top) is average of all working devices, red (bottom) is average of best three devices (based on μ); Conditions: [1] 3000 rpm for 3 min, annealed 100 °C for 1 h; [2] 3000 rpm for 3 min, annealed 140 °C for 1 h; [3] 5000 rpm for 3 min, annealed 100 °C for 1 h; [4] 5000 rpm for 3 min, annealed 140 °C for 1 h.

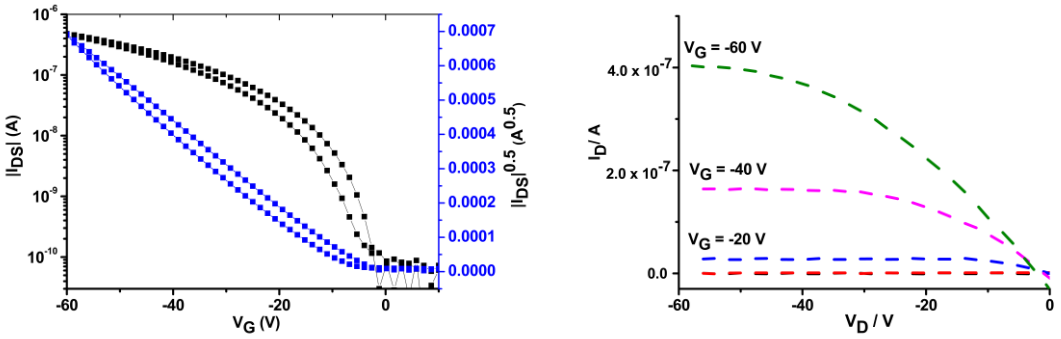
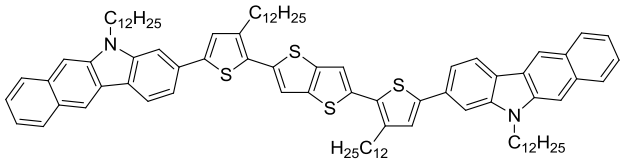


Figure 18 Transfer (left) and output (right) curves for compound **127** (Table 12, Entry 3).

Higher temperature annealing post deposition appeared to lower the performance of devices based on compound **127** and had an inconsistent effect on devices based on **126**. Increasing the spin speed during deposition of devices based on compound **127** had no impact on the mobility observed, whereas the mobility observed for devices based on **126** increased by an order of magnitude.



126

Conditions	μ / cm^2 Vs^{-1}	I_{on}/I_{off}	V_T / V	Hysteresis / V	No. working devices
1	2.12×10^{-5} ($\pm 2 \times 10^{-5}$)	1×10^3	-17	12	4/9
	2.63×10^{-5} ($\pm 3 \times 10^{-5}$)	1×10^3	-17	9	
2	1.59×10^{-4} ($\pm 1 \times 10^{-4}$)	1×10^3	-18	7	5/9
	2.29×10^{-4} ($\pm 4 \times 10^{-5}$)	2×10^3	-18	6	
3	**1.65×10^{-3} ($\pm 4 \times 10^{-4}$)**	**6×10^3**	**-15**	**4**	**5/9**
	1.84×10^{-3} ($\pm 4 \times 10^{-4}$)	**5×10^3**	**-17**	**5**	
4	1.28×10^{-3} ($\pm 6 \times 10^{-4}$)	4×10^3	-17	7	7/9
	1.78×10^{-3} ($\pm 6 \times 10^{-4}$)	6×10^3	-18	6	

Table 13 Summary of the performance of devices based on **126**; 0.4% w/w **126** in toluene at 110 °C deposited onto a heated substrate (110 °C); Black (top) is average of all working devices, red (bottom) is average of best three devices (based on μ); Conditions: [1] 3000 rpm for 3 min, annealed 100 °C for 1h; [2] 3000 rpm for 3 min, annealed 140 °C for 1 h; [3] 5000 rpm for 3 min, annealed 100 ° C for 1 h; [4] 5000 rpm for 3 min, annealed 140 °C for 1 h.

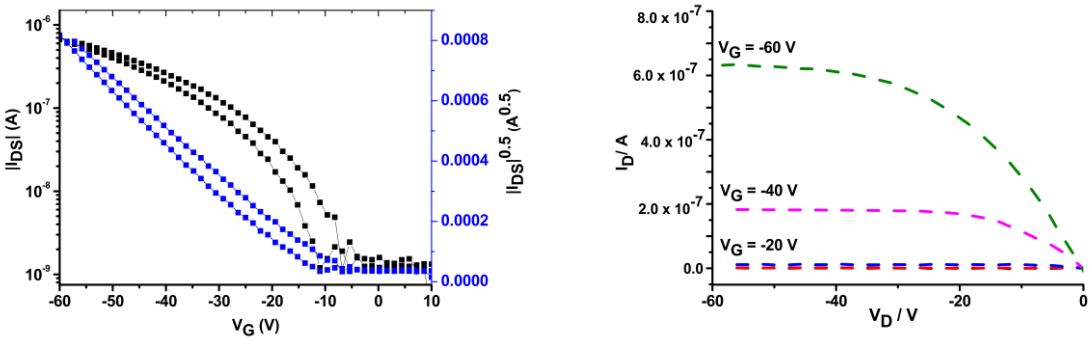
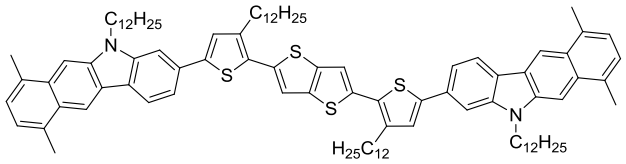


Figure 19 Transfer (left) and output (right) curves for compound **126** (Table 13, Entry 3).

Devices based on compound **128** all displayed very low mobility and I_{on}/I_{off} ratios, with the majority of the devices fabricated showing no transfer behaviour at all.



128

Conditions	μ / cm^2 Vs^{-1}	I_{on}/I_{off}	V_T / V	Hysteresis / V	No. working devices
1	**1.30×10^{-5} ($\pm 1 \times 10^{-6}$)**	**1×10^2**	**-11**	**5**	**8/9**
	1.40×10^{-5} ($\pm 2 \times 10^{-7}$)	**1×10^2**	**-14**	**4**	
2	1.14×10^{-5} ($\pm 2 \times 10^{-6}$)	9×10^1	-10	9	3/9
3	1.73×10^{-5} ($\pm 2 \times 10^{-6}$)	1×10^2	0	9	2/9
4	1.42×10^{-5} ($\pm 5 \times 10^{-6}$)	2×10^2	-16	10	**8/9**
	1.92×10^{-5} ($\pm 7 \times 10^{-6}$)	1×10^2	-16	7	

Table 14 Summary of the performance of devices based on **128**; 0.5% w/w in **128** trichloroethylene at 85 °C deposited onto a heated substrate (85 °C); Black (top) is average of all working devices, red (bottom) is average of best three devices (based on μ); Conditions: [1] 3000 rpm for 3 min, annealed 100 °C for 1h; [2] 3000 rpm for 3 min, annealed 140 °C for 1 h; [3] 5000 rpm for 3 min, annealed 100 ° C for 1 h; [4] 5000 rpm for 3min, annealed 140 °C for 1 h.

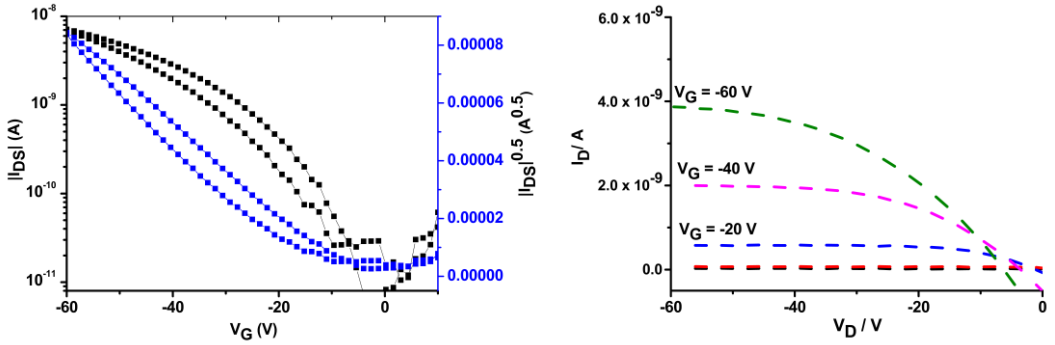
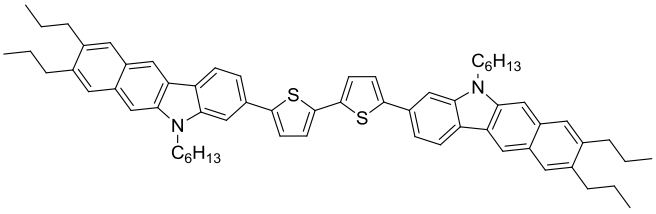


Figure 20 Transfer (left) and output (right) curves for compound **128** (Table 14, Entry 1).

Compounds **124** and **125** exhibited a difference in mobility of two orders of magnitude, with highest mobility and I_{on}/I_{off} ratios of 2.05×10^{-2} and 1×10^5 observed for **124**, whilst **125** displayed much lower performance with a mobility of only 1.5×10^{-4} and I_{on}/I_{off} of 2×10^2 observed. The annealing temperature appeared to have a dramatic effect on the mobility observed for **124**, with a 40 °C higher annealing temperature increasing the mobility and I_{on}/I_{off} ratio dramatically. Study of the films by polarised light microscopy indicated an increase in the crystallinity of the film (See Appendix D for POM images).



124

Conditions	μ / cm^2 Vs^{-1}	I_{on}/I_{off}	V_T / V	Hysteresis / V	No. working devices
1	2.62×10^{-4} ($\pm 1 \times 10^{-4}$)	6×10^2	-2	3	5/9
	3.24×10^{-4} ($\pm 4 \times 10^{-5}$)	8×10^2	-2	3	
2	**1.65×10^{-2} ($\pm 4 \times 10^{-3}$)**	**6×10^4**	**-6**	**3**	**8/9**
	2.05×10^{-2} ($\pm 3 \times 10^{-3}$)	**1×10^5**	**-7**	**3**	
3	2.70×10^{-4} ($\pm 9 \times 10^{-5}$)	3×10^2	-3	3	2/9

Table 15 Summary of the performance of devices based on **124**; 0.5% w/w **124** in $CHCl_3$ at 45 °C deposited onto a ambient temperature substrate; Black (top) is average of all working devices, red (bottom) is average of best three devices (based on μ); Conditions: [1] 5000 rpm for 3 min, annealed 100 °C for 1h; [2] 5000 rpm for 3 min, annealed 140 °C for 1 h; [3] 3000 rpm for 3 min, annealed 100 ° C for 1 h.

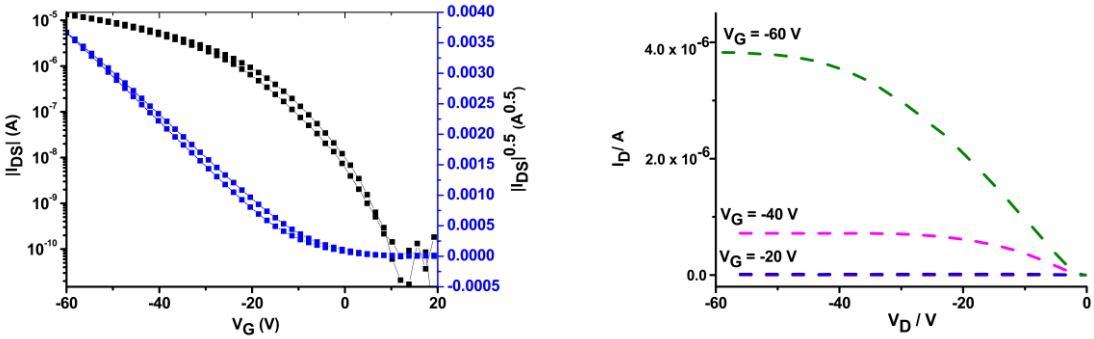
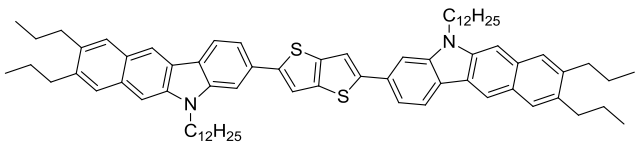


Figure 21 Transfer (left) and output (right) curves for compound **124** (Table 15, Entry 2).

Compound **125** exhibited significantly poorer performance. A higher annealing temperature was again found to improve the performance, although in this instance the films could not be distinguished by either optical microscopy or XRD.



125

Conditions	μ / cm^2 Vs^{-1}	I_{on}/I_{off}	V_T / V	Hysteresis / V	No. working devices
1	-	-	-	-	0/9
2	**9.4×10^{-5} ($\pm 6 \times 10^{-5}$)**	**2×10^2**	**-27**	**14**	**7/9**
	1.5×10^{-4} ($\pm 5.0 \times 10^{-5}$)	**2×10^2**	**-34**	**10**	
3	4.7×10^{-5} ($\pm 4 \times 10^{-5}$)	4×10^2	-27	10	5/9
	6.5×10^{-5} ($\pm 4 \times 10^{-5}$)	7×10^2	-24	13	
4	1.1×10^{-4} ($\pm 5 \times 10^{-5}$)	5×10^2	-32	13	5/9
	1.4×10^{-4} (1×10^{-5})	7×10^2	-31	10	

Table 16 Summary of the performance of devices based on **125**; 0.5% w/w **125** in $CHCl_3$ at 45 °C deposited onto a ambient temperature substrate; Black (top) is average of all working devices, red (bottom) is average of best three devices (based on μ); Conditions: [1] 5000 rpm for 3 min, annealed 100 °C for 1h; [2] 5000 rpm for 3 min, annealed 140 °C for 1 h; [3] 3000 rpm for 3 min, annealed 100 ° C for 1 h; [4] 3000 rpm for 3 min, annealed 140 °C.

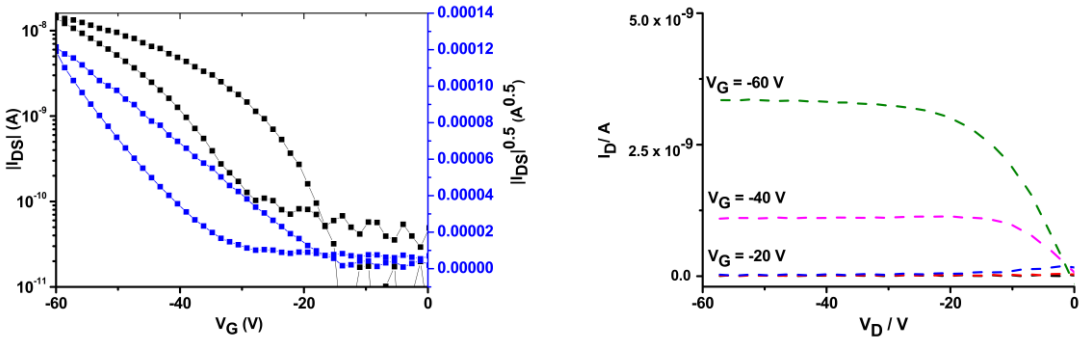
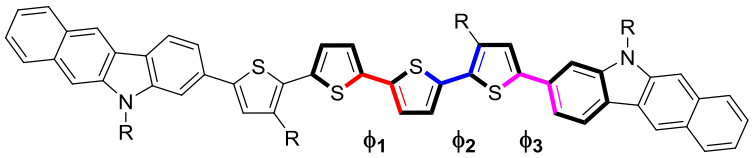


Figure 22 Transfer (left) and output (right) curves for compound **125** (Table 16, Entry 2).

Devices fabricated using **119**, **120** and **121** with the head-to-head alkyl chain arrangement in the thiophene linker failed to give any working devices. This is most likely a consequence of the very poor crystallinity of these compounds (as evidenced by DSC, and XRD of the films) which is in turn related to their non-planar structures; Energy minimised structures provided by Dr Iain Grace indicated that these compounds may exhibit non-planar structures, with a twist in the structure existing between the two central rings of the thiophene linker (Table 17).



Compound	Φ_1/ °	Φ_2 /°	Φ_3 / °
119	**22.8**	-	11.9
120	**29.7**	-	17.2
121	**26.4**	-	15.2
122	6.8	5.3	9.5
123	13.9	5.5	13.3
124	2.3	-	7.39
125	-	-	22.5
126	-	10.5	13.1
127	-	6.0	4.8
128	-	6.1	7.4

Table 17 Calculated Ar-Ar torsional angles for compounds **119**-**128**; Φ_1 = Torsional angle between central two rings of linker; Φ_2 = Torsional angle between central rings and outer rings of linker; Φ_3 = Torsional angle between linker rings and end-caps; Measured from energy minimised (DFT) structures provided by Dr Iain Grace [See SI of *Org Lett*, **2012**, 5744 for a discussion of the method used in the calculations].[216]

2.6 Conclusion and future work

A route to benzo[*b*]carbazoles with functionality in the 3-position appropriate for use in standard palladium-catalysed cross coupling has been developed, with the key steps being a fluorous connective-Pummerer cyclisation in which the regioselectivity of cyclisation is determined by a nonaflyloxy group, which is then later used to enable cross coupling of the final compound, and a SmI_2 mediated cleavage-cyclisation cascade in which SmI_2 both removes the fluorous tag and triggers a key cyclisation event (Figure 23).

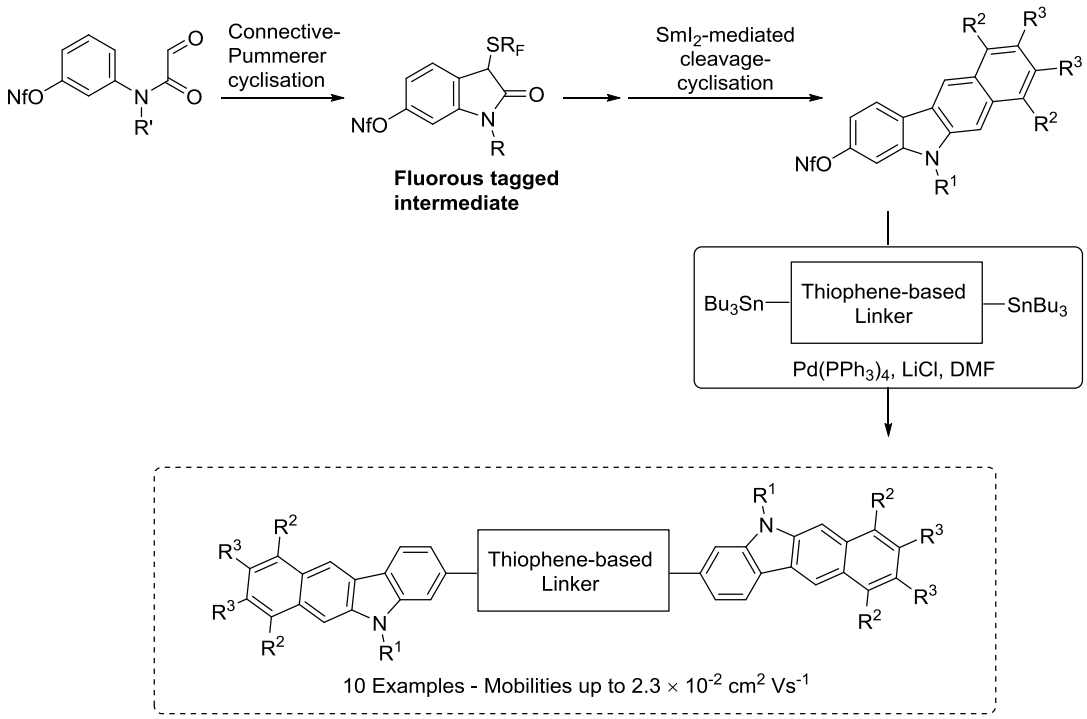


Figure 23 Summary of route to benzo[*b*]carbazole end-capped oligothiophenes.

During the course of this work the SmI_2-mediated cleavage-cyclisation cascade has been studied in more detail. Studies showed that the use of an appropriate proton source during the reaction is essential for conversion through to the desired cyclised products. The SmI_2-mediated reaction tolerates the inclusion of alkyl groups on the section of the substrates introduced during the previous alkylation step but any other modifications resulted in poor conversion through to the cyclised products. It would be of interest to investigate the substrate scope further with a wider range of *bis*-bromomethyl alkylating agents (Figure 24).

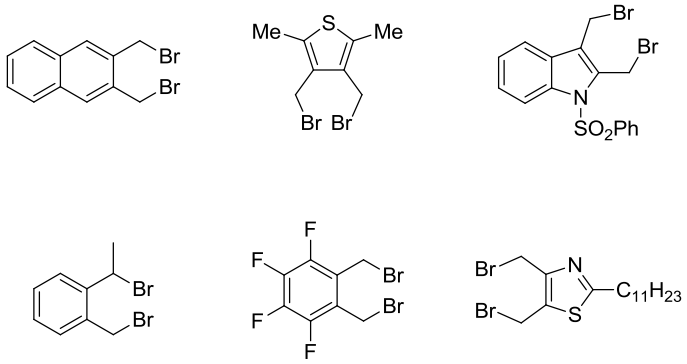


Figure 24 *bis*-Bromomethyl alkylating agents to further investigate substrate scope of the SmI_2-mediated reaction.[217-222]

It has been demonstrated that the nonaflyloxy-substituted benzo[*b*]carbazoles can be effectively coupled through aromatic linkers to generate a small library of novel organic semiconducting materials, whose performance has been assessed in OFET devices. The performance obtained from the materials is comparable to the most closely related literature materials.[75] The benzo[*b*]carbazole moiety in the current materials does not offer any advantage over the alternative acene end-capping groups used by other groups. Further work tuning both the nature of the solubilising chain on nitrogen, in order to improve solubility, and the structure of the linker may lead to future improvements in performance.

3 Two-directional synthesis of dibenzoindolo[3,2-*b*]carbazoles

3.1 Indolo[3,2-*b*]carbazoles

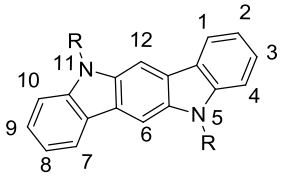


Figure 25 Structure of 5,11–disubstituted indolo[3,2–*b*]carbazole

Over the past decade a new class of organic semiconductor (5,11–disubstituted indolo[3,2–*b*]carbazoles) has emerged based on a tertiary diamine structure (Figure 25). It has been shown that these nitrogen containing analogues of pentacene exhibit good *p*-type semiconductivity, with the advantages of good ambient stability (lower HOMO level than pentacene), and relatively easy modification of solubility, molecular packing and electronic properties via alteration of the group attached to nitrogen.

3.1.1 OFET devices based on indolo[3,2-*b*]carbazoles

Ong et al. were the first to show the usefulness of indolo[3,2-*b*]carbazoles as organic semiconductors,[223] first as components in OLEDs, then later with OFET devices based on **OPICZ**, which displayed mobilities of up to 0.12 $cm^2 Vs^{-1}$ and I_{on}/I_{off} ratios of 10^7 in devices using an OTS-8 treated substrate (Figure 26). It was found that the compound packed in an intimate co-facial manner, with additional edge–to–face interactions existing between the phenyl appendages of one molecule and the end of the aromatic core of another.[163,197] A similar compound **OICZ**, lacking the hole stabilising phenyl substitution on nitrogen displayed much lower mobilities of $1.3\text{-}3.0 \times 10^{-3}$ $cm^2 Vs^{-1}$ despite still forming highly ordered crystalline films. Similar mobilities were also obtained when additional methyl groups were incorporated on the central ring (**MOICZ**), which interestingly leads to the adoption of an all parallel, co-facial arrangement in single crystals (in contrast to **OICZ** which exhibits herringbone-type packing). The introduction of chloro groups in the 2- and 8-positions (**CICZ**) was found to provide the necessary stabilisation to offset the removal of the phenyl groups on nitrogen, resulting in mobilities of up to 0.14 $cm^2 Vs^{-1}$

obtained for devices produced by vacuum evaporation.[197] Similar results were obtained by Dong et al. (0.12 cm^2 Vs^{-1} by vacuum evaporation onto OTS-SiO_2/Si^{++}) with a slightly shorter alkyl chain (R = C_6H_{13}), notably they were able to obtain a crystal structure, which showed that the compound packed preferentially face–to–face in one-dimensional columns, in contrast to the same compound but without the hexyl chains on nitrogen, which did not display any field-effect, and was found to pack in a herringbone arrangement.[224]

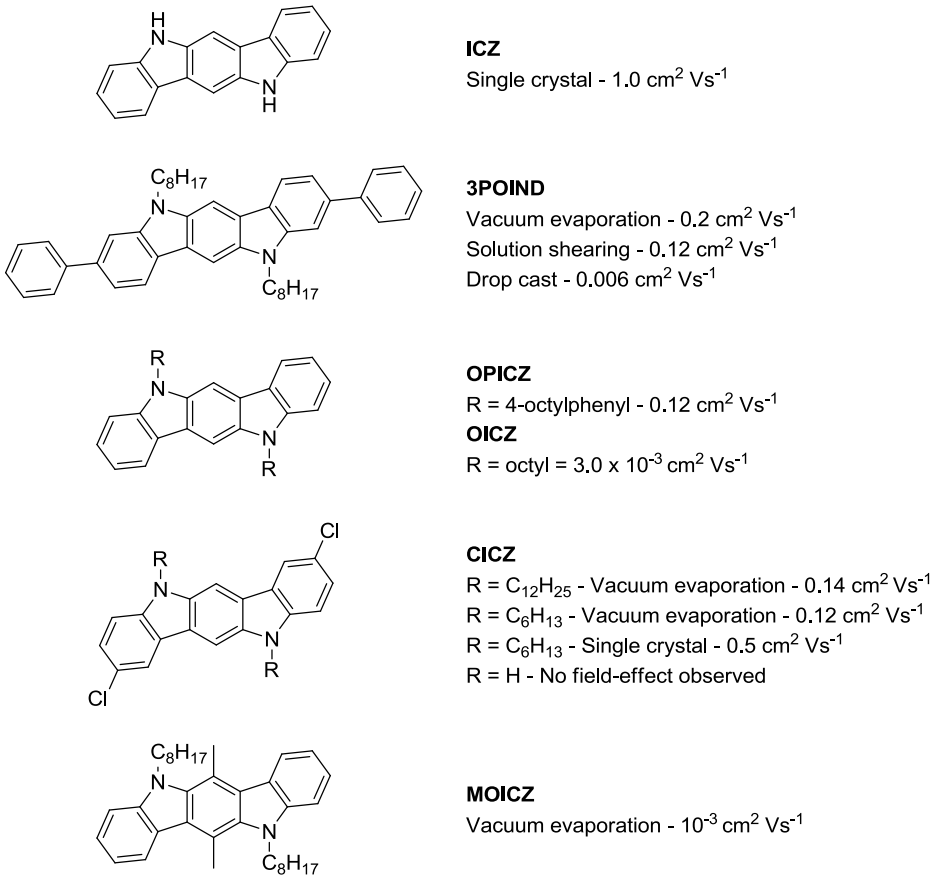


Figure 26 Summary of charge mobilities observed for devices based on indolo[3,2-*b*]carbazoles.

The diphenyl-substituted indolo[3,2-*b*]carbazole **3POIND** showed mobilities up to 0.2 cm^2 Vs^{-1} and I_{on}/I_{off} ratios of 10^6 when devices on OTS-SiO_2/Si wafers were fabricated by vacuum evaporation.[162] Slightly lower values were obtained when an alternative solution shearing technique was utilised on a phenyltrimethoxysilane-treated substrate.[49] This technique, which involves dragging a second substrate on top of the one on which the material in solution is placed, was said to form much larger and more highly orientated crystalline grains relative to those produced by drop-casting or spin-coating. The same

group has synthesised a range of other compounds, altering the end-capping group (phenyl and thienyl) and its position on the indolo[3,2-*b*]carbazole core (3- or 2-position). These compounds were all found to exhibit maximum mobilities an order of magnitude lower than that of **3POIND,** which was cited to be a consequence of the tighter packing structure and higher crystallinity of **3POIND**.[162]

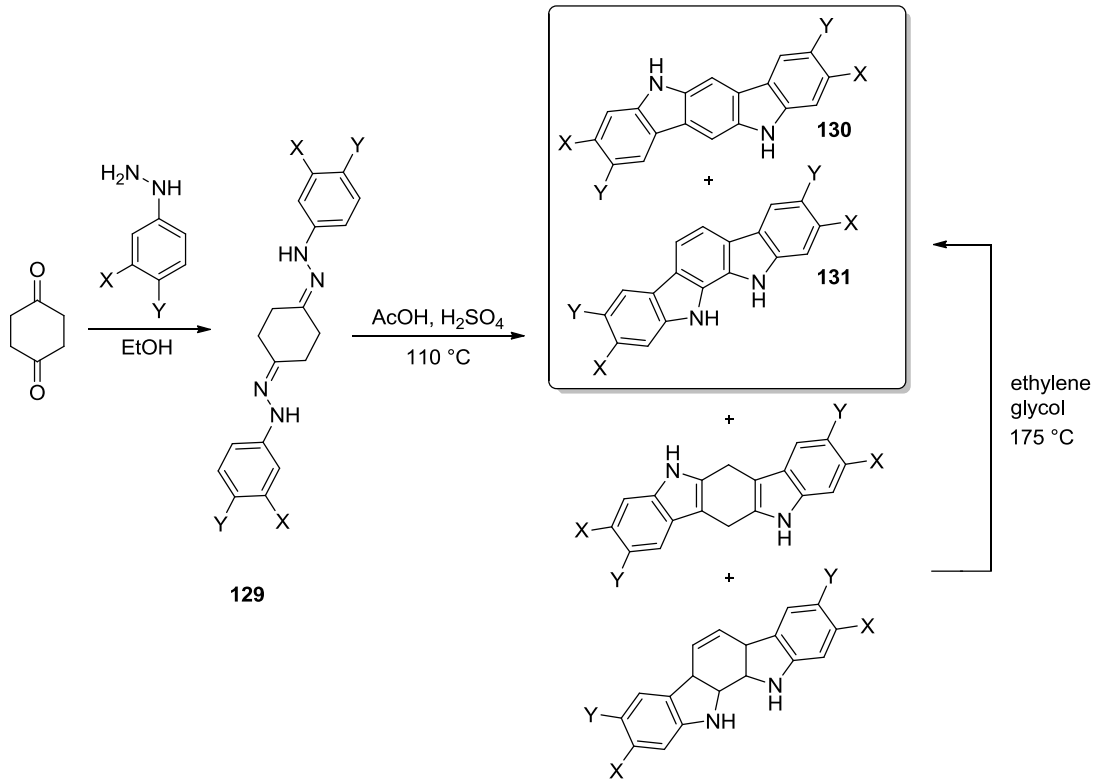
These studies all demonstrate the large changes in performance that can be brought about by small modifications in structure, when these changes have a significant impact on the electronic properties and crystal packing of the compounds.

To date the highest performance for an indolo[3,2-*b*]carbazole based device was reported by Jiang et al.,[225] who demonstrated a mobility of 1.0 cm^2 Vs^{-1} with an I_{on}/I_{off} ratio of 10^6 obtained from single crystal devices using **ICZ** on an OTS-SiO_2 dielectric.

3.1.2 Synthetic approaches to indolo[3,2-*b*]carbazoles

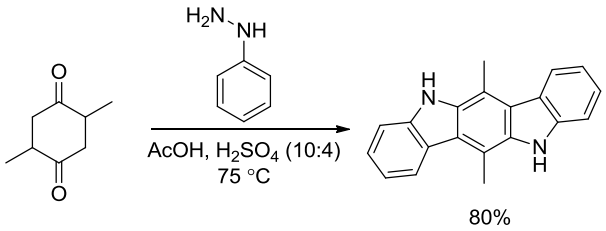
There are relatively few synthetic routes to indolo[3,2-*b*]carbazoles published in the literature, and most of these suffer from problems of regioselectivity (resulting in either poor yields or the necessity for blocking groups), or involve harsh reaction conditions which limit the opportunity for incorporation of additional diversity.

The most widely used approach is based on the double Fischer indolisation of cyclohexane-1,4-dione *bis*(phenylhydrazone) **129** under harsh acidic conditions (Scheme 34).[197,226-228] Unfortunately, the reaction also leads to the formation of the regioisomeric indolo[2,3-*a*]carbazole **131**, with the yield of the desired regioisomer **130** being low after separation.



Scheme 34

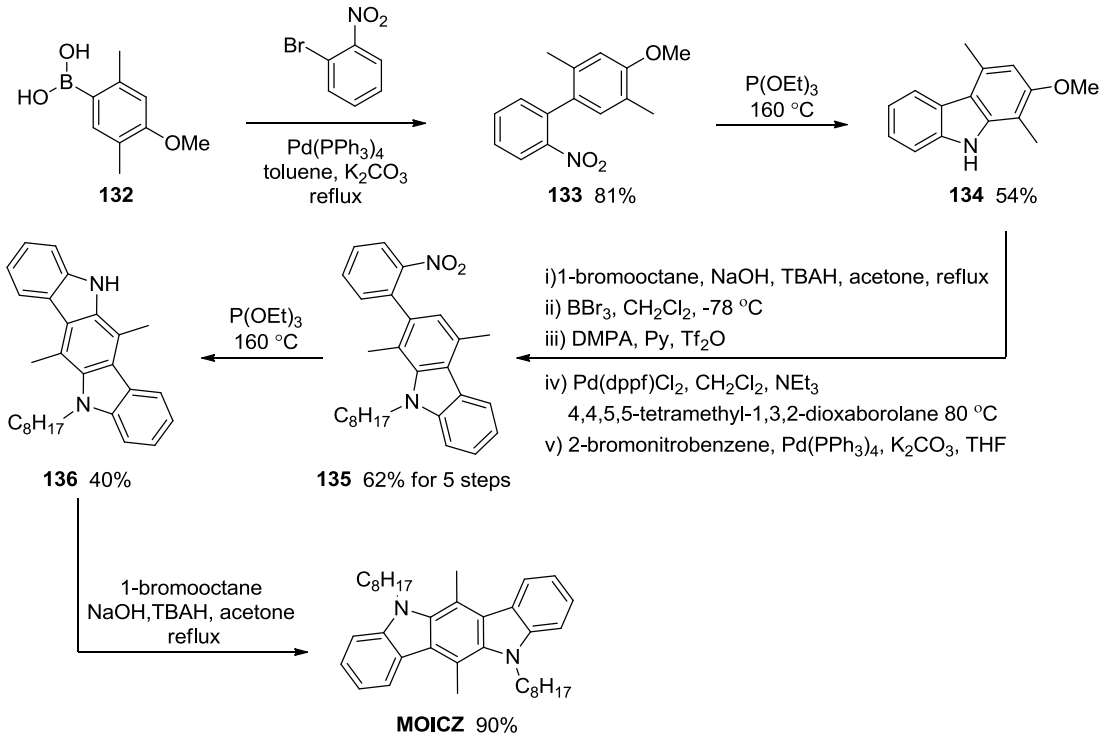
This approach, however, is advantageous over other published procedures in that the synthesis involves very few steps, and synthetically useful groups such as bromine, chlorine, fluorine and methoxy groups can be tolerated in the starting materials to give the 2,8- or 3,9-disubstituted products, which can then be further elaborated. The regioselectivity and yield can be improved through the use of blocking groups (Scheme 35).[229]



Scheme 35

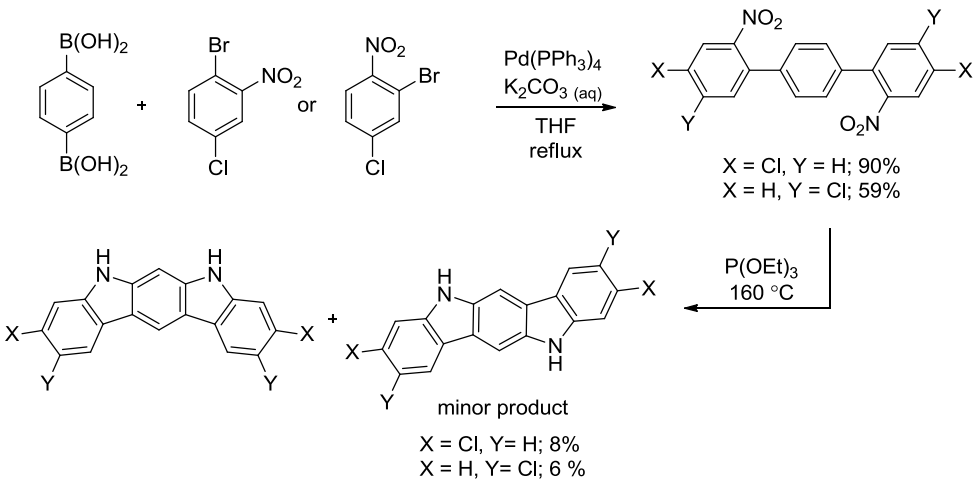
An alternative approach utilising two consecutive reductive Cadogen cyclisations [230,231] has been reported by Leclerc et al. (Scheme 36).[230-232] Substrate **133** is synthesised efficiently by Suzuki-Miyaura cross coupling of **132** with 2-bromonitrobenzene, a Cadogen cyclisation then gives **134** and after further manipulation **135**. A second Cadogen

cyclisation and functionalisation of nitrogen gives the product **MOICZ**. This route is unfortunately limited due to moderate yields for the key cyclisation reactions, harsh reaction conditions, and the requirement for blocking groups to prevent the formation of unwanted regioisomers.[233]



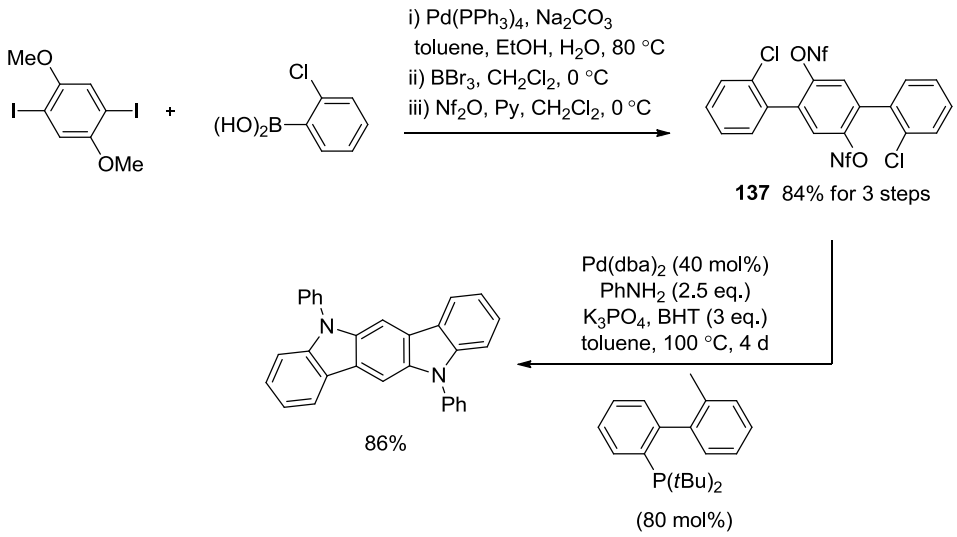
Scheme 36

A similar approach based on a double Cadogen cyclisation without methyl blocking groups has been reported by the same group; this was found to give the desired product, albeit in low yield (6-8%), via a much quicker route involving only two steps (Suzuki-Miyaura coupling and Cadogen cyclisation) from commercially available starting materials (Scheme 37).[234] It was shown that the resulting product can be further modified by alkylation, and then taken on to generate polymers using Yamamoto Ni(0) polymerisation.



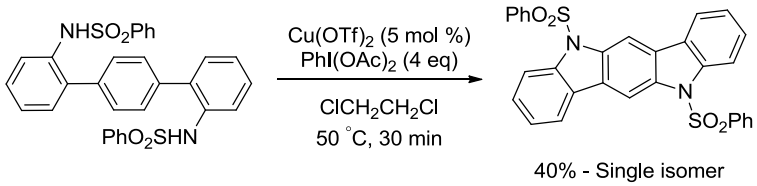
Scheme 37

The highest yielding method is that of Kawaguchi et al., who have developed an approach to indolo[3,2-*b*]carbazoles based on a double palladium(0) catalysed *N*-arylation reaction, which was found to give the desired indolo[3,2-*b*]carbazole product efficiently in excellent yield (Scheme 38).[235] The starting material for the key *N*-arylation step (**137**) is synthesised in excellent overall yield via Suzuki-Miyaura coupling, deprotection and nonaflate formation. This approach has been used in the synthesis of indolo[3,2-*b*]carbazole derivatives with alkyl and cyano groups in the 3,9-positions.



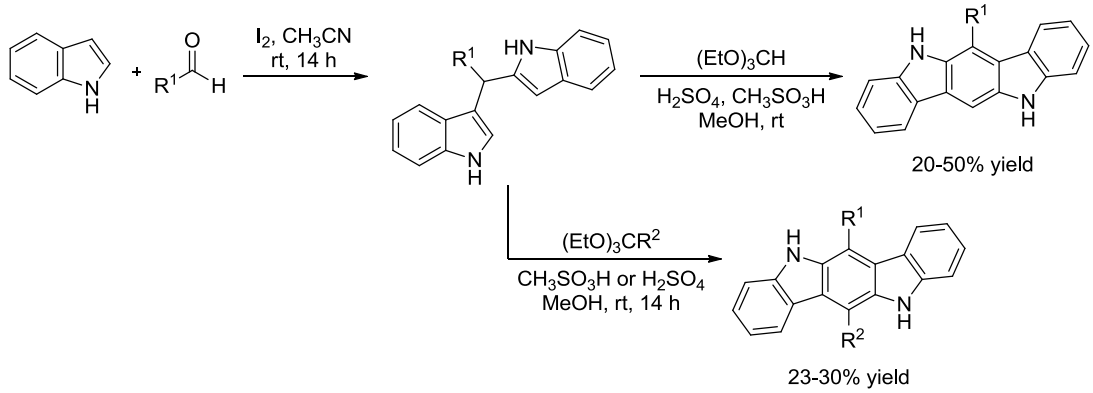
Scheme 38

Chang et al. demonstrated a short synthesis (3 steps) of *N*-protected indolo[3,2-*b*]carbazoles, using a copper-catalysed key step with phenyliodonium diacetate as a stoichiometric oxidant (Scheme 39). This approach gave the desired product as a single regioisomer in good overall yield.[236]



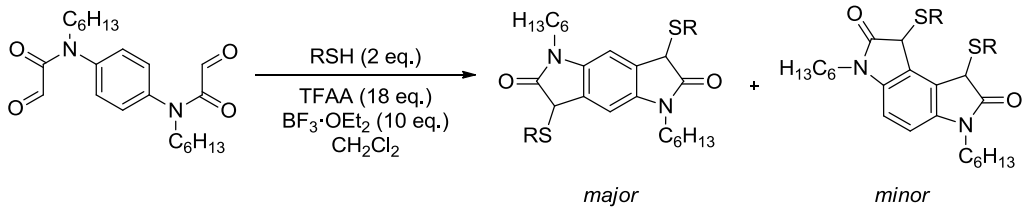
Scheme 39

Within the Dehaen group a procedure for the generation of 6-mono and 6,12-disubstituted indolo[3,2-*b*]carbazoles has been developed.[237-239] The method involves the condensation of indoles and aldehydes in the presence of iodine. A range of different derivatives have been synthesised in moderate yields using this method by utilising different indole and aldehyde components (Scheme 40). The group demonstrated that the products could easily be alkylated or arylated using Ullmann coupling reactions. Unfortunately, this methodology is strictly limited to 6-monosubstituted or 6,12-disubstituted materials. Closely related methods have also been developed by other groups.[240]



Scheme 40

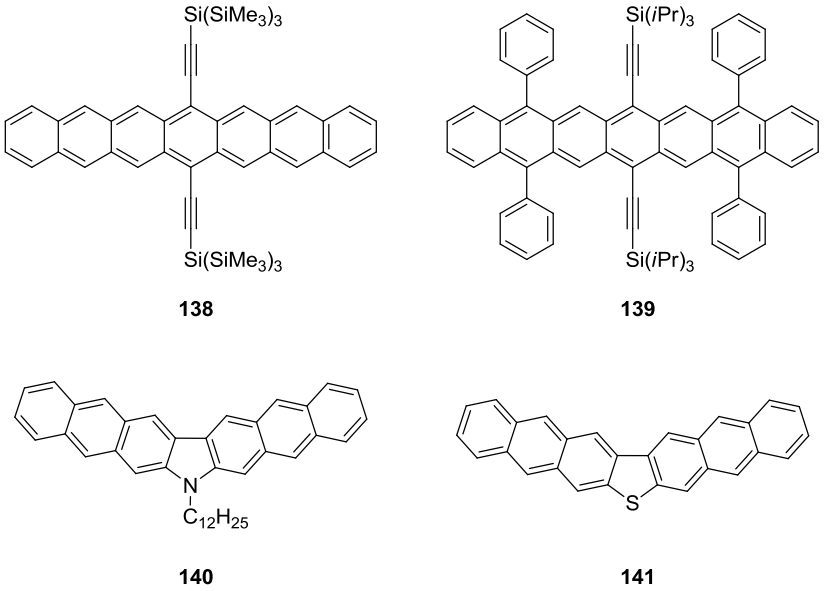
Importantly, it has been demonstrated within the Procter group that the connective-Pummerer reaction can be used in the two-directional fluorous synthesis of linear *bis*-oxindoles (Scheme 41).[117,118] The two-directional Pummerer cyclisation was generally found to occur with good regioselectivity, predominantly favouring the linear product. It was hoped within the Procter group that the linear product could be used in the construction of extended indolo[3,2-*b*]carbazole aza-heptacene structures.



Scheme 41

3.1.3 Heptacenes and heteroheptacenes

The higher acenes, beyond pentacene, are less well studied than their smaller counterparts owing to a decrease in stability and solubility as the number of fused rings is increased.[5,57,58,241-243] The desire to synthesise higher acenes is due to the gradual increase in intermolecular electronic coupling, and tighter crystal packing which is observed in going from benzene to pentacene and beyond. Hexacene has recently been shown to display good performance in single crystal devices, displaying a mobility of 4.3 $cm^2\ Vs^{-1}$, in comparison to 1.2 $cm^2\ Vs^{-1}$ shown by a pentacene based device fabricated under identical conditions.[57] Heptacene meanwhile is very unstable in the presence of oxygen and light, spontaneously forming an oxygen photoadduct in solution, as a consequence of a high HOMO energy. Heptacene and the higher acenes are also prone to dimerisation making the isolation of pure heptacene under normal conditions impossible. Unsubstituted heptacene has been synthesised photochemically when trapped within a polymer (PMMA) matrix to prevent decomposition, but even under these conditions the compound was only stable for several hours.[244,245]



138 **139**

140 **141**

Figure 27 Examples of substituted heptacenes (**138** [246] and **139** [247]) and heteroheptacenes (**140** [248] and **141** [249]).

Studies have instead focused primarily on the development of stabilised heptacene derivatives (Figure 27). The incorporation of bulky sterically hindering and electronically protecting side groups onto the aromatic core has been used to produce stabilised heptacene derivatives.[247,250,251] The incorporation of heteroatoms into the aromatic core of heptacene to generate heteroheptacenes has also yielded structures which are isoelectronic with heptacene but display much improved stability under ambient conditions.[33,248,249,252-261]

3.2 A two-directional fluorous approach to dibenzoindolo[3,2-*b*]carbazoles

Aza-heptacenes based on an extended indolo[3,2-*b*]carbazole core are unstudied. It was anticipated that by extending previous work on benzo[*b*]carbazole synthesis in a two-directional manner, dibenzoindolo[3,2-*b*]carbazoles (**DBIC**) could be accessed, via a two-directional connective-Pummerer cyclisation, followed by a two-directional SmI_2-mediated cleavage-cyclisation reaction (Figure 28).

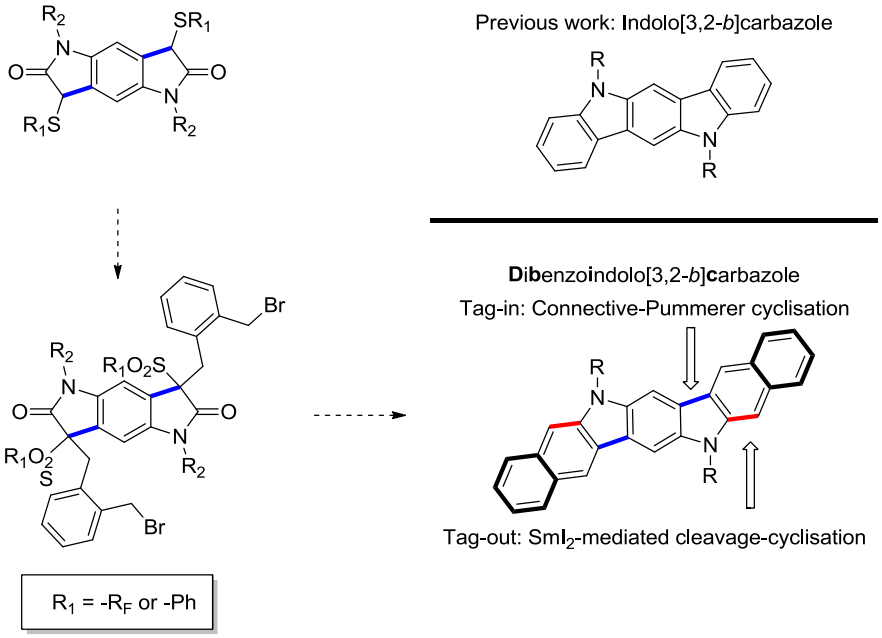
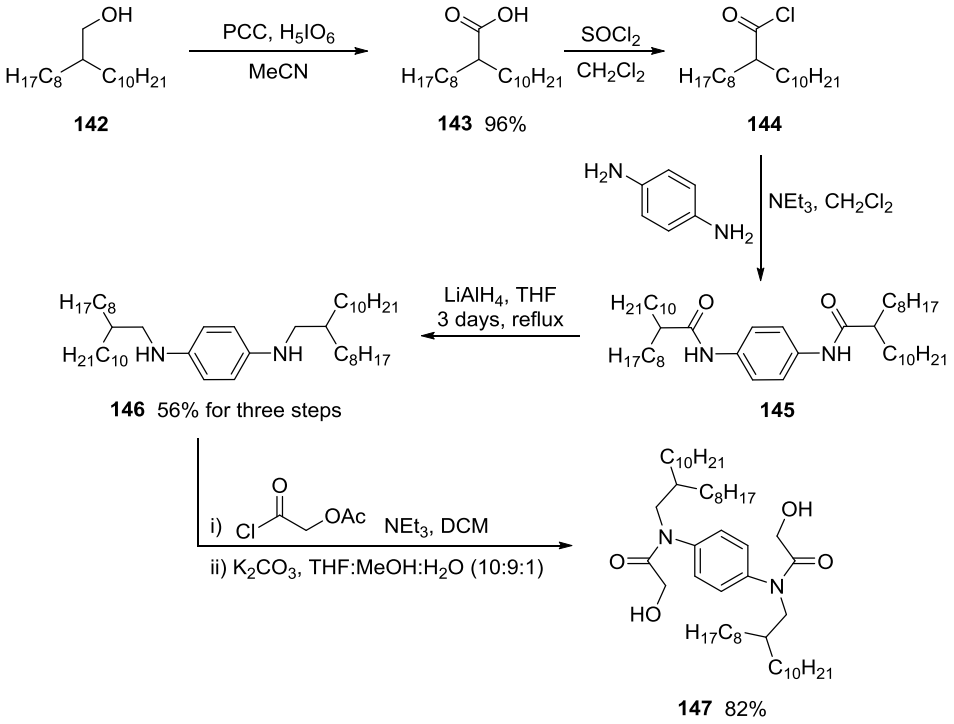


Figure 28 Potential route to dibenzoindolo[3,2-*b*]carbazoles (**DBIC**).

In order to generate soluble compounds it was anticipated that the incorporation of long branched alkyl chains would be necessary. The initial choice of solubilising group, 2-octyldodecanyl, was chosen due to the low cost of the starting material and its prevalent use in organic electronics.[262-265]

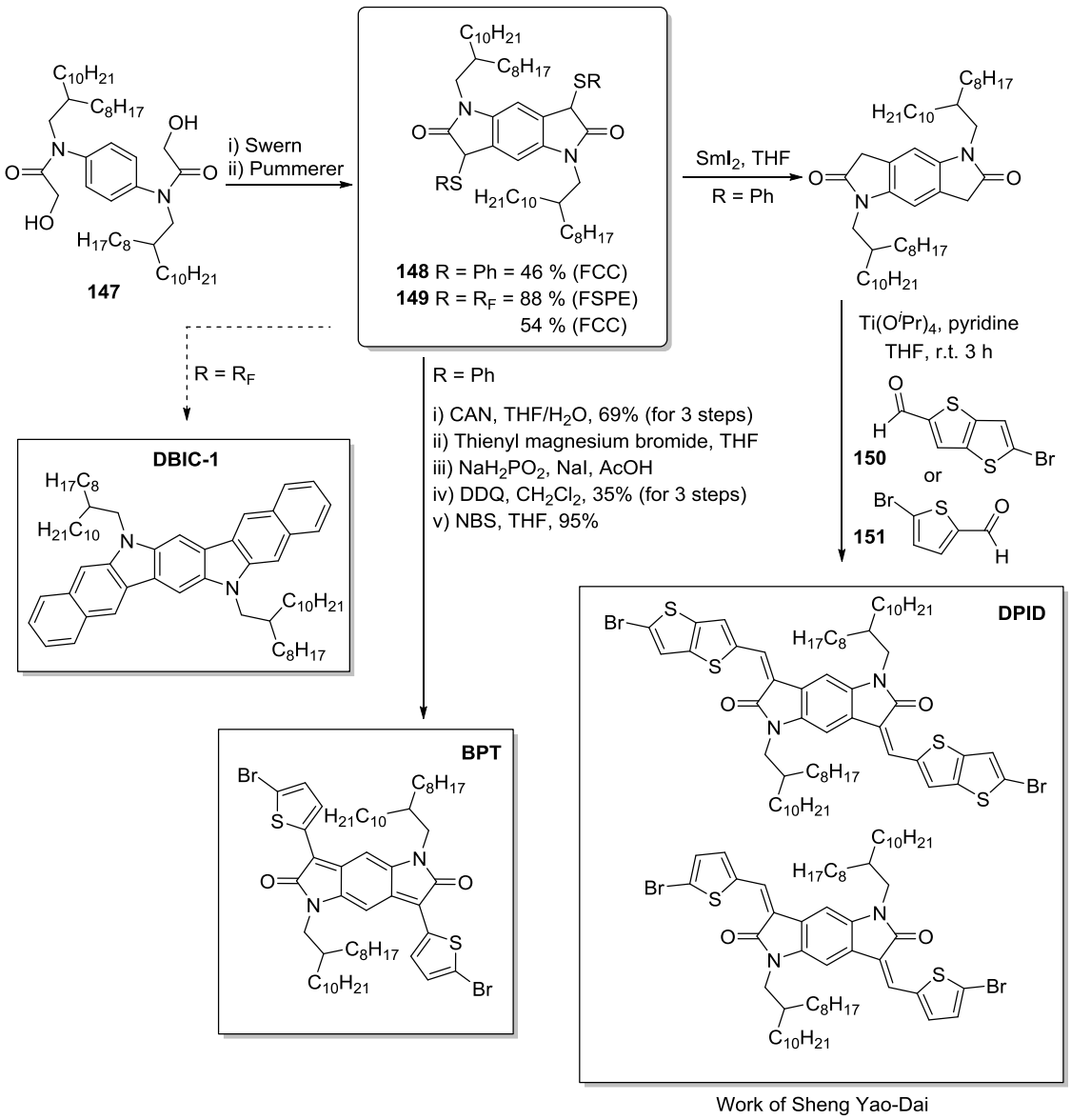


Scheme 42

Commercially available alcohol **142**, was initially converted through to the corresponding acid **143** using catalytic pyridinium chlorochromate (PCC) and excess periodic acid. This was then converted to the acid chloride **144** and coupled with *p*-phenylenediamine in a manner analogous to earlier work. Reduction of the amide to the corresponding amine using $LiAlH_4$, followed by amide coupling with acetoxyacetyl chloride and deprotection of the acetate, provided the *bis*-hydroxyamide **147** in good overall yield (Scheme 42).

After Swern oxidation, compound **147** readily underwent the Pummerer cyclisation using the standard procedure with both thiophenol and the fluorous thiol to give predominantly the desired linear isomers (>5:1) as inconsequential 1:1 mixtures of diastereoisomers in moderate yields after purification on silica gel. The product was then utilised in three different ways; either onwards towards indolo[3,2-*b*]carbazole-type materials, which constitutes the majority of the work described below, or towards novel monomers **BPT** and **DPID** via either reductive (SmI_2) or oxidative (ceric(IV) ammonium nitrate [CAN]) removal of the organosulfanyl groups. These different transformations illustrate the synthetic utility of *bis*-oxindole intermediates such as **148** and **149** in the synthesis of a range of semiconducting compounds (Scheme 43).

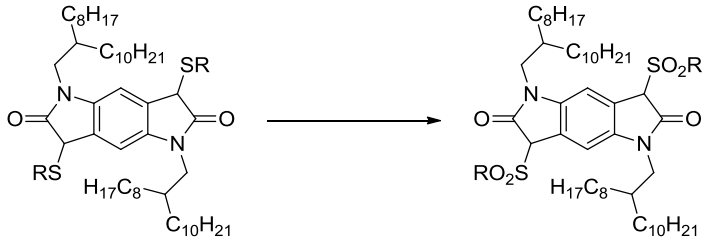
In collaboration with the McCulloch group two new monomers were devised for incorporation into semiconducting polymers. A synthetic route to dihydropyrroloindoledione (**DPID**) monomers was developed by Sheng-Yao Dai, and comprises of initial reduction of compound **148** with SmI_2, followed by Knoevenagal condensation with aromatic aldehydes **150** or **151**.[266-268] Alternatively oxidation with ceric(IV) ammonium nitrate led to a *bis*-isatin intermediate, which could then be converted to thiophene-flanked benzodipyrrolidone **(BPT)** monomers in three quick steps; Grignard addition, reduction with NaH_2PO_2 and oxidation with DDQ, in 35% yield over the three steps. Work within the MuCulloch group has shown the **DPID** and **BPT** monomers to be useful building blocks in the fabrication of new semiconducting polymers for application in organic photovoltaic cells and OFETs.[267-269]



Scheme 43

3.2.1 Synthesis of substrates for the investigation of the two-directional SmI_2-mediated cleavage-cyclisation reaction

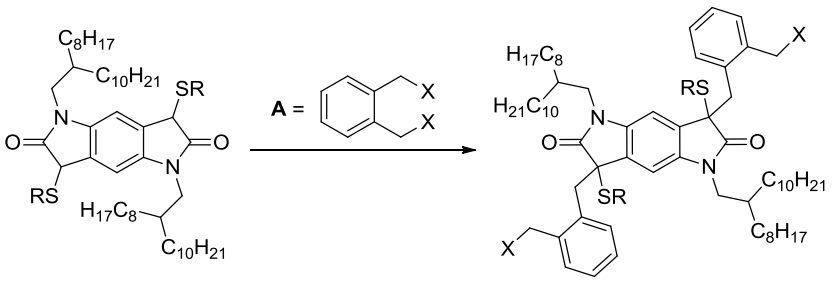
The oxidation and alkylation of intermediates **148** and **149** proved to be less straight forward than in previous one-directional work; applying the previously utilised conditions for the oxidation of the sulfide to sulfone resulted in decomposition of the starting material. Other standard conditions were investigated but these also resulted in complex mixtures of products from which no pure compounds could be isolated (Table 18).



R	Conditions	Yield / %
R_F	*m*CPBA(4.4 eq.), CH_2Cl_2, 2 h, rt	0 (Decomp.)
R_F	Purified[a] dry *m*CPBA(4.4 eq.), CH_2Cl_2, 16 h, rt	0 (Decomp.)
Ph	Purified[a] dry *m*CPBA(4.4 eq.), CH_2Cl_2, 4 h, rt	0 (Decomp.)
Ph	Oxone® (6.0 eq.), THF / H_2O, 2 h, rt	0 (Decomp.)
Ph	OsO_4 (5 mol%), NMO (8.0 eq.), *t*BuOH, THF, 16 h, rt	0 (Decomp.)

Table 18 Conditions for the unsuccessful oxidation of **148** and **149**; [a] Purified according to "Purification of Laboratory Chemicals".[270]

Investigation of the alkylation of the oxindole at the sulfide oxidation state was commenced, using the thiophenol tagged oxindole **148**. Using similar conditions to the one-directional work on sulfones (substituting acetone for DMF for solubility reasons) resulted in complete decomposition of the starting material, giving none of the desired product. Utilising a stronger base and lower temperature, LDA, proved more successful and a small amount of the desired product was obtained. Suspecting that the product was not entirely stable on silica, the same set of conditions were applied to the fluorous tagged oxindole **149**. Pleasingly, the desired product was obtained in good yield and acceptable purity after quick purification by FSPE (Table 19). Further purification of this product by flash column chromatography on silica gel gave the pure product in 54% yield. Alternative conditions using either LiHMDS/HMPA[271]gave a similar yield after FSPE. The alkylation was also attempted with benzylic chlorides using LDA, LiHMDS/HMPA, or NaH, in all cases the desired alkylated product was not obtained.



R	X	Conditions[b]	Yield / %
R_F	Cl	NaH (4.0 eq.), THF at rt then **A** reflux o/n	0
R_F	Cl	LiHMDS (2.1 eq.), HMPA (10 eq), THF, -78 °C 30 min then **A** and warmed to rt	0
R_F	Br	LiHMDS (2.1 eq.), HMPA (10 eq), THF, -78 °C 30 min then **A** and warmed to rt	84 (FSPE)
R_F	Cl	LDA (2.1 eq.) THF, -78 °C 30 min then **A** and warmed to rt	0
R_F	Br	LDA (2.1 eq.) THF, -78 °C 30 min then **A** and warmed to rt	82 (FSPE) 54 (Silica gel)
H[a]	Br	LDA (2.1 eq.) THF, -78 °C 30 min then **A** and warmed to rt	0
Ph	Br	K_2CO_3 (10 eq.), acetone, **A**	0
Ph	Br	LDA (2.1 eq.) THF, -78 °C 30 min then **A** and warmed to rt	13
Ph	Cl	LDA (2.1 eq) THF, -78 °C 30 min then **A** and warmed to rt	0

Table 19 Optimisation of two-directional alkylation conditions; [a] Sulfide cleaved reductively using SmI_2 (material was generated as part of the BPT project and was provided by Sheng Y. Dai [MRes student]); [b] 10 equivalents of **A**.

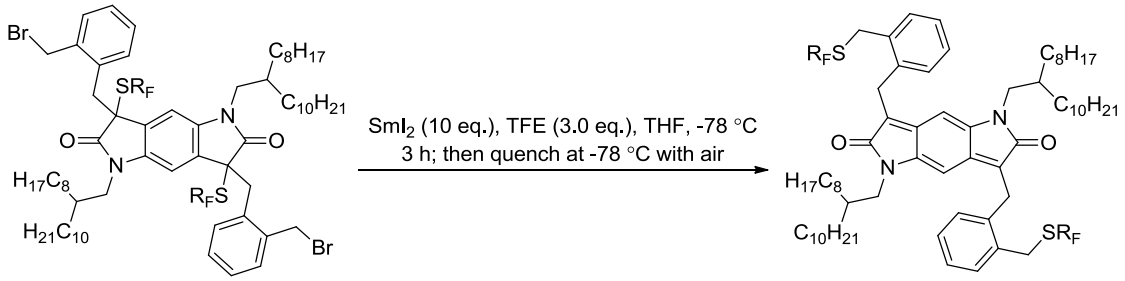
3.2.2 Optimisation of the two-directional SmI_2-mediated cleavage–cyclisation reaction

With the alkylated intermediate **152** in hand, the viability of the two-directional cleavage cyclisation process was assessed using material purified only by FSPE (Table 20). Using the previously developed reaction conditions, with trifluoroethanol as the proton source,

the desired product **DBIC-1** was obtained in an overall yield of 17% after oxidation of the crude (Table 20, Entry 7). The product after the initial SmI_2-mediated step exists in a mixture of oxidation states and was readily oxidised to the fully aromatised product after stirring with *p*-benzoquinone for 1 h.

The necessity of trifluoroethanol was demonstrated by the absence of product when the proton source was omitted from the reaction mixture. Alternative proton sources (MeOH, *t*BuOH) gave considerably lower yields, as was previously seen in the benzo[*b*]carbazole work (Table 20, Entries 1 and 2). Modifying the conditions, using a higher number of equivalents of trifluoroethanol and heating the reaction, appeared to give a very slight increase in the yield of the desired product. Using a more acidic proton source, hexafluoroisopropanol (HFIP), resulted in an increase in yield from 21% (trifluoroethanol) to 27% (Table 20, Entry 16).

Carrying out the addition at -78 °C and leaving the reaction to stir at this temperature for a further 3 h resulted in conversion to an interesting by-product **153**, in which tag cleavage appeared to have occurred (via reaction with just 2.0 equivalents of SmI_2 leading to *p*-quinodimethane formation) followed by re-attachment of the tag in the benzylic position (Scheme 44). It appears that even at low temperatures tag-cleavage proceeds rapidly (as indicated by complete consumption of the starting material by TLC at the end of the addition of SmI_2), whilst the formation of the benzylic organosamarium intermediate does not occur at this temperature. Formation of **153** appeared to occur over several hours when monitored by TLC. Carrying out the addition at -78 °C, stirring for 10 min at -78 °C, then warming rapidly to room temperature resulted in the formation of product **DBIC-1** in 18% yield.



152 **153** 67%

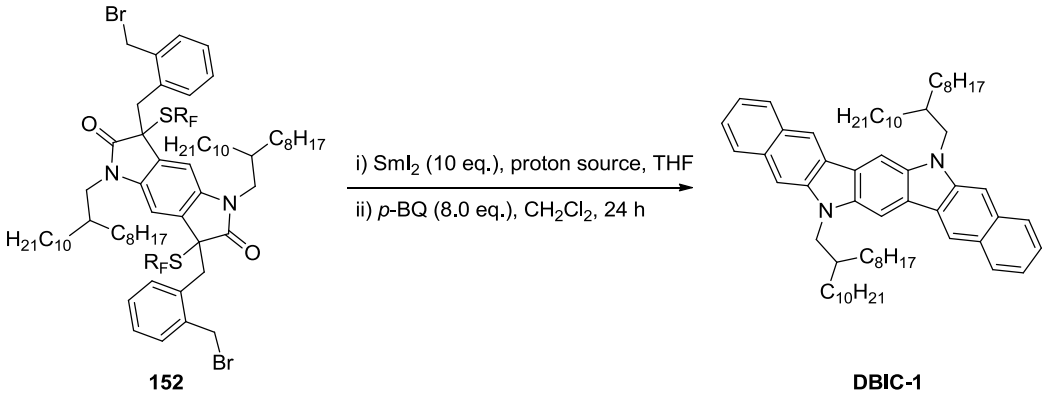
Scheme 44

Performing the reaction at -40 °C failed to give either the desired product or the tag-handover byproduct **153**, but instead resulted in a complex mixture of products. At -20 °C a small amount of cyclised product was formed (10%) (Table 20, Entry 11).

Following the procedure of Molander et al.,[158] using catalytic NiI_2 and visible light irradiation (Mercury lamp), did not result in any significant increase in yield when performed at either room temperature or -20 °C (Table 20, Entries 13 and 14).

The reaction was attempted using both material purified just by FSPE, and by FSPE followed by silica gel chromatography. The silica gel purified material gave a better yield in the SmI_2-mediated cleavage-cyclisation reaction as would be expected, but the overall yield for the three steps (alkylation, SmI_2-mediated cleavage-cyclisation and oxidation) was comparable (15% FSPE then silica gel, 14% just FSPE).

The oxidation of sulfide to sulfone was also re-investigated. It was found that the alkylated sulfide could easily be oxidised up to the sulfone oxidation state in 99% yield using *m*CPBA, indicating that the previous problems experienced had been related to the presence of the α-hydrogen. No significant difference in yield was observed between using the sulfide or sulfone starting material in the SmI_2-mediated reaction (Table 20, Entry 17).



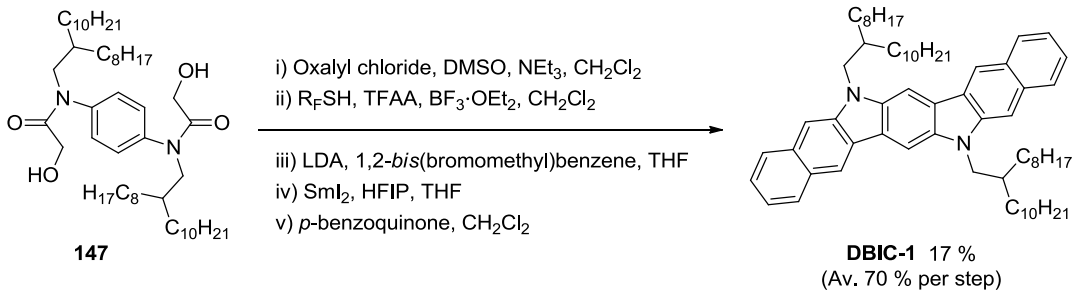
152 **DBIC-1**

Entry	Proton Source (eq.)	Temp.	Conditions / Notes[a]	Yield[d] / %
1	*t*BuOH (3.0)	rt	A	5
2	MeOH (3.0)	rt	A	6
3	No proton source	rt	A	< 1
4	TFE (1.5)	rt	A	17
5	TFE (3.0)	rt	A	21
6	TFE (2.2)	60 °C	A	24
7	TFE (2.2)	rt	A	17
8	TFE (2.2)	rt	A[b]	28
9	TFE (3.0)	-78 °C	A	0[c]
10	TFE (3.0)	-40 °C	A	0
11	TFE (3.0)	-20 °C	A	10
12	TFE (3.0)	-78 °C	B	18
13	TFE (3.0)	rt	C	23
14	TFE (3.0)	-20 °C	C	10
16	HFIP (3.0)	rt	A	27
17	TFE (3.0)	rt	D	25

Table 20 Optimisation of the two-directional SmI_2-mediated cleavage-cyclisation cascade; [a] A = SmI_2 addition dropwise (over 1 min) to substrate + proton source in THF at temperature indicated then maintained at this temperature until end of reaction as indicated by TLC; B = Same conditions as A but stirred for 15 min at the indicated temperature post addition, then warmed to room temperature; C = Same as for A but with added NiI_2 (2 mol%) and visible light irradiation; D = Same as for A but with sulfone used as starting material; [b] Starting material purified using silica gel; [c] Impurity **153** formed see Scheme 43. [d] Isolated yield.

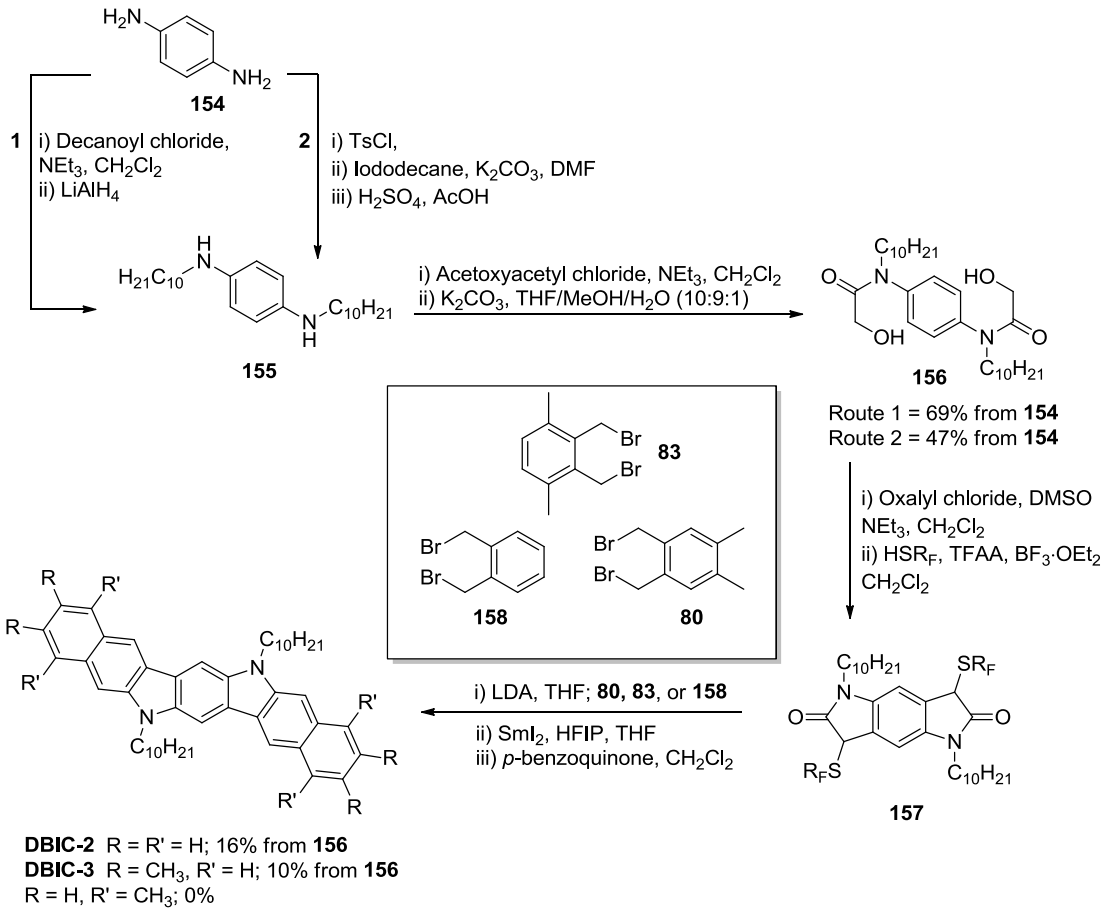
The optimised route is summarised below (Scheme 45), the intermediates between *bis*-hydroxyamide **147** and the final dibenzoindolo[3,2-*b*]carbazole (**DBIC-1**) are purified only

by FSPE, this offers benefits in both speed and convenience but more importantly facilitates isolation of the intermediate products, which appear unstable on silica gel, in reasonable purity. The final product is obtained in a moderate overall yield of 17% from the introduction of the tag (Swern oxidation/connective-Pummerer) to the removal of the tag (SmI_2-mediated cleavage-cyclisation/aromatisation), which over five steps equates to an average yield per step of ~70%. It is worth noting that some of the fluorous tag could be recovered (as the disulfide), which Dr Coote has previously demonstrated can be re-cycled by conversion back to R_FSH using nBu$_3$P in H_2O/THF.[123]



Scheme 45

This route was also utilised to access the same dibenzoindolo[3,2-*b*]carbazole core structure with shorter linear -$C_{10}H_{21}$ chains. In this instance, two different approaches to the *bis*-hydroxyamide **147** were investigated; one via our previous amide formation / reduction route, and another via tosylation and alkylation, in an attempt to bypass the poorly soluble diamide intermediate. Protection of the phenylenediamine **154** with tosylchloride, alkylation with iododecane and K_2CO_3 in DMF, followed by deprotection with H_2SO_4, and then formation of the hydroxyamide gave the desired product **147** in 47% yield, and offered no improvement over our previous route in terms of practicality. By comparison, our standard synthetic approach for the introduction of the solubilising chain (via amide coupling with phenylene diamine, followed by reduction) gave the desired hydroxyamide product in 69% yield (Scheme 46).



Scheme 46

Using the previously described approach, the desired fluorous tagged *bis*-oxindole **157** could be obtained in good yield and selectivity (>5:1) after purification by FSPE. Alkylation was then peformed with three different electrophiles. Using **80** and **158** gave good conversion to the desired cyclisation substrates, with yields of 74% and 63% obtained respectively after FSPE. Unfortunately when the alkylation was attempted with **83** none of the desired alkylated product could be distinguished in the initial fluorous FSPE fraction by either MALDI-MS or ^{1}H NMR.

The cyclisation substrates proceeded to give the desired heteroheptacenes **DBIC-2** and **DBIC-3** in yields of 16% and 10% (5 steps) respectively upon reaction with SmI_2/HFIP followed by *p*-benzoquinone, the lower yield observed for **DBIC-3** is thought to be due to poorer stability during purification rather than a difference in reactivity between the two substrates during the SmI_2-mediated processes. Alongside the two products the fluorous disulfide was recovered in 14-37% yield.

3.3 Physical properties of dibenzoindolo[3,2-*b*]carbazoles

3.3.1 Optical and electrical properties

Cyclic voltammetry revealed two reversible oxidation peaks for all three compounds, the low onset indicating HOMO energies of -5.13 eV, -5.19 eV and -4.99 eV for **DBIC-1**, **DBIC-2**, and **DBIC-3** respectively (Figure 29). These values are all significantly higher than those reported for indolo[3,2-*b*]carbazoles in the literature (HOMO = -5.43 to -5.6 eV for **3POIND** and related compounds),[162] and are instead similar to those of substituted heptacenes and heteroheptacenes such as **139** (-5.1 eV),[247] **140** (-5.3 eV),[248] and **141** (-5.18 eV) (Figure 26).[249]

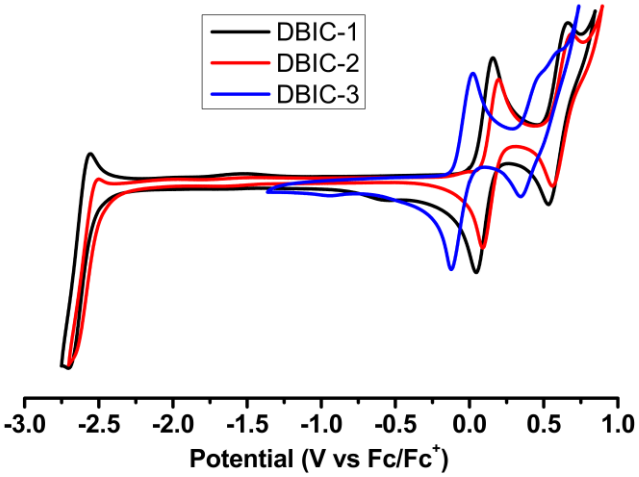


Figure 29 Cyclic voltammograms of **DBIC-1**, **DBIC-2**, and **DBIC-3**; Cyclic voltammetry was carried out using 0.001 M solutions of the compounds of interest, with a supporting electrotype of 0.1 M tetrabutylammonium hexafluorophosphate in THF, a Pt wire working electrode, and a $Ag/AgNO_3$ reference electrode, using a scan speed of 100 mVs^{-1}.

Irreversible reduction peaks were also observed for compounds **DBIC-1** and **DBIC-2**, corresponding to LUMO energies of -2.58 eV and -2.63 eV respectively.

UV-Vis spectra showed that all three compounds possessed slightly smaller band gaps (2.4 eV) than observed for indolo[3,2-*b*]carbazole derivatives with aromatic end caps such as **3POIND** and **3TOIND** (2.6 eV and 2.8 eV respectively), and much larger than observed for heptacene (1.5 eV) (Figure 30). The LUMO energies calculated indirectly from the optical band gap and HOMO energy level, and those estimated directly from cyclic

voltammetry were in good agreement, with the values obtained from the optical band gaps lying at -2.72 eV and –2.79 eV for **DBIC-1** and **DBIC-2** respectively.

The experimental data obtained for all three compounds, along with HOMO and LUMO energies calculated using DFT by Dr Iain Grace are summarised below in Table 21.[216] The calculated values underestimate the HOMO and overestimate the LUMO energy, predicting a lower energy HOMO and higher energy LUMO, but the relative differences between the materials is accurately reflected.

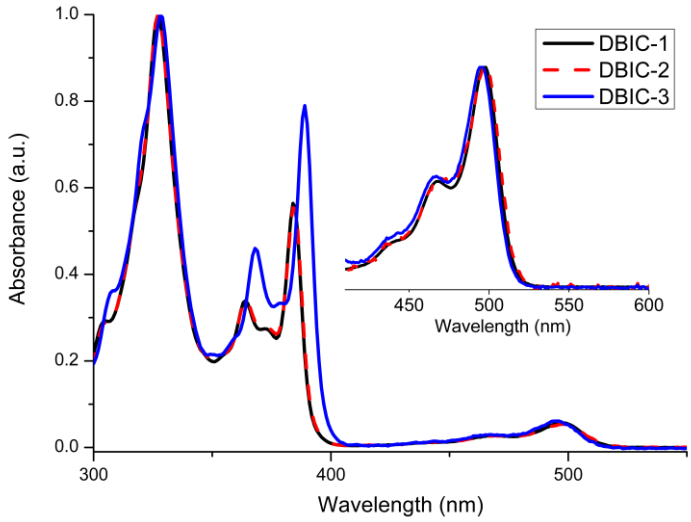


Figure 30 Compiled UV-Vis Spectra.

	HOMO / eV[a]	LUMO / eV[b]	HOMO calc / eV[c]	LUMO calc / eV[c]	λ_{onset} / nm[d]	E_g / eV[e]
DBIC-1	-5.13	-2.72	-5.70	-0.77	515	2.41
DBIC-2	-5.19	-2.79	-5.70	-0.77	516	2.40
DBIC-3	-4.99	-2.57	-5.52	-0.67	513	2.42

Table 21 Summary of electronic properties of **DBIC-1**, **DBIC-2**, and **DBIC-3** obtained by cyclic voltammetry and UV-Vis spectroscopy; [a] Calculated using E_{HOMO} (eV) = -(5.1 + E_{Ox} - $E_{Fc/Fc+}$); [b] Calculated using E_{LUMO} (eV) = E_{HOMO} (eV) + Eg (eV); [c] Calculated values provided by Dr I. Grace using the DFT code SIESTA [See SI of *Org Lett*, **2012**, 5744 for a discussion of the method used]; [d] Obtained by UV-Vis spectroscopy of a dilute solution of the compound in CH_2Cl_2; [e] Calculated using $E=hc/\lambda_{onset}$.

3.3.2 Thermal properties

Analysis by TGA indicated that all three compounds possess good thermal stability with the onset of decomposition (T_{onset}) occurring above 400 °C (Table 22).

Compound	Decomposition T_{onset} / °C	T_m / °C
DBIC-1	444	106
DBIC-2	423	194
DBIC-3	415	229

Table 22 Summary of melting points (T_m) and decomposition temperatures (T_{onset}), measured by DSC and TGA respectively.

Analysis by DSC indicated that **DBIC-1** possesses a low melting point, and showed the presence of liquid crystalline phases. After further study through collaboration with Nicholas Kasch (School of Physics and Astronomy-The University of Manchester) it was suggested that the following phase transitions are present: crystalline solid - 100 °C - crystal E phase - 104 °C - smectic B or crystal B phase - 106 °C - isotropic liquid (See Appendix E for POM images). **DBIC-2** and **DBIC-3** showed single melting endotherms at much higher temperatures (194 °C and 229 °C respectively), a consequence of substituting the chiral branched -C_8/C_{10} chain for a shorter linear -C_{10} chain (Figure 31).

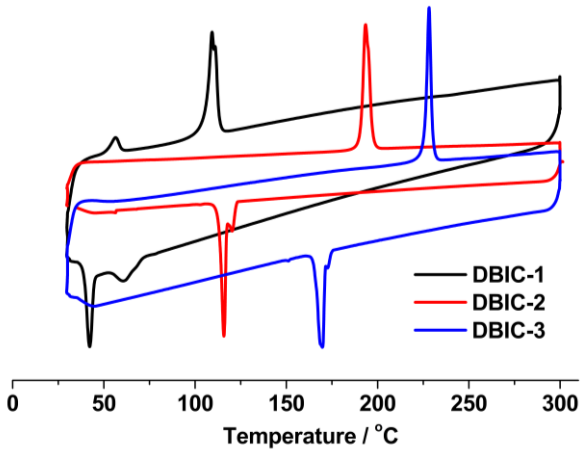


Figure 31 Compiled DSC traces.

3.3.3 X-ray crystal structures

Single crystals of both **DBIC-2** and **DBIC-3** were grown from THF. The single crystal of **DBIC-2** was found to pack in a P $2_1/c$ type space group, with unit cell parameters; a = 15.6742(10) Å, b = 5.4689(4) Å, and c = 21.5676(15) Å; and α = 90.00, β = 90.055(6), and γ = 90.00 (Figure 32). Segregation of the alkyl chains and aromatic cores is observed and the crystal shows a lamellar-type structure (with the aromatic cores arranged in layers separated by regions of aggregated alkyl chains with an inter-lamellar spacing of 15.67 Å), in which the aromatic cores pack in a herringbone-like manner similar to pentacene but offset along the long axis of the molecule such that only three rings from each molecule are overlapping in the edge-to-face orientation. Each molecule is surrounded by six others via a shortest carbon–carbon distance of 3.5 Å, two in a completely offset parallel face-to-face arrangement and four in an edge–to–face manner.[37] Within the herringbone motif the closest face-to-face centroid-to-centroid distance is 5.47 Å, which is too large a distance for any displaced face-to-face interactions; however, several short contacts are observed, such that each aromatic core is connected to four surrounding cores via edge–to-face C-H$^{\cdots}\pi$ interactions (2.59 Å). The centroid-to-centroid distance between the closest aromatic rings in this arrangement is 4.75 Å in an edge–to–face arrangement. NC-H$^{\cdots}\pi$ interactions (2.80 -2.99 Å) and a C-H$^{\cdots}\pi$ interaction (2.87 Å) between the alkyl chains and adjacent aromatic cores are also observed. A slight torsional twist of 3.83° (measured from C13-C13 to C8-C9) is observed along the aromatic core. The overall packing structure and intermolecular distances are similar to those seen for **3POIND** (intermolecular distances of 3.5-3.6 Å) and **OPIND** (intermolecular distances of 3.5-3.7 Å).[162]

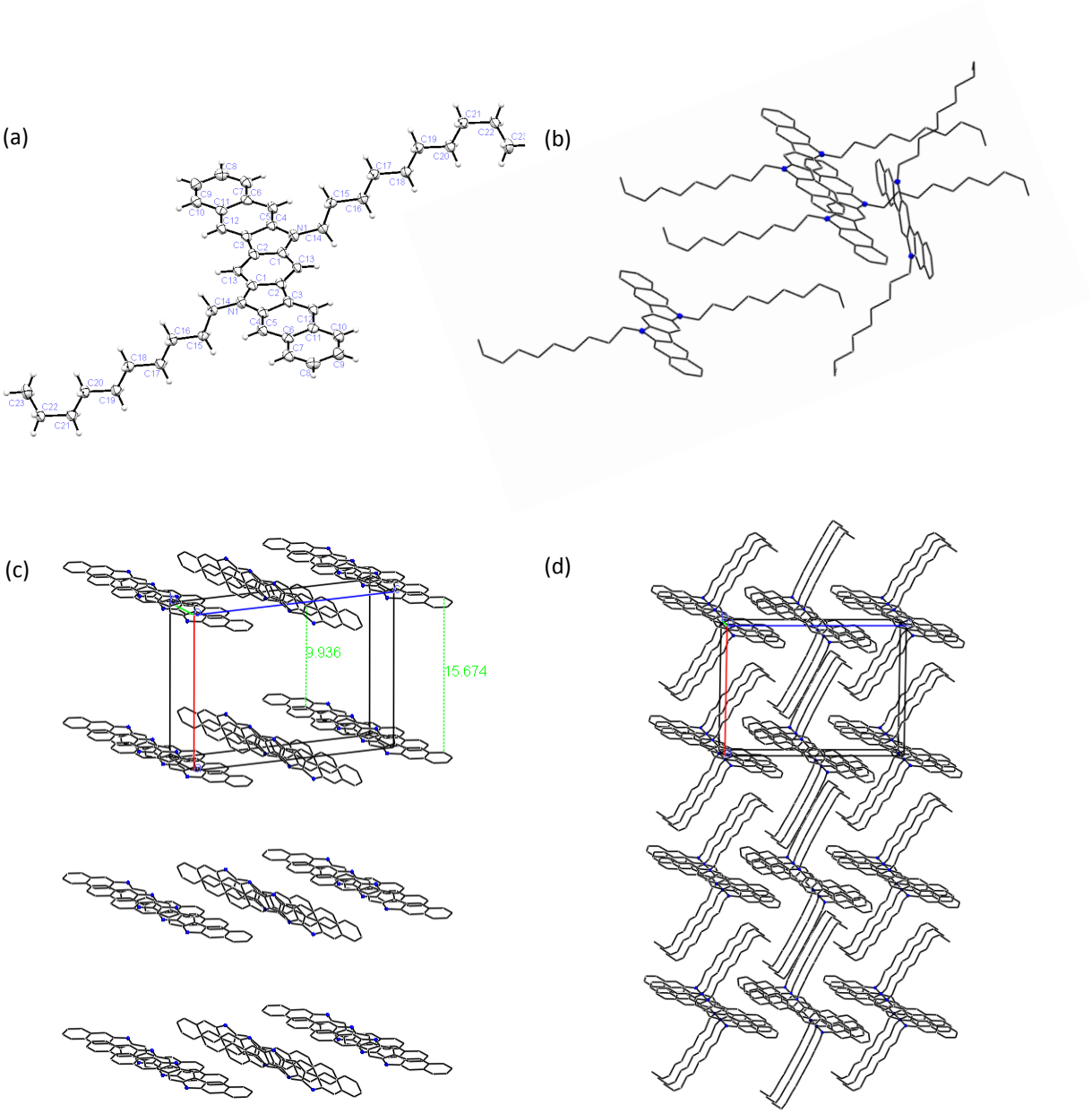


Figure 32 Crystal structure of **DBIC-2** showing; (a) structure with thermal ellipsoids, (b) herringbone structure, and lamellar structure without (c), and with (d) alkyl chains.

The crystal of **DBIC-3** was found to pack in a P -1 space group with cell constants of a = 5.9862(5) Å, b = 16.452(2) Å, c = 20.7760(18) Å and α = 95.482(9)°, β = 94.572(7)°, γ = 97.856(9)° (Figure 33). The compound stacks in a herringbone motif, and segregation of the alkyl chains is again observed with an interlayer spacing of 16.45 Å, with the unit cell containing two molecules. The closest face–to–face, centroid–to-centroid stacking distances of 5.78 and 5.94 Å are again too great for any face-to-face interactions, whilst the closest edge–to–face centroid–to–centroid distances of 4.91 Å and 5.29 Å indicate weaker intermolecular interactions than for **DBIC-2**. Each molecule is surrounded by six

others in the same manner observed for **DBIC-2** (except with only two rings on each adjacent molecule overlapping in the edge-to-face orientation) via a shortest carbon–carbon distance between 3.7-3.8 Å, four of these in an edge-to-face arrangement and two in a completely offset parallel face-to-face arrangement. Short contacts (CH···π and CH···CH hydrophobic interactions) exist between the alkyl chains / capping methyl groups, and the aromatic cores, and between the alkyl substituents themselves. The two molecules in the unit cell also exhibit torsional twists of 4.72 ° and 5.88 ° (measured in the same manner as for **DBIC-2**).

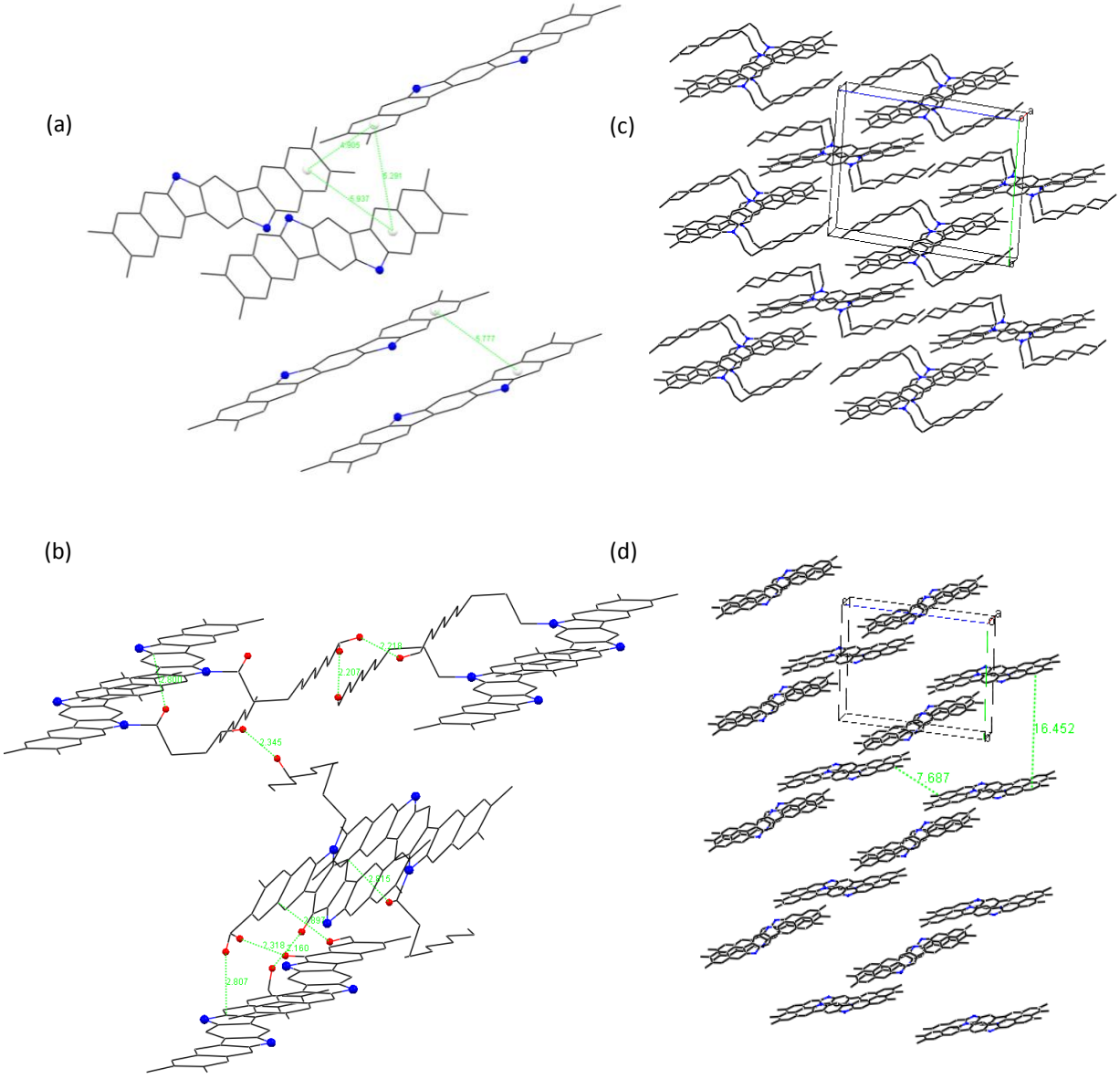


Figure 33 Crystal structure of **DBIC-3** showing (a) herringbone packing structure, (b) structure indicating short contacts [selected alkyl chains omitted for clarity], and lamellar structure with (c), and without (d) alkyl chains.

The crystal structures of both compounds show twisting of the alkyl chains, which implies that the packing structure is dominated by the aromatic cores, with the alkyl chains twisting to accommodate the packing of the aromatic core.

3.4 OFET Devices based on dibenzoindolo[3,2-*b*]carbazoles

3.4.1 Devices based on branched chain materials

The synthesised aza-heptacenes were investigated as the transport layer in OFET devices. Several sets of OFETs were produced from **DBIC-1**, via spin coating from 0.5% w/w solutions in a range of solvents (anisole, toluene, and THF) onto both bare SiO_2 and OTS-18 treated SiO_2. Initially a top-contact geometry was investigated, but poor device performance was observed. Upon inspection of the devices by optical microscopy it was evident that the high temperature generated during the gold evaporation process, coupled with the low melting point of **DBIC-1**, was causing the films to crack and in some cases melt around the gold contacts (Figure 34). The working OFETs obtained showed an average mobility of 2.6×10^{-3} ($\pm 5 \times 10^{-4}$) $cm^2\ Vs^{-1}$, and an average I_{on}/I_{off} ratio of 1.3×10^3, with a large degree of hysteresis (18 ± 4 V).

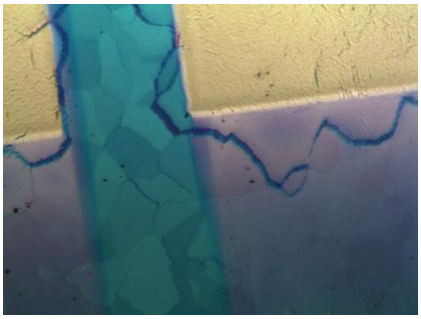
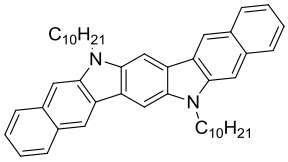


Figure 34 Optical microscope image of film cracking (channel width = 60 μM).

Bottom-contact devices were briefly investigated, in order to avoid any heating of the film once deposited. Unfortunately devices fabricated by both spin-coating and drop-casting onto bare-SiO_2 and OTS-SiO_2 failed to generate any working devices.

3.4.2 Devices based on linear chain materials

Devices were next fabricated from **DBIC-2** and **DBIC-3** by vacuum sublimation (Table 23). Two different substrate temperatures were investigated (25 °C and 100 °C) along with three different dielectric layers (SiO_2, OTS-SiO_2, and PMMA-SiO_2).



Conditions	μ / cm^2 Vs^{-1}	I_{on}/I_{off}	V_T / V	Hysteresis / V	No. working devices
OTS-SiO_2; substrate heated at 100 °C	**3.22×10^{-3} ($\pm 1 \times 10^{-3}$)**	**2×10^4**	**-20**	**11**	**7/9**
	4.04×10^{-3} ($\pm 1 \times 10^{-3}$)	**4×10^4**	**-19**	**11**	
SiO_2; substrate heated at 100 °C	1.07×10^{-4} ($\pm 2 \times 10^{-4}$)	2×10^2	-25	8	5/9 [a]
	1.73×10^{-4} ($\pm 2 \times 10^{-4}$)	2×10^2	-26	12	
OTS-SiO_2; substrate heated at 25 °C	1.99×10^{-2} ($\pm 8 \times 10^{-3}$)	4×10^4	-35	10	5/9 [a]
	2.43×10^{-2} ($\pm 7 \times 10^{-3}$)	4×10^4	-39	8	
SiO_2; substrate heated at 25 °C	1.26×10^{-4} (9×10^{-5})	4×10^2	-30	12	7/9 [a]
	2.07×10^{-4} (7×10^{-5})	5×10^2	-30	12	

Table 23 Summary of the performance of devices based on **DBIC-2**; [a] Devices do not function correctly (bad shape to transfer curves particularly on the reverse scan); Black (top) is average of all working devices, red (bottom) is average of best three devices (based on μ).

The best performance was observed with OTS-SiO_2 treated substrates, which gave I_{on}/I_{off} values and mobilities an order of magnitude higher than for the untreated substrate. When PMMA was used, no working devices were observed. The devices fabricated with a substrate temperature of 25 °C did not show normal transfer behaviour, thus making it hard to accurately assess the mobility (Table 23). Meanwhile devices fabricated on OTS-SiO_2, with a substrate temperature of 100 °C, showed good transfer characteristics from which the mobility was calculated to be 4.04×10^{-3} ($\pm 1 \times 10^{-3}$) cm^2 Vs^{-1} (Figure 35 and

Table 23). All the devices were found to exhibit fairly large hysteresis between the forward and reverse V_G sweeps, as was observed for **DBIC-1**.

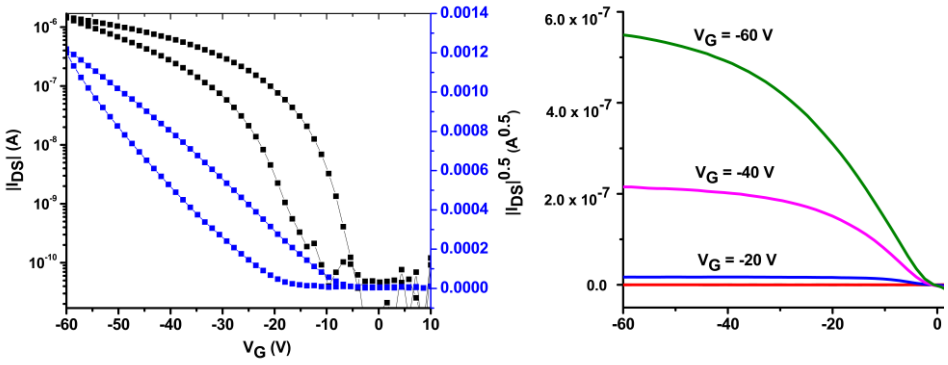


Figure 35 Transfer and output curves for **DBIC-2**

Devices fabricated from **DBIC-3** were found to perform much more poorly, with only one set of devices showing any transfer characteristics (Table 24). Devices fabricated on a OTS-SiO_2 substrate heated at 25 °C, displayed mobilities of 3.1×10^{-5} ($\pm 2.8 \times 10^{-5}$) cm^2 Vs^{-1}, and I_{on}/I_{off} ratios of 4×10^3.

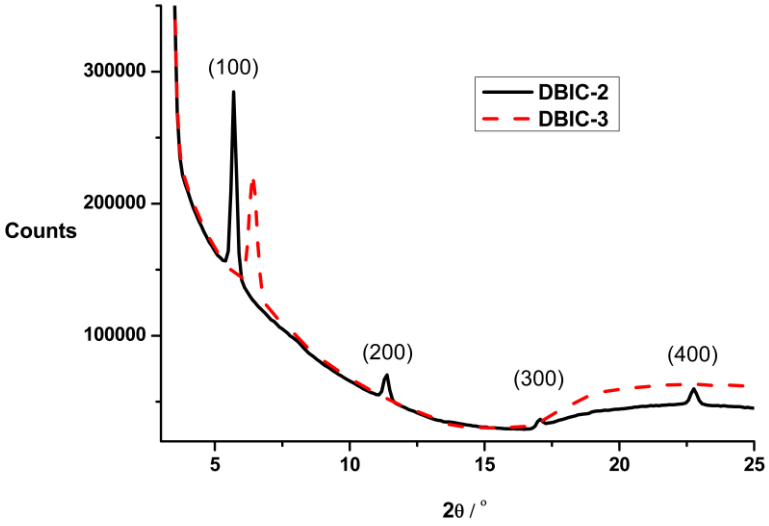


Figure 36 XRD diffractograms of thin films of **DBIC-2** and **DBIC-3** on SiO_2 substrates.

Analysis by powder XRD indicates that changing between the two substrate temperatures has little impact on the bulk orientation of the compound within the film. For compound **DBIC-2** a primary diffraction peak is observed at 2θ = 5.70° (100 °C) and 5.72° (25 °C), with second, third and fourth-order diffraction peaks visible at both temperatures (Figure 36). The primary diffraction peaks correspond to a d-spacing of 15.5 Å, this matches closely

with the predicted (1, 0, 0) reflection from the single crystal data, which predicts a d-spacing of 15.7 Å. This hints that the compound may be adopting an orientation in which the alkyl chains are pointing both downwards towards the substrate and upwards away from the substrate, with the aromatic core laid with its longest axis off parallel by an angle of ~ 35° relative to the substrate (Figure 37). **DBIC-3** displays a primary diffraction peak of 6.39°, corresponding to a d-spacing of 13.8 Å. This matches with the predicted primary diffraction peak at 6.56° (0,1,-1), estimated from the single crystal data, suggesting the aromatic core of the compound may be adopting a conformation with its long axis at an angle of ~50° relative to the substrate.

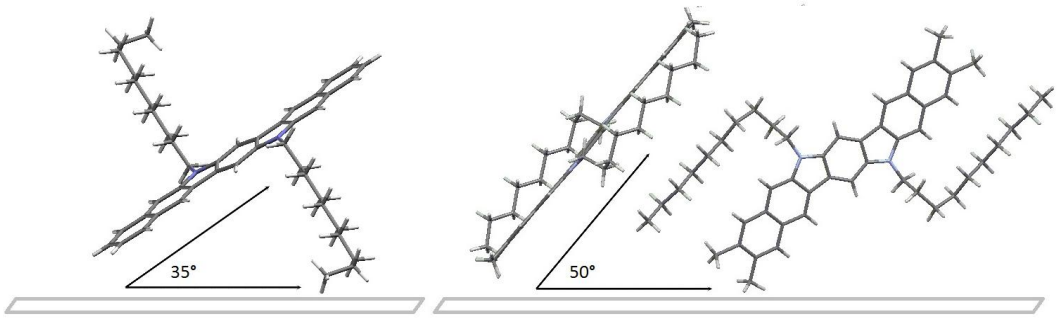


Figure 37 Potential orientation of **DBIC-2** (left) and **DBIC-3** (right) in thin films on SiO_2 substrates.

Upon examination of the films of **DBIC-2** by optical microscopy it was clear that with the higher substrate temperature (100 °C) larger crystalline grains had formed (Figure 38).

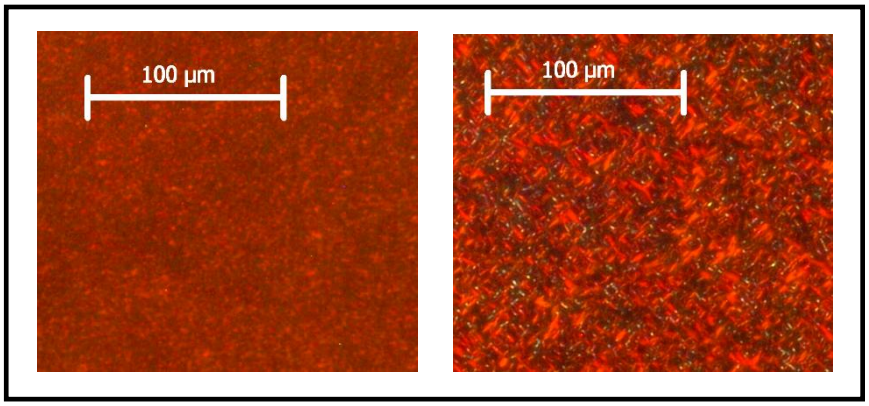


Figure 38 Polarised optical microscopy images of thin films of **DBIC-2** deposited onto OTS-SiO_2 subtrates heated at 25 °C (left) and 100 °C (right).

Using the coordinates from the crystal structures, Dr Iain Grace at the University of Lancaster calculated estimates of both the transfer integrals (t) and reorganisation

energies (λ) for charge transfer in the edge-to-face direction for both **DBIC-2** and **DBIC-3** (Table 24). Using the semi-classical Marcus hopping model, the rates of charge transfer at rt (hole) were then calculated to be 0.22 s^{-1} and 0.02 s^{-1} for **DBIC-2** and **DBIC-3** respectively.[9] The calculated reorganisation energies are low and close in value (0.076 eV and 0.074 eV), with the source of the differing rates being derived from the large difference in the respective transfer integrals (0.11 eV Vs 0.05 eV). This correlates with the observed relative mobilities of **DBIC-2** and **DBIC-3**, and is likely to be a participating factor in the differences in performance of these two compounds.

	μ / $cm^2 Vs^{-1}$	I_{on}/I_{off}	V_T	t / eV[a]	$\lambda_{(hole)}$ / eV[a]	$k_{(hole)}$ / s^{-1}
DBIC-1	2.6×10^{-3} ($\pm 5 \times 10^{-4}$)	1×10^3	-1	-	-	-
DBIC-2	4.0×10^{-3} ($\pm 1 \times 10^{-3}$)	4×10^4	-19	0.11	0.076	0.22
DBIC-3	3.1×10^{-5} ($\pm 2.8 \times 10^{-5}$)	4×10^3	-13	0.05	0.074	0.02

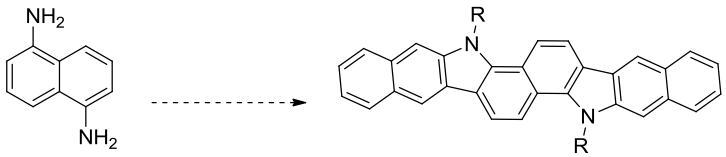
Table 24 Summary of device characteristics, and calculated transfer integrals (t) and reorganizational energies (λ).

3.5 Conclusion and future work

The utility of the two-directional Pummerer reaction in the synthesis of novel organic semiconductors has been demonstrated. It has been shown that the *bis*-oxindole products can be taken forwards in a variety of ways to access three different classes of organic semiconductor. Primarily the two-directional SmI_2-mediated cleavage-cyclisation reaction has been studied and shown to work in a similar manner to the analogous one-directional reaction developed previously, allowing access to novel aza-heptacene compounds in overall yields of 10-17% for five steps from *bis*-hydroxyamides **147** and **156**.

The dibenzoindolo[3,2-*b*]carbazoles described in this work displayed good stability under ambient conditions, the measured HOMO energies seeming to suggest that further extension of the conjugation length may still yield stable materials. With this in mind it would be interesting to assess the stability of the aza-octacene **162** which could

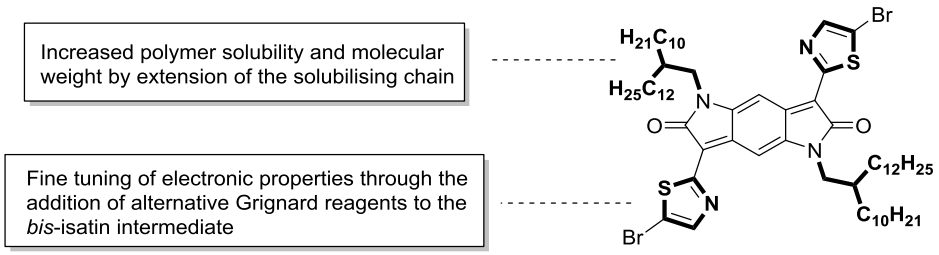
potentially be accessed from commercially available naphthalene-1,5-diamine via our current procedure without any modifications (Scheme 47). The twisted nature of **162** possibly generating a more stable material and allowing for straight forward synthesis without any issue arising from the regioselectivity of the Pummerer cyclisation.[248,260]



162

Scheme 47

Based on work within the McCulloch group it is apparent that further work fine-tuning the solubilising chain utilised for the **BPT** monomer is needed in order to improve the solubility of the resulting polymer, which will in turn lead improved polymerisations giving polymers of higher molecular weight. It would also be interesting to alter the Grignard used (for example chloro(1,3-thiazol-2-yl)magnesium) in order to assess the impact of differing aromatic groups on the resulting polymer and to allow fine tuning of electronic properties (Scheme 48).



Scheme 48

4 Experimental

4.1 General experimental

All experiments were performed under an atmosphere of N_2, using anhydrous solvents unless otherwise stated. All reactions were carried out using oven dried glassware. Tetrahydrofuran was distilled from sodium/benzophenone. CH_2Cl_2, toluene and NEt_3 were distilled from CaH_2. Petroleum ether refers to the fraction of petroleum ether boiling in the range 40-60 °C. All other solvents were purchased from commercial sources and used as supplied. Anhydrous DMF and dioxane used in Stille cross couplings was purchased commercially then further dried over activated 3Å molecular sieves. *p*-Benzoquinone was purified by sublimation under reduced pressure at room temperature using a liquid N_2 filled cold finger. NBS was purified by recrystallisation from H_2O. HMPA was dried and purified using 13X molecular sieves. *n*BuLi, LiHMDS and LDA (Freshly prepared from *n*BuLi and DIPA in THF) were titrated immediately prior to use by addition to menthol in THF using either 1,10-phenanthroline or fluorene as indicator. LiCl, LiBr, NiI_2 and molecular sieves were flame dried under vacuum before use. $Fe(DBM)_3$ was prepared according to *Tetrahedron Lett*, 1996, **37**, 2577 (mp 245-250 °C [Lit. 240 °C][138]).

All commercially available reagents were purchased and used without further purification unless otherwise stated.

^1H, ^{13}C, and ^{19}F NMR were recorded using 300, 400, or 500 MHz spectrometers with chemical shift values reported in ppm relative to either residual undeuterated solvent ($CHCl_3$ δ_H = 7.27, δ_C = 77.0, C_6H_6 δ_H = 7.15, δ_C = 128.6, C_7H_8 δ_H = 2.11, δ_C = 21.4) as an internal standard or $CFCl_3$ (δ_F = 0.00) as an external standard unless otherwise stated. All coupling constants (*J*) are reported in Hertz (Hz). ^1H and ^{13}C NMR assignments were made on the basis of COSY, HMQC, and DEPT-135 spectra. In the ^{13}C NMR spectra, discrete CF_2 shifts are not observed due to carbon-fluorine coupling which results in low intensity multiplets which cannot be accurately distinguished from the background noise. Infrared spectra were recorded using an FTIR spectrometer as evaporated films or using an ATR accessory. Melting points are uncorrected. Mass spectrometry was performed by the

Mass Spectrometry service in the School of Chemisty at the University of Manchester, and the EPSRC National Mass Spectrometry Facility. HRMS determined masses of bromine containing compounds refer to the ^{79}Br isotope.

Routine TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. Plates were visualised by UV and/or by staining with aqueous potassium permanganate, ethanolic *p*-anisaldehyde or ethanolic phosphomolybdic acid. Column chromatography was carried out using 35-70μ, 60A silica gel.

UV-Vis spectra were run as dilute solutions in CH_2Cl_2 or THF on a Cary 5000 UV-Vis-NIR Spectrophotometer using a quartz cuvette (10 mm × 10 mm). Cyclic voltammetry was carried out using a BASi C3 cell using a scan speed of 100 mVs^{-1} and a supporting electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate in MeCN, a Pt wire counter electrode, an $Ag/AgNO_3$ reference electrode and a Pt foil working electrode upon which the compounds to be measured were spin coated from a 1% w/w solution of toluene to give a thin film; or alternatively as 0.001 M solutions in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in THF using a Pt wire working electrode. TGA was performed on a TGA Q5000 IR Thermogravimetric analyser, heating at a rate of 10 °C/min from room temperature to 600 °C in an aluminium pan. DSC was performed on a PerkinElmer Jade DSC apparatus heating at a rate of 10 °C/min. Powder-XRD was performed on a Bruker D8 Discover with a Cu source.

4.2 Device fabrication procedures

Substrate cleaning and preparation:

Si^{++}/SiO_2 wafer was cut to size as appropriate by scoring with a silicon carbide scriber and snapping across a straight edge. Samples were first rinsed with deionised water and then ultrasonicated for 5 min in each of acetone, isopropanol and methanol. Samples were blown dry with a stream of dry nitrogen and treated with UV/O_3 for 20 min to remove organic contaminants.

TFT Fabrication:

Top Contact - Spincoating was carried out inside a nitrogen glove box and unless otherwise stated substrates were approximately 10 x 10 mm and 50 µl coating solution was used.

Source and drain contacts were deposited by evaporation using an Edwards Auto 500 metal evaporator inside a nitrogen glove box. All contacts were 100 nm gold and patterned by shadow masking. Unless otherwise stated, substrates were patterned with nine sets of source and drain contacts, with channels from 20 µm to 100 µm in increments of 10 µm all TFTs had a channel width of 2000 µm.

Bottom Contact - Source and drain contacts were deposited by evaporation (Chromium (~4 nm), followed by gold (~50 nm) through a shadow mask (20 x 20 mm). After deposition of the OSC, the contacts were cleared of excess OSC using an appropriate solvent.

Octadecyltrichlorosilane Self-Assembled-Monolayer (SAM) formation:

Using the method of Z. Bao et al.,[27] a solution of 4.5 µL octadecyltrichlorosilane in 4 mL TCE was prepared in a glove box. Freshly UV/Ozone treated wafer samples were placed in a spincoater and 50 µL of the OTS solution were added. Th wafer was allowed to stand for 10 sec before spinning at 3000 rpm for 10 sec, this application procedure was then repeated three times for each substrate. The samples were next placed on a hotplate and heated to 105 °C for 20 min. To remove visible residual OTS from the surface of the substrates, they were swabbed using a lint-free clean-room wipe soaked in methanol. The substrates were then sonicated for 5 min in both $CHCl_3$, *i*PrOH and MeOH and blown dry with a stream of dry nitrogen before being placed into a nitrogen glovebox for storage prior to use. The quality of OTS-treatment was assessed by contact angle measurement, which using this procedure was found to be 109° (± 2) (Figure 39). This value is consistent with values obtained by others within the Turner group and the values originally published in the literature cited above.

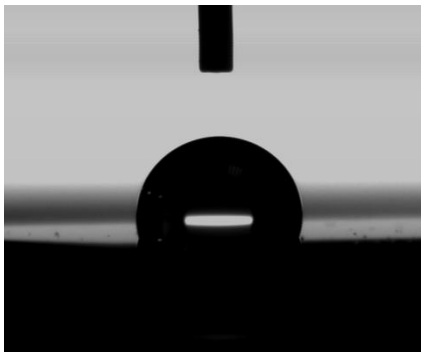


Figure 39 De-ionised water droplet on OTS-treated SiO_2/Si wafer

PMMA dielectric formation:

A 1% w/w solution of PMMA (average M_W = 996,000) in anisole was prepared then spin coated at 3000 rpm for 3 min onto the SiO_2/Si wafer, followed by cross-linking at 220 °C for 1 h. The quality of PMMA-treatment was assessed by contact angle measurement, which was found to be 76° (± 2). This value is consistent with values observed in the literature.[272,273]

TFT characterization:

Thin film transistors were characterised under an N_2 atmosphere at 20 °C in order to obtain comparable results between different compounds. Unless otherwise stated, OFETs were characterised by transfer measurements at V_{SD} = -60 V (saturation regime) and V_G was swept from 10 to -60 V and back. The gradient of the linear portion of the graph of the square root of I_{SD} against V_G was used to calculate the field effect mobility of the device according to the standard MOSFET equation. The intercept of this gradient line with the V_G axis (at I_{SD} = 0) was used to obtain V_T.

4.3 Procedure for the use of fluorous solid-phase extraction (FSPE)

A glass column was packed with fluorous silica gel using 60 or 80% aqueous MeCN. The mixture to be purified was dry loaded onto the fluorous silica gel. Elution with either 60

or 80% aqueous MeCN (2-3 column volumes) separated the non-fluorous components of the mixture. Elution with 100% MeCN or THF (2-3 column volumes) provided the fluorous components of the mixture. The fluorous column could be recycled up to 30 times by rinsing with THF and MeOH and then drying with compressed air.

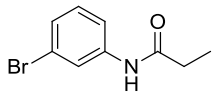
4.4 Preparation of samarium diiodide (SmI_2)[274]

Samarium diiodide was prepared by a modification of the procedure of Imamoto and Ono. Samarium powder (2.00 g, 13.8 mmol, 1.2 eq.) was added to an oven-dried round-bottomed flask and the flask was sealed and flushed with nitrogen gas for 20 min. THF (110 mL) was added and the resulting suspension was bubbled with nitrogen gas for 15 min. Finally, iodine (2.80 g, 10.8 mmol, 1.0 eq.) was added and the flask flushed again with nitrogen gas for 10 min. The flask was covered in aluminium foil and heated at 60 °C for 18 hours. The ~0.1 M solution was allowed to cool to room temperature and then used directly.

4.5 Synthetic Procedures

General procedure A: Preparation of propionamides

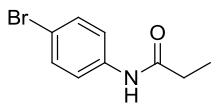
34 *N*-(3-Bromophenyl)-propionamide



To a stirred solution of *m*-bromoaniline (3.04 g, 17.7 mmol) in CH_2Cl_2 (90 mL) was added NEt_3 (2.68 g, 26.5 mmol) and propanoic anhydride (4.60 g, 35.3 mmol) at 0 °C. The resulting solution was then allowed to warm to 20 °C and stirred for 16 h. The solution was then washed with a saturated solution of $NaHCO_3$ (3 × 20 mL), dried ($MgSO_4$), and concentrated *in vacuo* to yield the crude product. Trituration with Et_2O:Hexane (1:1, 20 mL) gave pure **34** (3.19 g, 14.0 mmol, 79%) as a white solid, mp (Et_2O/hexane) 89-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.25 (3 H, t, *J* = 7.5 Hz; C*H*$_3$), 2.40 (2 H, q, *J* = 7.5 Hz; C*H*$_2$), 7.14 (1 H, s; N*H*), 7.16-7.24 (2 H, m; 2 × Ar*H*), 7.42 (1 H, d, *J* = 7.82 Hz; Ar*H*), 7.80 (1 H, s; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 9.6 (*C*H$_3$), 30.7 (*C*H$_2$), 118.2 (Ar*C*H), 122.6 (Ar*C*),

122.7 (Ar*C*H), 127.1 (Ar*C*H), 130.3 (Ar*C*H) 139.1 (Ar*C*), 172.1 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 3289, 3241, 3175, 3103, 3067, 2974, 2938, 2879, 1682, 1652 (C=O), 1587, 1528, 1471, 1435, 1416, 1380, 1362, 1303, 1267, 1242, 1194, 1165, 1091, 1068, 1017; MS *m/z* (ES^+) 249 ($[M+Na]^+$, 100); HRMS (ES^+): $C_9H_{10}ONBrNa$ requires 249.9849, found 249.9839. Elemental analysis: Expected, %: C, 47.39; H, 4.42; N, 6.14; Found, %: C, 47.59; H, 4.19; N, 6.08.

33 *N*-(4-Bromo-phenyl)-propionamide[121]

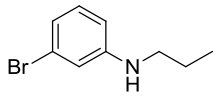


Following general procedure *A*, using *p*-bromoaniline (6.00 g, 34.8 mmol), NEt_3 (5.29 g, 52.3 mmol), and propanoic anhydride (9.07 g, 69.7 mmol) in CH_2Cl_2 (180 mL) gave the crude product. Trituration with Et_2O:Hexane (1:1, 40 mL) yielded pure **33** (7.47 g, 32.8 mmol, 94%) as an amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.26 (3 H, t, *J* = 7.5 Hz; C*H*$_3$), 2.40 (2 H, q, *J* = 7.5 Hz; C*H*$_2$), 7.26 (1 H, s; N*H*), 7.44 (4 H, s; 4 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.3 (*C*H$_3$), 21.0 (*C*H$_2$), 109.3 (Ar*C*), 115.6 (2 × Ar*C*H), 130.4 (2 × Ar*C*H), 141.3 (Ar*C*), 163.5 (*C*=O).

[Data consistent with literature]

General Procedure B: Preparation of propylamines

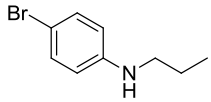
36 (3-Bromophenyl)-propylamine



To a stirred solution of **34** (10.7 g, 46.9 mmol) in THF (200 mL) under N_2 at 0 °C was added $LiAlH_4$ (3.91 g, 103 mmol) over 2 h. The resulting suspension was then warmed to 20 °C and stirred for 6 h. The suspension was then cooled to 0 °C and 15% NaOH:H_2O (1:1, 50 mL) was added dropwise resulting in the formation of a thick precipitate. The mixture was filtered and the solid washed with EtOAc (3 × 50 mL). The filtrate was then washed with H_2O (2 × 150 mL), dried ($MgSO_4$), and concentrated *in vacuo* to yield **36** (7.66 g, 35.8 mmol, 76%) as a brown oil, which was used without further purification; ^{1}H NMR (400

MHz, $CDCl_3$) δ ppm 1.00 (3 H, t, J = 7.4 Hz; CH_3), 1.60-1.69 (2 H, m; CH_2), 3.06 (2 H, t, J = 7.1 Hz; NCH_2), 3.77 (1 H, s; NH), 6.51 (1 H, dd, J = 8.1, 2.3 Hz; ArH), 6.73-6.74 (1 H, m; ArH), 6.78-6.81 (1H, m; ArH), 6.99-7.03 (1 H, m; ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.6 (CH$_3$), 22.5 (CH$_2$), 45.5 (NCH$_2$), 111.4 (ArCH), 115.0 (ArCH), 119.7 (ArCH), 123.3 (ArC), 130.4 (ArCH), 149.7 (ArC); IR (ATR): ν_{max}/cm^{-1} 3410 (NH), 3051, 2960, 2931, 2873, 1597, 1573, 1504; MS (ES$^+$): *m/z* (%) 214 ([M+H]$^+$, 100); HRMS (ES$^+$): $C_9H_{13}NBr$ requires 214.0226, found 214.0217.

35 (4-Bromophenyl)-propylamine[121]

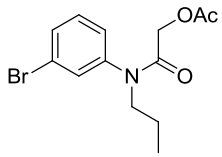


Following general procedure *B*, using **33** (7.72 g, 33.8 mmol) and $LiAlH_4$ (2.83 g, 74.6 mmol) in THF (140 mL) gave **35** (6.41 g, 29.9 mmol, 88%) as a brown oil, which was used without further purification; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.00 (3 H, t, J = 7.4 Hz; CH_3), 1.60-1.67 (2 H, m; CH_2), 3.02-3.08 (2 H, m; NCH_2), 3.66 (1 H, s; NH), 6.48 (2 H, d, J = 8.8 Hz; 2 × ArH), 7.25 (2 H, d, J = 8.8 Hz; 2 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.6 (CH$_3$), 22.5 (CH$_2$), 45.8 (NCH$_2$), 108.5 (ArC), 114.2 (2 × ArCH), 131.9 (2 × ArCH), 147.4 (ArC).

[Data consistent with literature]

General Procedure C: Preparation of acetyl protected hydroxyamides (EDCI Method)

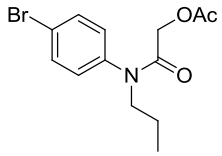
38a 2-((3-Bromophenyl)(propyl)amino)-2-oxoethyl acetate



To a stirred solution of **36** (7.66 g, 35.8 mmol) in CH_2Cl_2 (250 mL) under N_2 was added HOBt (0.97 g, 7.18 mmol), EDCI (8.23 g, 42.9 mmol), and acetoxyacetic acid (5.02 g, 42.5 mmol). The resulting solution was stirred for 19 h, then washed with 1M HCl (3 × 50 mL), dried ($MgSO_4$), and concentrated *in vacuo* to yield **38a** (11.1 g, 35.3 mmol) as a pale yellow oil, which was used immediately in the next step without further purification; ^{1}H

NMR (500 MHz, $CDCl_3$) δ ppm 0.91 (3 H, t, J = 7.4 Hz; CH_2CH_3), 1.41-1.62 (2 H, m; CH_2CH_3), 2.16 (3 H, s; CH_3), 3.55-3.72 (2 H, m; NCH_2), 4.38 (2 H, s; OCH_2), 7.21 (1 H, d, J = 7.9 Hz; Ar*H*), 7.32 (1 H, t, J = 7.9 Hz; Ar*H*), 7.43 (1 H, s; Ar*H*), 7.57 (1 H, d, J = 7.9 Hz; Ar*H*).

37a 2-((4-Bromophenyl)(propyl)amino)-2-oxoethyl acetate[121]

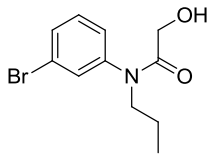


Following general procedure *C*, using **35** (6.41 g, 29.9 mmol), EDCI (6.89 g, 35.9 mmol), HOBt (0.81 g, 6.0 mmol), and acetoxy acetic acid (4.24 g, 35.9 mmol) in CH_2Cl_2 (250 mL) gave crude **37a** (9.3 g, 30 mmol) as a brown oil, which was used immediately without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.89 (3 H, t, J = 7.4 Hz; CH_2CH_3), 1.44-1.60 (2 H, m; CH_2CH_3), 2.13 (3 H, s; CH_3), 3.55-3.72 (2 H, t, J = 7.6 Hz; NCH_2), 4.32 (2 H, s; OCH_2), 7.13 (2 H, d, J = 8.6 Hz; 2 × Ar*H*), 7.58 (2 H, d, J = 8.6 Hz; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.1 (CH_2CH_3), 20.5 (CH_3), 20.7 (CH_2CH_3) 51.1 (NCH_2), 61.6 (OCH_2), 122.6 (Ar*C*) 129.9 (2 × Ar*C*H), 133.26 (2 × Ar*C*H), 139.5 (Ar*C*), 166.2 (*C*=O), 170.6 (*C*=O).

[Data consistent with literature]

General Procedure D: Preparation of hydroxamides

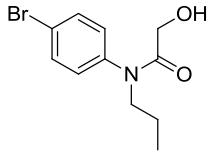
38 *N*-(3-Bromo-phenyl)-2-hydroxy-*N*-propylacetamide



To a solution of **38a (**11.1 g, 35.3 mmol) in MeOH (100 mL) and H_2O (50 mL) was added K_2CO_3 (19.5 g, 141 mmol). The resulting suspension was stirred for 3 h at rt and then H_2O (20 mL) and EtOAc (40 mL) were added. The layers were separated, and the organic layer washed with EtOAc (3 × 40 mL), dried ($MgSO_4$) and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 50% EtOAc in petroleum ether gave the product **38** (7.88 g, 29.0 mmol, 81% for 2 steps)

as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.81 (3 H, t, *J* = 7.4 Hz; C*H*$_3$) 1.40-1.50 (2 H, m; C*H*$_2$CH$_3$), 3.32-3.46 (1 H, m; O*H*), 3.59 (2 H, t, *J* = 7.6 Hz; NC*H*$_2$), 3.69 (2 H, d, *J* = 4.5 Hz; C*H*$_2$OH), 7.04 (1 H, d, *J* = 7.8 Hz; Ar*H*), 7.22-7.28 (2 H, m; 2 × Ar*H*), 7.46 (1 H, d, *J* = 8.1 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.0 (*C*H$_3$), 20.6 (*C*H$_2$CH$_3$), 51.1 (N*C*H$_2$), 60.4 (*C*H$_2$OH), 123.0 (Ar*C*), 126.8 (Ar*C*H), 131.0 (Ar*C*H), 131.1 (Ar*C*H) 131.8 (Ar*C*H), 140.8 (Ar*C*), 171.3 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 3245 (OH), 2963, 2930, 2875, 1653 (C=O), 1586, 1568; MS (ES$^+$): *m/z* (%) 272 ([M+H]$^+$, 20), 194 ([M-Br]$^+$, 100); HRMS (ES$^+$): $C_{11}H_{15}O_2NBr$ requires 272.0281, found 272.0276.

37 *N*-(4-Bromophenyl)-2-hydroxy-*N*-propylacetamide[123]



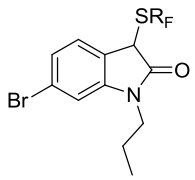
Following general procedure *D*, using crude **37a** (9.2 g) and K_2CO_3 (16.3 g, 118 mmol) in MeOH (90 mL) and H_2O (45 mL), stirring for 16 h gave **37** (5.49 g, 20.2 mmol, 68% for 2 steps) as a colourless oil after purification by flash column chromatography on silica gel eluting with 30% EtOAc in petroleum ether; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.92 (3 H, t, *J* = 7.3 Hz; C*H*$_3$), 1.35-1.75 (2 H, m; C*H*$_2$CH$_3$), 3.37 (1 H, s; O*H*), 3.69 (2 H, t, *J* = 7.6 Hz; NC*H*$_2$), 3.76 (2 H, s; C*H*$_2$OH), 7.06 (2 H, d, *J* = 8.4 Hz; 2 × Ar*H*), 7.59 (2 H, d, *J* = 8.4 Hz; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.1 (*C*H$_3$), 20.8 (*C*H$_2$CH$_3$), 51.2 (N*C*H$_2$), 60.5 (*C*H$_2$OH), 122.7 (Ar*C*), 129.8 (2 × Ar*C*H), 133.2 (2 × Ar*C*H), 138.6 (Ar*C*), 171.4 (*C*=O).

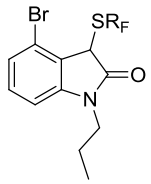
[Data consistent with literature]

General procedure E: Preparation of oxindoles / bis-oxindoles

40 6-Bromo-5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-1-propyl-1,3-dihydro-indol-2-one

41 4-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-1-propyl-1,3-dihydro-indol-2-one



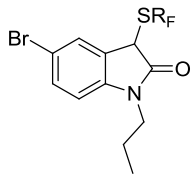


A solution of DMSO (0.57 g, 7.30 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of oxalyl chloride (0.52 g, 4.02 mmol) in CH_2Cl_2 (10 mL) at -78 °C under nitrogen. The resulting solution was stirred at -78 °C for 30 min, then a solution of **38** (1.00 g, 3.67 mmol) in CH_2Cl_2 (14 mL) was added dropwise at -78 °C via cannula. The resulting solution was stirred at -78 °C for 1 h, then Et_3N (1.86 g, 18.4 mmol) was added dropwise at -78 °C. The mixture was allowed to warm to rt and stirred at rt for 3 h. CH_2Cl_2 (75 mL) was then added and the organic layer washed with a saturated aqueous solution of $NaHCO_3$ (3 × 100 mL), dried ($MgSO_4$), and concentrated *in vacuo* to give the crude glyoxamide, which was used directly in the next step without further purification.

To a solution of the crude glyoxamide in CH_2Cl_2 (40 mL) was added R_FSH (1.24 g, 2.58 mmol), followed by stirring for 16 h. TFAA (4.63 mL, 33.3 mmol) was added followed by $BF_3{\cdot}OEt_2$ (2.32 mL, 18.5 mmol) after 1 h. The resulting solution was stirred for 6 h at rt. The reaction was then quenched carefully with a saturated aqueous solution of $NaHCO_3$ (100 mL) and the layers were separated and the organic layer washed further with aqueous $NaHCO_3$ (3 × 25 mL), before drying ($MgSO_4$), and concentrating *in vacuo*. Purification by FSPE (eluting with MeCN) gave the fluorous-tagged oxindoles **40** and **41** (1.81 g, 2.47 mmol, 96%) as an inseparable 1.1:1 mixture of regioisomers respectively; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.98 (6 H, t, J = 7.4 Hz; 2 × CH_3, both regiosiomers), 1.71 (4 H, m; 2 × CH_2CH$_3$ [both regiosiomers]), 2.21-2.62 (4 H, m; 2 × CF_2CH_2 [both regiosiomers]), 2.72-2.91 (2 H, m; 2 × SCH_AH$_B$ [both regiosiomers]), 2.92-3.13 (2 H, m; 2 × SCH$_A$$H_B$ [both regiosiomers]), 3.55-3.82 (4 H, m; 2 × NCH_2 [both regiosiomers]), 4.27 (1 H, s; CH [one

regioisomer]), 4.27 (1 H, s; C*H* [one regioisomer]), 6.80 (1 H, dd, *J* = 6.3, 2.3 Hz; Ar*H* [one regioisomer]), 7.00 (1 H, s; Ar*H* [one regioisomer]), 7.13-7.32 (4 H, m; Ar*H* [both regiosiomers]); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.2 (2 × CH_3 [both regiosiomers]), 20.6 (CH_2CH_3 [one regioisomer]), 20.7 (CH_2CH_3 [one regioisomer]), 21.0 (SCH_2 [one regioisomer]), 21.1 (SCH_2 [one regioisomer]), 31.8 (t, *J* = 21 Hz, 2 × CF_2CH_2 [both regiosiomers]), 42.0 (NCH_2 [one regioisomer]), 42.1 (NCH_2 [one regioisomer]), 44.3 (*C*H [one regioisomer]), 46.1 (*C*H [one regioisomer]), 107.6 (Ar*C*H [one regioisomer]), 112.1 (Ar*C*H [one regioisomer]), 120.5 (Ar*C* [one regioisomer]), 123.0 (Ar*C* [one regioisomer]), 124.0 (Ar*C* [one regioisomer]), 124.6 (Ar*C* [one regioisomer]), 125.7 (Ar*C*H [one regioisomer]), 126.4 (Ar*C*H [one regioisomer]), 126.5 (Ar*C*H [one regioisomer]), 130.8 (Ar*C*H [one regioisomer]), 144.8 (Ar*C* [one regioisomer]), 145.1 (Ar*C* [one regioisomer]), 174.0 (*C*=O [one regioisomer]), 174.8 (*C*=O [one regioisomer]); IR (ATR): ν_{max}/cm^{-1} 2973, 1719 (C=O), 1604; MS (ES^-): *m/z* (%) 730 ($[M-H]^-$, 100); HRMS (ES^-): $C_{21}H_{14}O_1N_1Br_1S_1F_{17}$ requires 729.9713, found 729.9713.

39 5-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-1-propyl-1,3-dihydro-indol-2-one[121]



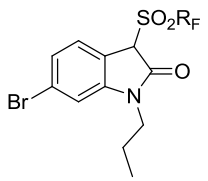
Following general procedure *E*, using **37** (1.79 g, 6.58 mmol), oxalyl chloride (0.63 mL, 7.24 mmol), DMSO (0.93 mL, 13.2 mmol), and NEt_3 (4.58 mL, 32.9 mmol) in CH_2Cl_2 (60 mL), followed by R_FSH (1.32 mL, 4.60 mmol), TFAA (8.23 mL, 59.2 mmol), and $BF_3{\cdot}OEt_2$ (4.13 mL, 32.9 mmol) in CH_2Cl_2 (70 mL) gave **39** (3.06 g, 4.18 mmol, 91%) after purification by FSPE (MeCN); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.97 (3 H, t, *J* = 7.4 Hz; CH_3), 1.63-1.78 (2 H, m; CH_2CH_3), 2.27-2.54 (2 H, m; CF_2CH_2), 2.75-2.90 (1 H, m; SCH_AH_B), 2.90-3.05 (1 H, m; SCH_AH_B), 3.55-3.81 (2 H, m; NCH_2), 4.32 (1 H, s; C*H*), 6.74 (1 H, d, *J* = 8.3 Hz; Ar*H*), 7.45 (1 H, dd, *J* = 8.3 Hz, 0.5 H; Ar*H*), 7.52 (1 H, s; Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 11.3 (CH_3), 20.6 (CH_2CH_3), 21.2 (t, *J* = 4 Hz, SCH_2), 31.9 (t, *J* = 21 Hz, CF_2CH_2), 42.0 (NCH_2), 44.6 (*C*H), 110.1 (Ar*C*H), 115.4 (Ar*C*), 127.3 (Ar*C*), 128.5 (Ar*C*H), 132.3 (Ar*C*H), 142.6 (Ar*C*), 174.3 (*C*=O).

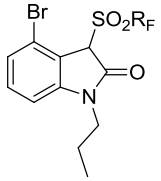
[Data consistent with literature]

General procedure F: Oxidation of oxindoles

43 6-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecane-1-sulfonyl)-1-propyl-1,3-dihydroindol-2-one;

X44 4-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecane-1-sulfonyl)-1-propyl-1,3-dihydroindol-2-one

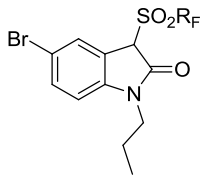




To a solution of **40** and **41** (0.43 g, 0.59 mmol, 1.1:1 mixture of regioisomers) in CH_2Cl_2 (20 mL) was added *m*CPBA (0.25 g, 1.13 mmol, 77% w/w). The resulting solution was stirred for 2 h at rt, then the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (3 × 20 mL), dried ($MgSO_4$), and concentrated *in vacuo* to give the crude products. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in petroleum ether gave **43** and **44** (0.33 g, 0.43 mmol, 75%) as a 1.1:1 mixture of regioisomers; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.96 (6 H, m; 2 × C*H*$_3$ [both regioisomers]), 1.57-1.85 (4 H, m; 2 × C*H*$_2$CH$_3$ [both regioisomers]), 2.47-2.98 (4 H, m; 2 × CF$_2$C*H*$_2$ [both regioisomers]), 3.34-4.09 (8 H, m; 2 × NC*H*$_2$ and 2 × SO$_2$C*H*$_2$ [both regioisomers]), 4.77 (1 H, s; C*H* [one regioisomer]), 4.93 (1 H, s; C*H* [one regioisomer]), 6.84 (1 H, dd, *J* = 6.6, 2.3 Hz; Ar*H* [one regioisomer]), 7.05 (1 H, d, *J* = 1.5 Hz; Ar*H* [one regioisomer]), 7.21-7.31 (3 H, m; 3 × Ar*H*), 7.46 (1 H, d, *J* = 8.1 Hz; Ar*H* [one regioisomer]); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.1 (*C*H$_3$ [one regioisomer]), 11.2 (*C*H$_3$ [one regioisomer]), 20.5 (*C*H$_2$CH$_3$ [one regioisomer]), 20.5 (*C*H$_2$CH$_3$ [one regioisomer]), 24.2 (t, *J* = 23 Hz, 2 × CF$_2$*C*H$_2$ [both regioisomers]), 42.4 (N*C*H$_2$ [one regioisomer]), 42.6 (N*C*H$_2$ [one regioisomer]), 43.9 (SO$_2$*C*H$_2$ [one regioisomer]), 44.1 (SO$_2$*C*H$_2$ [one regioisomer]), 65.2 (*C*H [one regioisomer]), 68.0 (*C*H [one regioisomer]), 108.2 (Ar*C*H [one regioisomer]), 112.9 (Ar*C*H [one regioisomer]), 115.1 (Ar*C* [one regioisomer]), 117.5 (Ar*C* [one regioisomer]), 121.7 (Ar*C* [one regioisomer]), 125.2 (Ar*C* [one regioisomer]), 126.4 (Ar*C*H [one regioisomer]), 127.7 (Ar*C*H [one regioisomer]), 128.4 (Ar*C*H [one regioisomer]), 132.3 (Ar*C*H [one

regioisomer]), 146.0 (Ar*C* [one regioisomer]), 146.9 (Ar*C* [one regioisomer]), 167.0 (*C*=O [one regioisomer]), 167.1 (*C*=O [one regioisomer]); IR (ATR): ν_{max}/cm^{-1} 2925, 2853, 1721 (C=O), 1604, 1487, 1447, 1432, 1330 (S=O),1145 (S=O); MS (ES^-): *m/z* (%) 762 ($[M-H]^-$, 100); HRMS (ES^-): $C_{21}H_{14}O_3N_1Br_1S_1F_{17}$ requires 761.9611, found 761.9609.

42 5-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecane-1-sulfonyl)-1-propyl-1,3-dihydroindol-2-one[121]

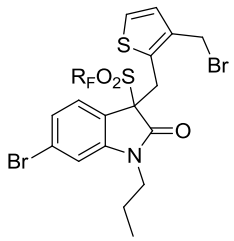


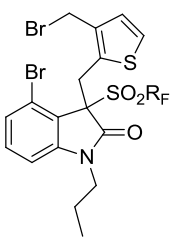
Following general procedure *F*, using **39** (1.89 g, 2.58 mmol) and *m*CPBA (1.16 g, 77% w/w, 5.18 mmol) in CH_2Cl_2 (75 mL) gave, after purification by FSPE, **42** (1.63 g, 2.13 mmol, 83%) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.97 (3 H, t, *J* = 7.3 Hz; CH_3), 1.54-1.99 (2 H, m; C*H*$_2$), 2.65-2.97 (2 H, m; CF_2CH_2), 3.38-4.27 (4 H, m; NC*H*$_2$ and (SO_2CH_2), 4.85 (1 H, s; C*H*), 6.82 (1 H, d, *J* = 8.3 Hz; Ar*H*), 7.57 (1 H, d, *J* = 8.3 Hz; Ar*H*), 7.77 (1 H, s; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.1 (*C*H$_3$), 20.5 (*C*H$_2$), 24.2 (CF_2CH_2, t, *J* = 23.1 Hz), 42.4 (N*C*H$_2$), 44.0 (SO_2CH_2), 65.2 (*C*H), 110.7 (Ar*C*H), 116.1 (Ar*C*), 118.1 (Ar*C*), 130.2 (Ar*C*H), 134.0 (Ar*C*H), 143.8 (Ar*C*), 166.6 (*C*=O).

[Data consistent with literature]

General procedure G: Preparation of alkylated oxindoles

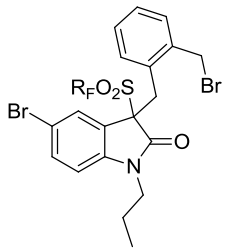
47 6-Bromo-3-(3-bromomethyl-thiophen-2-ylmethyl)-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecane-1-sulfonyl)-1-propyl-1,3-dihydroindolo-2-one





To a solution of **43** and **44** (86 mg, 0.11 mmol, 1.1:1 mixture of regioisomers) in DMF (10 mL), was added 2,3-*bis*-bromomethyl-thiophene (0.15 g, 0.56 mmol) and K_2CO_3 (78 mg, 0.56 mmol). The resulting suspension was stirred at rt for 2 h, then EtOAc (20 mL) was added and the organic layer washed with water (5 × 10 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The products were then isolated from the excess alkylating agent by FSPE (MeCN) to give the crude product as a mixture of isomers. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in petroleum ether gave **47** (11 mg, 0.012 mmol, 11%) as a white waxy solid and **48** (21 mg, 0.022 mmol, 20%) as a white waxy solid; **47**: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.72 (3 H, t, J = 7.4 Hz; CH_2CH_3), 1.37-1.52 (2 H, m; CH_2CH_3), 2.59-2.82 (2 H, m; CF_2CH_2), 3.43-3.54 (2 H, m; $SO_2CH_AH_B$ and NCH_AH_B), 3.55-3.65 (1 H, m; NCH_AH_B), 3.81- 3.87 (1H, m; $SO_2CH_AH_B$), 3.83 (1 H, d, J = 14.5 Hz; $ArCH_AH_B$), 4.09 (1 H, d, J = 14.5 Hz; $ArCH_AH_B$), 4.38 (1 H, d, J = 11.0 Hz; $ArCH_AH_B$), 4.57 (1 H, d, J = 11.0 Hz; $ArCH_AH_B$), 6.88 (1 H, d, J = 5.4 Hz; thiophene Ar*H*), 6.97 (1 H, d, J = 1.6 Hz; Ar*H*), 7.00 (1 H, d, J = 5.4 Hz; thiophene Ar*H*), 7.38 (1 H, dd, J = 8.2, 1.6 Hz; Ar*H*), 7.58 (1 H, d, J = 8.2 Hz; Ar*H*); IR (ATR): ν_{max}/cm^{-1} 2969, 1715 (C=O), 1602, 1578, 1454, 1332, 1237, 1202, 1143, 1092, 1063, 1046, 1001; MS (ES^+): *m/z* (%) 977 (50), 976 ($[M+NH_4]^+$, 100), 974 (50%); HRMS (ES^+): $C_{27}H_{20}O_3N_1Br_2S_2F_{17}Na$ ($[M+Na]^+$) requires 973.8872, found 973.8879; Single crystal XRD: See Appendix A; **48**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.67 (3 H, t, J = 7.4 Hz; CH_3), 1.36-1.55 (2 H, m; CH_2), 2.56-2.84 (2 H, m; CF_2CH_2), 3.50-3.72 (3 H, m; SO_2CH_2 and NCH_AH_B), 3.73-3.86 (1 H, m; NCH_AH_B), 4.03 (1 H, d, J = 14.6 Hz; $ArCH_AH_B$), 4.49 (1 H, d, J = 11.0 Hz; $ArCH_AH_B$), 4.59 (1 H, d, J = 14.6 Hz; $ArCH_AH_B$), 4.75 (1 H, d, J = 11.0 Hz; $ArCH_AH_B$), 6.81 (1 H, dd, J = 8.1, 0.9 Hz; Ar*H*), 6.90 (1 H, d, J = 5.2 Hz; thiophene Ar*H*), 6.99 (1 H, d, J = 5.2 Hz; thiophene Ar*H*), 7.30 (1 H, app. t, J = 8.1 Hz; Ar*H*), 7.40 (1 H, dd, J = 8.1, 0.9 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 10.7 (CH_3), 20.1 (CH_2), 24.2 (t, J = 23 Hz; CF_2CH_2), 25.4 ($ArCCH_2$), 26.4 ($ArCCH_2$), 41.8 (t, J = 4 Hz; SO_2CH_2), 42.4 (NCH_2), 58.0 (C_{quat}), 108.5 (Ar*C*H), 119.2 (Ar*C*), 122.2 (Ar*C*), 125.3 (Ar*C*H), 128.6 (Ar*C*H), 129.1 (Ar*C*H), 131.7 (Ar*C*), 132.6 (Ar*C*H), 136.9 (Ar*C*), 147.1 (Ar*C*), 169.3 (*C*=O); MS (ASAP): *m/z* (%) 954 ($[M+H]^+$, 100), 873 (35), 556 (20), 270 (80); HRMS (ES^+): $C_{27}H_{21}O_3NBr_2S_2F_{17}$ ($[M+H]^+$) requires 953.9032, found 953. 9023.

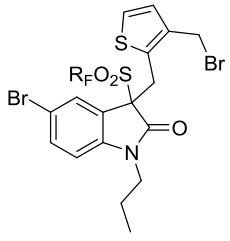
26 5-Bromo-3-(2-bromomethylbenzyl)-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecane-1-sulfonyl)-1-propyl-1,3-dihydroindolo-2-one[121]



Following general procedure *G*, using **42** (0.498 g, 0.652 mmol), 2-*bis*(bromomethyl)benzene (0.86 g, 3.3 mmol), and K_2CO_3 (0.45 g, 3.3 mmol) in DMF (50 mL) gave after purification by FSPE **26** (0.492 g, 0.519 mmol, 80%) as a pale brown waxy solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.63 (3 H, t, *J* = 7.4 Hz; CH_2CH_3), 1.19-1.51 (2 H, m; CH_2CH_3), 2.59-3.01 (2 H, m; CF_2CH_2), 3.23-3.47 (1 H, m; NCH_AH_B), 3.55-3.64 (2 H, m; NCH_AH_B and $SO_2CH_AH_B$), 3.74 (1 H, d, *J* = 13.9 Hz; $ArCH_AH_B$), 3.85-4.01 (1 H, m; $SO_2CH_AH_B$), 4.07 (1 H, d, *J* = 13.9 Hz; $ArCH_AH_B$), 4.44 (1 H, d, *J* = 10.7 Hz; $ArCH_AH_B$), 4.89 (1 H, d, *J* = 10.7 Hz; $ArCH_AH_B$), 6.66 (2 H, d, *J* = 8.3 Hz; 2 × Ar*H*), 6.98 (1 H, t, *J* = 7.5 Hz; Ar*H*), 7.13 (1 H, t, *J* = 7.5 Hz; Ar*H*), 7.21-7.31 (1 H, m; Ar*H*), 7.54 (1 H, dd, *J* = 8.3, 1.9 Hz; Ar*H*), 7.92 (1 H, d, *J* = 1.9 Hz; Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.8 (CH_2CH_3), 20.2 (CH_2CH_3), 24.1 (t, *J* = 22.6 Hz; CF_2CH_2), 31.6 ($ArCCH_2$), 32.7 ($ArCCH_2$), 40.8 (SO_2CH_2), 42.3 (NCH_2), 74.7 (C_{quat}), 110.6 (ArCH), 116.0 (ArC), 122.7 (ArC), 128.4 (ArCH), 128.6 (ArCH), 129.8 (ArCH), 130.6 (ArCH), 131.1 (ArCH), 131.1 (ArC), 134.2 (ArCH), 137.0 (ArC), 143.4 (ArC), 169.6 (C=O).

[Data consistent with literature]

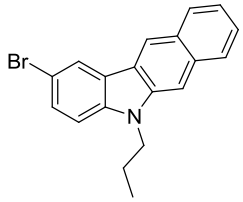
46 5-Bromo-3-(3-bromomethyl-thiophen-2-ylmethyl)-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecane-1-sulfonyl)-1-propyl-1,3-dihydroindolo-2-one



Following general procedure *G*, using **42** (1.31 g, 1.71 mmol), K_2CO_3 (0.47 g, 3.4 mmol), 2,3-*bis*-bromomethyl-thiophene (0.92 g, 3.4 mmol) in DMF (150 mL), followed by

purification by flash column chromatography eluting with 20% EtOAc in petroleum ether gave **46** (0.80 g, 0.84 mmol, 49%) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.71 (3 H, t, *J* = 7.4 Hz; CH_3), 1.34-1.52 (2 H, m; CH_2CH$_3$), 2.56-2.85 (2 H, m; CF_2CH_2), 3.46-3.54 (2 H, m; $SO_2CH_AH_B$ and NCH_AH_B), 3.57-3.64 (1 H, m; NCH_AH_B) 3.79-3.92 (1 H, m; $SO_2CH_AH_B$) 3.82 (1 H, d, *J* = 14.6 Hz; $ArCH_AH_B$), 4.09 (1 H, d, *J* = 14.6 Hz; $ArCH_AH_B$), 4.39 (1 H, d, *J* = 11.1 Hz; $ArCH_AH_B$), 4.58 (1 H, d, *J* = 11.1 Hz; $ArCH_AH_B$), 6.71 (1 H, d, *J* = 8.3 Hz; Ar*H*), 6.88 (1 H, d, *J* = 5.3 Hz; thiophene Ar*H*), 6.99 (1 H, d, *J* = 5.3 Hz; thiophene Ar*H*), 7.57 (1 H, dd, *J* = 8.3, 1.9 Hz; Ar*H*), 7.85 (1 H, d, *J* = 1.9 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 10.8 (CH_3), 20.2 (CH_2CH_3), 24.0 (CF_2CH_2), 24.9 ($ArCCH_2$), 29.5 ($ArCCH_2$), 40.8 (SO_2CH_2), 42.4 (NCH_2), 74.0 (C_{quat}) 110.8 (Ar*C*H), 116.3 (Ar*C*), 122.0 (Ar*C*), 125.4 (Ar*C*H), 128.7 (Ar*C*H), 129.8 (Ar*C*H), 130.8 (Ar*C*), 134.5 (Ar*C*H), 137.0 (Ar*C*), 143.7 (Ar*C*), 169.2 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2971, 1716 (C=O), 1607, 1332, 1146; MS (ES$^+$): *m/z* (%) 975 ([M+Na]$^+$, 100); HRMS (ES$^+$): $C_{27}H_{24}O_3N_2Br_2S_2F_{17}$ ([M+NH$_4$]$^+$) requires 968.9318, found 968.9328.

27 5-Bromo-5-propyl-5*H*-benzo[*b*]carbazole[121]



To a solution of **26** (0.251 g, 0.265 mmol) in degassed THF (13 mL) was added TFE (0.64 mL of a 0.041 g mL^{-1} solution in degassed THF, 0.26 mmol). To this was added SmI_2 (10.6 mL of a 0.1 M solution in THF, 1.06 mmol) dropwise over 20 min via syringe pump. The resulting suspension was then allowed to stir for a further 30 min at 20 °C, before opening to air and quenching with a saturated aqueous solution of $NaHCO_3$ (20 mL) and extracting with EtOAc (4 × 20 mL). The combined organic fractions were then dried (Na_2SO_4) and concentrated *in vacuo* to yield a yellow oil containing an inseparable mixture of the non-aromatised intermediate **32** and product **27**.

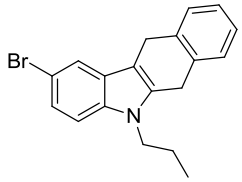
To a solution of the crude material in toluene (10 mL) was added DDQ (60 mg, 0.26 mmol), the resulting suspension was heated for 30 min at reflux. CH_2Cl_2 (10 mL) was then added and the organic layer was washed with H_2O (3 × 5 mL), dried ($MgSO_4$), and

concentrated *in vacuo.* Purification by flash column chromatography on silica gel eluting with 3% EtOAc in petroleum ether gave **27** (67 mg, 0.20 mmol, 75%).

Data for **27**: ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.02 (3 H, t, *J* = 7.4 Hz; CH_2CH_3), 1.67-2.17 (2 H, m; CH_2CH_3), 4.31 (2 H, t, *J* = 7.2 Hz; NCH_2), 7.27 (1 H, d, *J* = 8.6 Hz; Ar*H*), 7.40 (1 H, td, *J* = 7.5, 1.0 Hz; Ar*H*), 7.51 (1 H, td, *J* = 7.5, 1.0 Hz; Ar*H*), 7.61 (1 H, dd, *J* = 8.6, 1.9 Hz; Ar*H*), 7.70 (1 H, s; Ar*H*), 7.99 (1 H, d, *J* = 8.2 Hz; Ar*H*), 8.05 (1 H, d, *J* = 8.2 Hz; Ar*H*), 8.33 (1 H, d, *J* = 1.9 Hz; Ar*H*), 8.54 (1 H, s; Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 11.8 (CH_3), 21.8 (CH_2CH_3), 44.9 (NCH_2), 103.6 (Ar*C*H), 109.7 (Ar*C*H), 111.3 (Ar*C*), 119.1 (Ar*C*H), 122.9 (Ar*C*H), 123.8 (Ar*C*), 124.0 (Ar*C*), 124.5 (Ar*C*H), 125.5 (Ar*C*H), 127.1 (Ar*C*H), 128.1 (Ar*C*H), 128.6 (Ar*C*), 129.7 (Ar*C*H), 132.8 (Ar*C*), 140.6 (Ar*C*), 141.8 (Ar*C*).

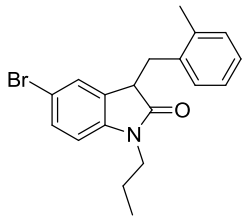
[Data consistent with literature]

32 2-Bromo-5-propyl-6,11-dihydro-5H-benzo[*b*]carbazole



Data for **32**: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.97 (3 H, t, *J* = 7.4 Hz; CH_2CH_3), 1.82 (2 H, app. sxt, *J* = 7.4 Hz; CH_2CH_3), 4.08 (2 H, t, *J* = 7.4 Hz; NCH_2), 4.12 (4 H, s; 2 × CH_2), 7.15-7.23 (1 H, m; Ar*H*), 7.25-7.31 (3 H, m; 3 × Ar*H*), 7.34 (1 H, d, *J* = 7.9 Hz; Ar*H*), 7.39 (1 H, d, *J* = 6.9 Hz; Ar*H*), 7.70 (1 H, s; Ar*H*); ^{13}C NMR ($CDCl_3$) δ ppm 11.5 (CH_2CH_3), 23.7 (CH_2CH_3), 26.7 (CH_2), 27.3 (CH_2), 45.0 (NCH_2), 106.4 (Ar*C*), 110.5 (Ar*C*H), 112.1 (Ar*C*), 120.7 (Ar*C*H), 123.6 (Ar*C*H), 126.1 (Ar*C*H), 126.5 (Ar*C*H), 128.4 (Ar*C*), 129.4 (Ar*C*H), 129.7 (Ar*C*H), 132.2 (Ar*C*), 134.0 (Ar*C*), 134.4 (Ar*C*), 135.5 (Ar*C*).

28 5-Bromo-3-(2-methylbenzyl)-1-propyl-1,3-dihydro-indol-2-one[121]

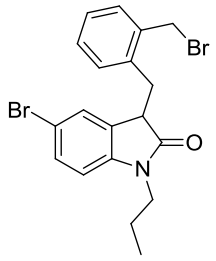


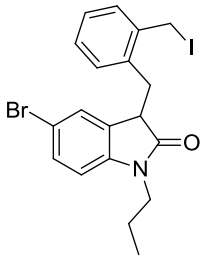
To a solution of **26** (59 mg, 0.062 mmol) in degassed THF (3 mL) was added SmI_2 (2.62 mL of a 0.1 M solution in THF, 0.26 mol) dropwise over 20 min via syringe pump. The resulting suspension was opened to air and quenched with a saturated aqueous solution of $NaHCO_3$ (8 mL) and extracted with EtOAc (3 × 12 mL). The combined organic extracts were then dried (Na_2SO_4) and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 5% EtOAc in petroleum ether gave **28** (15 mg, 0.042 mmol, 71%) as a yellow residue; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.94 (3 H, t, *J* = 7.4 Hz; CH_2CH_3), 1.54-1.71 (2 H, m; CH_2), 2.23 (3 H, s; $ArCCH_3$), 2.69 (1 H, dd, *J* = 14.0, 10.6 Hz; $ArCH_AH_B$), 3.43 (1 H, dd, *J* = 14.0, 4.7 Hz; $ArCH_AH_B$), 3.50-3.70 (3 H, m; NCH_2 and CH), 6.56-6.66 (2 H, m; 2 × ArH), 7.01-7.17 (4 H, m; 4 × ArH), 7.28 (1 H, dd, *J* = 8.3, 1.5 Hz; ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 11.3 (CH_3), 19.9 ($ArCCH_3$), 20.6 (CH_2CH_3), 34.3 ($ArCCH_2$), 41.6 (NCH_2), 45.6 (CH), 109.2 (ArCH), 114.0 (ArC), 125.9 (ArCH), 127.7 (ArCH), 128.0 (ArC), 130.1 (ArCH), 130.5 (ArCH), 130.6 (ArCH), 130.7 (ArCH), 136.1 (ArC), 136.6 (ArC), 142.7 (ArC), 176.5 (C=O).

[Data consistent with literature]

52 5-Bromo-3-(2-(bromomethyl)benzyl)-1-propylindolin-2-one;

53 5-Bromo-3-(2-(iodomethyl)benzyl)-1-propylindolin-2-one

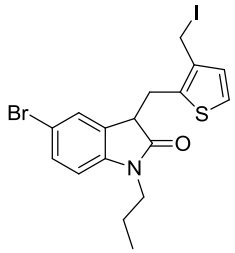




To a solution of **26** (0.529 g, 0.558 mmol) in degassed THF (26 mL) was added trifluoroethanol (0.81 mL of a 0.069 g/mL solution in degassed THF, 0.56 mmol), followed by SmI_2 (11.2 mL, 0.1 M solution in degassed THF, 1.12 mmol) dropwise over 10 min. The

resulting mixture was stirred for a further 10 min then quenched by opening to air. A saturated aqueous solution of $NaHCO_3$ (50 mL) was then added, and the mixture extracted with CH_2Cl_2 (3 × 50 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield the crude product (0.264 g). A portion of this (0.198 g) was further purified by flash column chromatography on silica gel eluting with a gradient of 5-20% EtOAc in hexane to afford the product as an inseparable mixture of **52** and **53** (0.146 g, 1.5:1 [**52**:**53**], 0.19 mmol **52**, 0.13 mmol **53**, 76%) as a yellow oil; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.57 (3 H, t, *J* = 7.4 Hz; C*H*$_3$ [**52**]), 0.58 (3 H, t, *J* = 7.4 Hz; C*H*$_3$ [**53**]), 1.10-1.32 (4 H, m; 2 × C*H*$_2$ [both compounds]), 3.02-3.13 (2 H, m; 2 × NC*H*$_A$H$_B$ [both compounds]), 3.21-3.36 (6 H, m; 2 × NCH$_A$*H*$_B$ [both compounds] and 2 × ArC*H*$_2$ [both compounds]), 3.39 (2 H, dd, *J* = 8.8, 4.5 Hz; 2 × C*H* [both compounds]), 4.12 (1 H, d, *J* = 9.8 Hz; C*H*$_A$H$_B$I [**53**]), 4.17 (2 H, d, *J* = 10.3 Hz; C*H*$_A$H$_B$Br [**52**]), 4.38 (2 H, d, *J* = 9.8 Hz; CH$_A$*H*$_B$I [**53**]), 4.50 (2 H, d, *J* = 10.3 Hz; CH$_A$*H*$_B$Br [**52**]), 5.94 (1 H, d, *J* = 8.3 Hz; Ar*H* [**53**]), 5.95 (1 H, d, *J* = 8.5 Hz; Ar*H* [**52**]), 6.65-6.74 (2 H, m; 2 × Ar*H* [both compounds]), 6.74-6.87 (6 H, m; 6 × Ar*H* [both compounds]), 6.91-6.98 (2 H, m; 2 × Ar*H* [both compounds]), 7.10-7.15 (2 H, m; 2 × Ar*H* [both compounds]); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 4.9 (*C*H$_2$I [**53**]), 11.5 (2 × *C*H$_3$), 21.0 (2 × C*H*$_2$CH$_3$), 32.3 (*C*H$_2$Br [**52**]), 33.2 (ArC*C*H$_2$ [**52**]), 33.6 (ArC*C*H$_2$ [**53**]), 41.5 (2 × N*C*H$_2$), 45.6 (*C*H [**53**]), 46.2 (*C*H [**52**]), 110.0 (2 × Ar*C*H), 114.7 (2 × Ar*C*), 127.9 (Ar*C*H), 128.0 (Ar*C*H), 128.4 (Ar*C*H), 128.5 (Ar*C*H), 128.7 (Ar*C*H), 129.0 (Ar*C*H), 131.0 (Ar*C*H), 131.25 (3 × Ar*C*H), 131.29 (Ar*C*), 131.31 (Ar*C*H), 131.5 (Ar*C*H), 136.5 (2 × Ar*C*), 137.2 (Ar*C*), 137.3 (Ar*C*), 138.6 (Ar*C*), 143.6 (2 × Ar*C*), 176.0 (2 × C=O); MS (ES$^+$): *m/z* (%) 486 ([M+H (**53**)]$^+$, 60) 437 ([M$^+$ (**52**)], 100), 358 (60); HRMS (ES$^+$): $C_{19}H_{20}NOBrI$ requires 483.9768, found 483.9774; HRMS (ES$^+$): $C_{19}H_{20}NOBr_2$ requires 435.9907, found 435.9918.

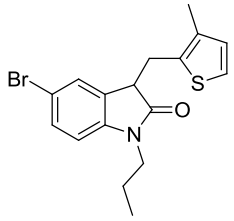
54 5-Bromo-3-(3-iodomethylthiophen-2-ylmethyl)-1-propyl-1,3-dihydro-indol-2-one



To a solution of **46** (58 mg, 0.061 mmol) in degassed THF (3 mL) was added TFE (1.33 mL of a 0.014 g mL^{-1} solution, 0.19 mmol). To this solution was then added SmI_2 (1.28 mL of a

0.1 M solution in THF, 0.128 mmol) dropwise over 20 min via syringe pump. The resulting suspension was opened to air, quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL) and extracted with EtOAc (4 × 5 mL). The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography on silica gel eluting with 100% CH_2Cl_2 gave **54** (12 mg, 0.024 mmol, 40%) as a yellow oily residue; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.82 (3 H, t, J = 7.4 Hz; CH_2CH_3), 1.47-1.67 (2 H, m; CH_2CH_3), 3.28-3.40 (1 H, m; $ArCH_AH_B$), 3.42-3.48 (1 H, m; $ArCH_AH_B$), 3.50-3.56 (1 H, m; NCH_AH_B), 3.62-3.70 (1H, m; NCH_AH_B), 3.80 (1 H, dd, J = 8.1, 4.5 Hz; C*H*), 4.26 (1 H, d, J = 10.0 Hz; CH_AH_BI), 4.36 (1 H, d, J = 10.0 Hz; CH_AH_BI), 6.60 (1 H, d, J = 8.3 Hz; Ar*H*), 6.87 (1 H, d, J = 5.2 Hz; thiophene Ar*H*), 6.99 (1 H, d, J = 5.2 Hz; thiophene Ar*H*), 7.03 (1 H, br. s; Ar*H*), 7.32 (1 H, dd, J = 8.3 Hz, 1.3 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm -2.2 (CH_2I), 11.1 (CH_3), 20.5 (CH_2), 28.7 ($ArCCH_2$), 41.6 (NCH_2), 45.8 (*C*H), 109.8 (Ar*C*H), 114.9 (Ar*C*), 123.9 (Ar*C*H) 127.8 (Ar*C*H), 128.7 (Ar*C*H), 129.7 (Ar*C*), 131.2 (Ar*C*H), 135.7 (Ar*C*), 136.4 (Ar*C*), 143.1 (Ar*C*), 175.6 (*C*=O); MS (ES$^+$): *m/z* (%) 512 ([M+Na]$^+$, 100).

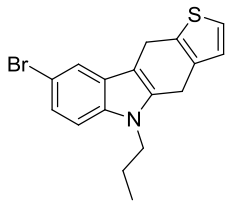
55 5-Bromo-3-(3-methyl-thiophen-2-ylmethyl)-1-propyl-1,3-dihydro-indol-2-one



To a solution of **46** (88 mg, 0.093 mmol) in degassed THF (4 mL), and trifluoroethanol (0.68 mL of a 0.014 g mL^{-1} solution in degassed THF, 0.095 mmol), was added SmI_2 (3.91 mL of a 0.1 M solution in THF, 0.39 mmol) dropwise over 20 min via syringe pump. The resulting suspension was opened to air and quenched with a saturated aqueous solution of $NaHCO_3$ (11 mL) and extracted with EtOAc (4 x 12 mL). The combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo* to yield a mixture of **55** and **56**. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in petroleum ether gave **55** (16 mg, 0.044 mmol, 47%) and **56** (3 mg, 0.009 mmol, 10%); Data for **55**: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.86 (3 H, t, J = 7.6 Hz; CH_2CH_3), 1.51-1.71 (2 H, m; CH_2CH_3), 2.11 (3 H, s; $ArCCH_3$), 3.22 (1 H, dd, J = 15.0, 8.7 Hz; $ArCH_AH_B$), 3.46-3.57 (2 H, m; $ArCH_AH_B$ and NCH_AH_B), 3.64-3.67 (2 H, m; C*H* and NCH_AH_B), 6.66 (1 H, d, J = 8.4 Hz;

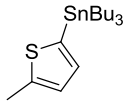
Ar*H*), 6.76 (1 H, d, *J* = 5.0 Hz; Ar*H*), 7.00-7.05 (2 H, m; 2 × Ar*H*), 7.37 (1 H, dd, *J* = 8.4, 1.3 Hz; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 11.2 ($CH_2\mathit{C}H_3$), 13.9 (ArC$\mathit{C}H_3$), 20.5 ($\mathit{C}H_2CH_3$), 28.8 (ArC$\mathit{C}H_2$), 41.6 (N$\mathit{C}H_2$), 46.9 (*C*H), 109.6 (Ar*C*H), 114.6 (Ar*C*), 122.6 (Ar*C*H), 127.8 (Ar*C*H), 129.7 (Ar*C*H), 130.2 (Ar*C*), 130.9 (Ar*C*H), 132.6 (Ar*C*), 135.0 (Ar*C*), 143.1 (Ar*C*), 175.9 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2918, 2850, 1712 (C=O), 1607; MS (ES$^+$): *m/z* (%) 386 ([M+Na]$^+$, 100); HRMS (ES$^+$) $C_{17}H_{18}ONBrNaS$ requires 386.0185, found 386.0183.

56 6-Bromo-9-propyl-9,10-dihydro-4H-3-thia-9-aza-cyclopenta[*b*]fluorene



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.96 (3 H, t, *J* = 7.3 Hz; CH_3), 1.75-1.90 (2 H, m, *J* = 7.3 Hz; CH_2CH$_3$), 4.00 (1 H, d, J = 5.7 Hz; CH_AH$_B$), 4.01 (1 H, d, J = 5.7 Hz; CH$_A\mathit{H}_B$), 4.07 (2 H, t, *J* = 7.3 Hz; NCH_2), 4.14 (1 H, d, *J* = 5.7 Hz; CH$_A\mathit{H}_B$), 4.15 (1 H, d, *J* = 5.7 Hz; CH$_A\mathit{H}_B$), 6.90 (1 H, d, *J* = 5.0 Hz; Ar*H*), 7.13 (1 H, d, *J* = 8.5 Hz; Ar*H*), 7.19 (2 H, m; Ar*H*), 7.59 (1 H, d, *J* = 1.9 Hz; Ar*H*); MS (ES$^+$): *m/z* (%) 366 ([M-H$_2$+Na]$^+$, 100).

58 Tributyl(5-methylthiophen-2-yl)stannane[275]

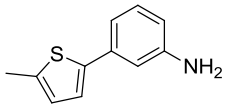


To a solution of 2-methylthiophene (0.202 g, 2.06 mmol) in THF (12 mL) at 0 °C was added *n*BuLi (0.81 mL of a 2.54 M solution, 2.06 mmol) dropwise. The solution was warmed to 20 °C followed by stirring for 1 h, before cooling back to 0 °C and the addition of $ClSnBu_3$ (0.56 mL, 2.06 mmol) dropwise. The solution was stirred at 20 °C for 16 h, then quenched with $NaHCO_3$ (4 mL), before separating the organic layer and washing with H_2O (2 × 4 mL). The combined solution was then dried (Na_2SO_4) and concentrated *in vacuo* to yield **58** (0.790 g, 2.04 mmol, 99%) as a clear oil which was used in the next step without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.87-0.95 (9 H, m; 3 × $CH_2C\mathit{H}_3$), 1.03-1.12 (6 H, m; 3 × Sn$\mathit{C}H_2$), 1.25-1.41 (6 H, m; 3 × $\mathit{C}H_2CH_3$), 1.45-1.69 (6 H, m; 3 × $\mathit{C}H_2CH_2CH_3$), 2.56 (3 H, d, *J* = 1.0 Hz; ArCH_3), 6.89-6.93 (1 H, m; Ar*H*), 6.99 (1 H, d, *J* = 3.3 Hz; Ar*H*); ^{13}C

NMR (101 MHz, $CDCl_3$) δ ppm 10.7 (3 × Sn*C*H_2), 13.7 (3 × CH_2*C*H_3), 15.0 (ArC*C*H_3), 27.3 (3 × *C*H_2CH_3), 28.9 (3 × *C*$H_2CH_2CH_3$), 126.6 (Ar*C*H), 134.3 (Ar*C*H), 135.5 (Ar*C*), 145.3 (Ar*C*).

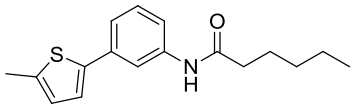
[Data consistent with literature]

59 3-(5-Methylthiophen-2-yl)aniline



To a microwave vial was added **58** (0.499 g, 1.29 mmol), 3-bromoaniline (0.222 g, 1.29 mmol) and $Pd(PPh_3)_4$ (74 mg, 0.064 mmol). The vial was then sealed and subjected to three vacuum-refill cycles with argon. Toluene (12 mL, degassed) was then added under argon and the vial sealed and heated at 95 ˚C for 24 h with stirring. The solution was then concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in petroleum ether yielded **59** (0.226 g, 1.19 mmol, 92%) as a pale brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.52 (3 H, s; ArCC*H*$_3$), 3.62 (2 H, br. s; N*H*$_2$), 6.53-6.65 (1 H, d, *J* = 7.9 Hz; Ar*H*), 6.71-6.76 (1 H, m; thiophene Ar*H*), 6.90 (1 H, s; Ar*H*), 7.00 (1 H, d, *J* = 7.9 Hz; Ar*H*), 7.09 (1 H, d, *J* = 3.5 Hz; thiophene Ar*H*), 7.16 (1 H, t, *J* = 7.9 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 15.4 (ArC*C*H_3), 112.0 (Ar*C*H), 113.9 (Ar*C*H), 116.0 (Ar*C*H), 122.7 (thiophene Ar*C*H), 126.0 (thiophene Ar*C*H), 129.7 (Ar*C*H), 135.6 (Ar*C*), 139.2 (Ar*C*), 142.1 (Ar*C*), 146.6 (Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3456 (NH), 3372 (NH), 2918, 1617, 1602, 1584; MS (ES$^+$): *m/z* (%) 413 (50), 190 ([M+H]$^+$, 100), 102 (60); HRMS (ES$^+$): $C_{11}H_{12}N_1S_1$ requires 190.0685, found 190.0687.

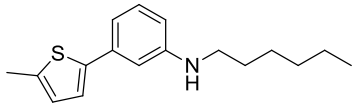
60a *N*-(3-(5-Methylthiophen-2-yl)phenyl)hexanamide



A solution of **59** (0.226 g, 1.31 mmol) in CH_2Cl_2 (6.8 mL) was cooled to 0 ˚C and NEt_3 (0.22 mL, 1.6 mmol) added, followed by hexanoyl chloride (0.20 mL, 1.4 mmol) dropwise over 15 min. The solution was stirred for 16 h at 20 ˚C, then washed with a saturated aqueous solution of $NaHCO_3$ (3 × 5 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield **60a**

(0.369 g, 1.28 mmol, 98%) as a white solid, which was used in the next step without any further purification, mp (EtOAc) 86-87 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.86-0.96 (3 H, m; CH_2CH_3), 1.28-1.42 (4 H, m; 2 × CH_2), 1.66-1.80 (2 H, m; $CH_2CH_2CH_2CH_3$), 2.37 (2 H, t, *J* = 7.6 Hz; (CO)CH_2), 2.50 (3 H, s; ArCH_3), 6.66-6.75 (1 H, m; thiophene Ar*H*), 7.10 (1 H, d, *J* = 3.2 Hz; thiophene Ar*H*), 7.22-7.33 (2 H, m; 2 × Ar*H*), 7.45 (1 H, d, *J* = 6.6 Hz; Ar*H*), 7.72 (1 H, br. s; N*H*), 7.77 (1 H, s; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.9 (CH_2CH_3), 15.3 (ArCCH_3), 22.4 (CH_2), 25.3 (CH_2), 31.4 ($CH_2CH_2CH_2CH_3$), 37.7 ((CO)CH_2), 116.7 (Ar*C*H), 118.4 (Ar*C*H), 121.2 (Ar*C*H), 123.2 (thiophene Ar*C*H), 126.1 (thiophene Ar*C*H), 129.3 (Ar*C*H), 135.4 (Ar*C*), 138.5 (Ar*C*), 139.6 (Ar*C*), 141.4 (Ar*C*), 171.8 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 3245, 2946, 2862, 1659 (C=O), 1603, 1556; MS (ES$^+$): *m/z* (%) 310 ([M+Na]$^+$, 100) 342 (40), 151 (20); HRMS (ES$^+$): $C_{17}H_{22}NOS$ ([M+H]$^+$) requires 288.1417, found 288.1413.

60 *N*-Hexyl-3-(5-methylthiophen-2-yl)aniline

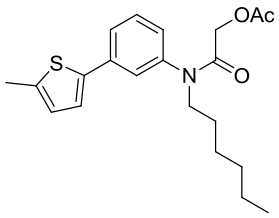


To a solution of **60a** (0.258 g, 0.898 mmol) in THF (4.4 mL) at 0 ˚C was added $LiAlH_4$ (75 mg, 1.98 mmol) over 30 min. The reaction mixture was allowed to warm to 20 ˚C and stirred for 16 h. H_2O (1 mL) and 15% aq. NaOH (1 mL) were added, and the resulting slurry filtered and the filtrand washed with EtOAc (10 mL). The filtrate was then washed with H_2O (5 mL) and brine (5 mL), dried ($MgSO_4$), and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 1% NEt_3 in hexane gave **60** (0.190 g, 0.695 mmol, 77%) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.77-1.05 (3 H, m; CH_2CH_3), 1.19-1.53 (6 H, m; 3 × CH_2), 1.53-1.77 (2 H, m; CH_2), 2.52 (3 H, d, *J* = 0.9 Hz; ArCH_3), 3.16 (2 H, t, *J* = 7.1 Hz; NCH_2), 3.67 (1 H, br. s; N*H*), 6.53 (1 H, ddd, *J* = 7.9, 2.3, 0.8 Hz; Ar*H*), 6.69-6.76 (1 H, m; thiophene Ar*H*), 6.78-6.81 (1 H, m; Ar*H*), 6.92 (1 H, d, *J* = 7.9 Hz; Ar*H*), 7.10 (1 H, d, *J* = 3.6 Hz; thiophene Ar*H*), 7.18 (1 H, t, *J* = 7.9 Hz; Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 14.0 (CH_2CH_3), 15.4 (ArCCH_3), 22.6 (CH_2), 26.8 (CH_2), 29.5 (CH_2), 31.6 (CH_2), 44.0 (NCH_2), 109.7 (Ar*C*H), 111.6 (Ar*C*H), 114.7 (Ar*C*H), 122.6 (thiophene Ar*C*H), 125.9 (thiophene Ar*C*H), 129.6 (Ar*C*H), 135.6 (Ar*C*), 139.0 (Ar*C*), 142.6 (Ar*C*), 148.8 (Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3407 (NH stretch), 2953, 2925, 2855, 1601

(NH bend), 1582; MS (ES^+): *m/z* (%) 274 ($[M+H]^+$,100); HRMS (ES^+): $C_{17}H_{24}N_1S_1$ ($[M+H]^+$) requires 274.1624, found 274.1628.

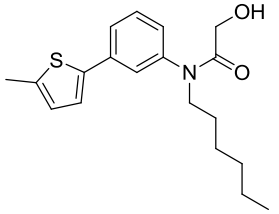
General Procedure H:

61a 2-(Hexyl(3-(5-methylthiophen-2-yl)phenyl)amino)-2-oxoethyl acetate



To a solution of **60** (0.190 g, 0.694 mmol) in CH_2Cl_2 (4.1 mL) was added acetoxy acetyl chloride (0.09 mL, 0.8 mmol) and NEt_3 (0.12 mL, 0.86 mmol). The solution was stirred for 18 h, then CH_2Cl_2 (10 mL) added. The solution was then washed with a saturated aqueous solution of $NaHCO_3$ (3 × 5 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield the crude intermediate **61a** (0.30 g), which was taken on immediately in the next step without further purification.

61 *N*-Hexyl-2-hydroxy-*N*-(3-(5-methylthiophen-2-yl)phenyl)acetamide

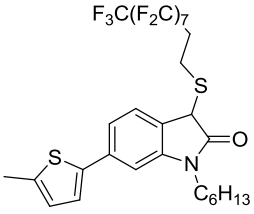


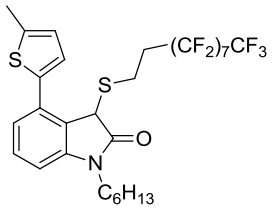
Following general procedure *D* using crude **61a** (0.30 g), K_2CO_3 (0.384 g, 2.78 mmol) in MeOH (2.4 mL) and H_2O (1.2 mL) gave **61** (0.220 g, 0.664 mmol, 96%) as a pale brown oil which was used in the next step without any further purification; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.78-0.98 (3 H, m; CH_2CH_3), 1.20-1.41 (6 H, m; 3 × CH_2), 1.47-1.61 (2 H, m; CH_2), 2.53 (3 H, s; $ArCCH_3$), 3.43 (1 H, t, *J* = 4.5 Hz; O*H*), 3.70-3.80 (2 H, m; NCH_2), 3.82 (2 H, d, *J* = 4.5 Hz; CH_2OH), 6.72-6.80 (1 H, m; thiophene Ar*H*), 6.97-7.06 (1 H, m; Ar*H*), 7.13 (1 H, d, *J* = 3.8 Hz; thiophene Ar*H*), 7.30-7.32 (1 H, m; Ar*H*), 7.42 (1 H, t, *J* = 7.8 Hz; Ar*H*), 7.54-7.61 (1 H, m; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 (CH_2CH_3), 15.5 ($ArCCH_3$), 22.6 (CH_2), 26.4 (CH_2), 27.6 (CH_2), 31.5 (CH_2), 49.7 (NCH_2), 60.6 (CH_2OH), 123.9 (thiophene Ar*C*H), 124.8 (Ar*C*H), 125.6 (Ar*C*H), 126.3 (thiophene Ar*C*H), 126.5 (Ar*C*H), 130.4 (Ar*C*H),

136.8 (Ar*C*), 140.0 (Ar*C*), 140.1 (Ar*C*), 140.8 (Ar*C*), 171.6 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 3452 (OH), 2955, 2927, 2857, 1659 (C=O), 1598; MS (ES$^+$): *m/z* (%) 354 ([M+Na]$^+$, 100) 258 (30); HRMS (ES$^+$): $C_{19}H_{26}N_1O_2S_1$ ([M+H]$^+$) requires 332.1679, found 332.1692.

62 1-Hexyl-6-(5-methylthiophen-2-yl)-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundecyl)thio)indolin-2-one;

63 1-Hexyl-4-(5-methylthiophen-2-yl)-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-nonadecafluoroundecyl)thio)indolin-2-one

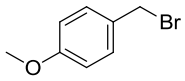




Following general procedure *E*, using **61** (33 mg, 0.10 mmol), oxalyl chloride (0.34 mL of a 0.0413 g mL^{-1} solution in CH_2Cl_2, 0.11 mmol), DMSO (0.022 mL of a 0.717 g mL^{-1} solution in CH_2Cl_2, 0.20 mmol) and NEt_3 (0.070 mL, 0.50 mmol) in CH_2Cl_2 (0.4 mL), followed by R_FSH (0.027 mL, 0.094 mmol) and TFAA (0.028 mL, 0.20 mmol) in CH_2Cl_2 (1.2 mL) gave an inseparable mixture of **62** and **63** (62 mg, 0.074 mmol, 82%, 1.2:1-**62**:**63**) as an oily residue after purification by flash column chromatography on silica gel eluting with 5% EtOAc in hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.89 (6 H, t, *J* = 6.7 Hz; 2 × C*H*$_3$), 1.19-1.48 (12 H, m; 6 × C*H*$_2$), 1.59-1.79 (4 H, m; 2 × C*H*$_2$ [both regioisomers]), 2.09-2.51 (4 H, m; 2 × CF_2CH_2 [both regioisomers]), 2.53 (3 H, s; ArC*H*$_3$ [one regioisomer]), 2.55 (3 H, s; ArC*H*$_3$ [one regioisomer]), 2.69 (1 H, ddd, *J* = 13.6, 11.6, 5.0 Hz; SC*H*$_A$H$_B$ [one regioisomer]), 2.83 (1 H, ddd, *J* = 13.1, 10.3, 7.1 Hz; SC*H*$_A$H$_B$ [one regioisomer]), 2.91-3.04 (2 H, m; 2 × SCH$_A$*H*$_B$ [both regioisomers]), 3.58-3.88 (4 H, m; 2 × NC*H*$_2$ [both regioisomers]), 4.33 (1 H, s; C*H* [**62**]), 4.58 (1 H, s; C*H* [**63**]), 6.67-6.86 (3 H, m; 3 × Ar*H* [2 from **63** and one from **62**]), 6.98 (1 H, s; Ar*H* [**62**]), 7.14 (1H, d, *J* = 3.5; Ar*H* [one regioisomer]), 7.12 (1 H, d, *J* = 3.5; Ar*H* [one regioisomer]), 7.20 (1 H, d, *J* = 7.9 Hz, [**63**]), 7.26-7.29 (1H, m; Ar*H* [**62**]), 7.33 (1 H, t, *J* = 7.9 Hz, Ar*H* [**63**]), 7.34-7.37 (1H, m; Ar*H* [**62**]); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 (2 x CH_2CH_3 [both regioisomers]), 15.3 (ArC*C*H$_3$ [one regioisomer]), 15.5 (ArC*C*H$_3$ [one regioisomer]), 20.8 (m, S*C*H$_2$ [one regioisomer]), 20.9-21.0 (m, S*C*H$_2$, [one regioisomer]), 22.5 (2 x *C*H$_2$ [both regioisomers]), 26.6 (2 x *C*H$_2$ [both regioisomers]), 27.3 (2 x NCH_2CH_2 [both regioisomers]), 31.4 (*C*H$_2$ [one regioisomer]), 31.4 (*C*H$_2$ [one regioisomer]), 31.7-32.0

(m, 2 x CF_2CH_2 [both regioisomers]) 40.3 (2 x NCH_2 [both regioisomers]), 44.7 (*C*H [**62**]), 44.9 (*C*H [**63**]), 105.7 (Ar*C*H [**62**]), 107.4 (Ar*C*H [**63**]), 120.1 (Ar*C*H [**62**]), 121.1 (Ar*C* [one regioisomer]), 122.9 (Ar*C*H [**63**]), 123.6 (Ar*C*H thiophene [one regioisomer]), 123.7 (Ar*C* [one regioisomer]), 125.5 (Ar*C*H [**62**]), 125.9 (Ar*C*H thiophene [one regioisomer]), 126.2 (Ar*C*H thiophene [one regioisomer]), 126.3 (Ar*C*H thiophene [one regioisomer]), 129.7 (Ar*C*H [**63**]), 132.7 (Ar*C* [one regioisomer]), 136.2 (Ar*C* [one regioisomer]), 137.9 (Ar*C* [one regioisomer]), 140.3 (Ar*C* [one regioisomer]), 141.1 (Ar*C* [one regioisomer]), 141.2 (Ar*C* [one regioisomer]), 144.0 (Ar*C* [one regioisomer]), 144.3 (Ar*C* [one regioisomer]), 174.8 (*C*=O [one regioisomer]), 175.0 (*C*=O [one regioisomer]); IR (ATR): ν_{max}/cm^{-1} 2964, 2934, 2864, 1713 (C=O), 1616, 1584, 1504; MS (ES^-): *m/z* (%) 790 ($[M-H]^-$,100); HRMS (ES^+): $C_{29}H_{27}N_1O_1F_{17}S_2$ requires 792.1258, found 792.1280.

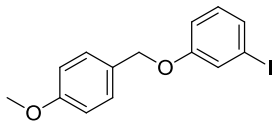
65 1-(Bromomethyl)-4-methoxybenzene[276]



To a solution of (4-methoxyphenyl)methanol (5.0 mL, 40 mmol) in CH_2Cl_2 (70 mL) under N_2 was added PBr_3 (4.52 mL, 48.1 mmol) at 0 ˚C. The resulting solution was stirred at 0 ˚C for 1 h followed by the addition of crushed ice (~15 g). The organic layer was separated and washed with $NaHCO_3$ (20 mL) at 0 ˚C, dried ($MgSO_4$), and concentrated *in vacuo* to yield **65** (7.66 g, 38.1 mmol, 95%) as a colourless oil, which was used without further purification; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 3.82 (3 H, s; O*C*H_3), 4.53 (2 H, s; *C*H_2Br), 6.89 (2 H, d, *J* = 8.7 Hz; 2 × Ar*H*), 7.35 (2 H, d, *J* = 8.7 Hz; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 34.0 (*C*H_2Br), 55.2 (O*C*H_3), 114.1 (2 × Ar*C*H), 129.9 (Ar*C*), 130.4 (2 × Ar*C*H), 159.6 (Ar*C*).

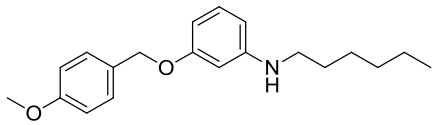
[Data consistent with literature]

66 1-Iodo-3-((4-methoxybenzyl)oxy)benzene



To a solution of 3-iodophenol (0.214 g, 0.973 mmol) in DMF (10 mL) at 0 ˚C was added NaH (65 mg, 60% w/w in mineral oil, 1.7 mmol) followed by **65** (0.444 g, 2.21 mmol) dropwise over 20 min. The mixture was stirred for 2 h at 0 ˚C, then for 16 h at 20 ˚C. To the solution was then added crushed ice (~10 g) resulting in the formation of a white solid which was collected by filtration, washed with water and dried thoroughly under vacuum. The crude product was purified by recrystallisation in Et_2O to yield **66** (0.228 g, 0.670 mmol, 69%) as a white crystalline solid, mp (Et_2O) 71-72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.83 (3 H, s; OCH_3), 4.96 (2 H, s; CH_2O), 6.89-6.96 (3 H, m; 3 × Ar*H*), 7.00 (1 H, app. t, *J* = 7.9 Hz; Ar*H*), 7.30 (1 H, d, *J* = 7.9 Hz; Ar*H*), 7.33-7.38 (3 H, m, 3 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 55.3 (O*C*H$_3$), 69.9 (O*C*H$_2$), 94.3 (Ar*C*), 114.0 (2 × Ar*C*H), 114.5 (Ar*C*H), 124.0 (Ar*C*H), 128.4 (Ar*C*H), 129.3 (2 × Ar*C*H), 130.0 (Ar*C*H), 130.8 (Ar*C*), 159.3 (Ar*C*), 159.6 (Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2954, 2930, 1611, 1580, 1513, 1513; MS (ES$^-$): *m/z* (%) 339 ([M-H]$^-$,100), 381 (50), 219 (50); HRMS (ES$^-$): $C_{14}H_{12}O_2I$ ([M-H]$^-$) requires 338.9887, found 338.9885.

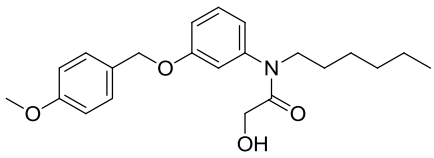
67 *N*-Hexyl-3-((4-methoxybenzyl)oxy)aniline[189]



To a microwave vial was added **66** (0.28 g, 0.82 mmol), copper powder (16 mg, 0.25 mmol) and K_3PO_4 (0.35 g, 1.64 mmol). The vial was then sealed and subjected to three vacuum-refill cycles with argon. Hexylamine (0.23 mL, 1.65 mmol) and dimethylaminoethanol (0.82 mL) were then added to the vial under argon. The sealed vial was then heated at 70 ˚C with vigorous stirring for 16 h. H_2O (8 mL) and Et_2O (8 mL) were then added, the layers separated and the aqueous layer washed with Et_2O (3 × 8 mL). The combined organic layers were then washed with brine (8 mL), dried ($MgSO_4$), and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in hexane gave **67** (0.17 g, 0.54 mmol, 66%) as a green solid, mp (EtOAc/Hexane) 33-35 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

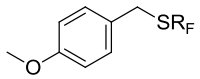
ppm 0.67-0.80 (3 H, t, *J* = 6.8; C*H*$_3$), 1.05-1.30 (6 H, m; 3 × C*H*$_2$), 1.40-1.54 (2 H, m; C*H*$_2$), 2.94 (2 H, t, *J* = 7.2 Hz; NC*H*$_2$), 3.52 (1 H, br. s; N*H*) 3.67 (3 H, s; OC*H*$_3$), 4.82 (2 H, s; OC*H*$_2$), 6.08-6.16 (2 H, m; 2 × Ar*H*), 6.16-6.28 (1 H, m; Ar*H*), 6.79 (2 H, d, *J* = 8.8 Hz; 2 × Ar*H*), 6.95 (1 H, t, *J* = 8.3 Hz; Ar*H*), 7.23 (2 H, d, *J* = 8.8 Hz; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 (*C*H$_3$), 22.5 (*C*H$_2$), 26.7 (*C*H$_2$), 29.3 (*C*H$_2$), 31.5 (*C*H$_2$), 43.8 (N*C*H$_2$), 55.1 (O*C*H$_3$), 69.4 (O*C*H$_2$), 99.3 (Ar*C*H), 102.8 (Ar*C*H), 106.0 (Ar*C*H), 113.8 (2 × Ar*C*H), 129.1 (Ar*C*H), 129.2 (2 × Ar*C*H), 129.7 (Ar*C*), 149.8 (Ar*C*), 159.2 (Ar*C*), 160.0 (Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3392 (NH), 3062, 2999, 2953, 2921, 2854, 2835, 1611, 1594, 1512, 1494; MS (ES$^+$): *m/z* (%) 314 ([M+H]$^+$, 100), 336 (20); HRMS (ES$^+$): $C_{20}H_{28}NO_2$ ([M+H]$^+$) requires 314.2115, found 314.2108.

68 *N*-Hexyl-2-hydroxy-N-(3-((4-methoxybenzyl)oxy)phenyl)acetamide



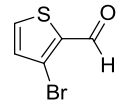
Following general procedures *D* and *H*, using **67** (0.21 g, 0.67 mmol), NEt_3 (0.058 mL, 0.79 mmol), and acetoxyacetyl chloride (0.084 mL, 0.78 mmol) in CH_2Cl_2 (4.1 mL), followed by K_2CO_3 (0.36 g, 2.60 mmol) in MeOH / H_2O (2:1, 3.0 mL), gave **68** (0.21 g, 0.57 mmol, 88% for 2 steps) as a colourless oil after purification by flash column chromatography on silica gel eluting with 20% EtOAc in hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.87 (3 H, t, *J* = 6.6 Hz; C*H*$_3$), 1.18-1.39 (6 H, m; 3 × C*H*$_2$), 1.50 (2 H, t, *J* = 6.7 Hz; C*H*$_2$), 3.71 (2 H, t, *J* = 7.8 Hz; NC*H*$_2$), 3.78 (2 H, s; C*H*$_2$OH), 3.82 (3 H, s; OC*H*$_3$), 4.99 (2 H, s; OC*H*$_2$), 6.71-6.77 (2 H, m; 2 × Ar*H*), 6.90-6.97 (2 H, m; 2 × Ar*H*), 6.98-7.05 (1 H, m; Ar*H*), 7.35 (3 H, m; 3 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 (*C*H$_3$), 22.5 (*C*H$_2$), 26.3 (*C*H$_2$), 27.5 (*C*H$_2$), 31.4 (*C*H$_2$), 49.6 (N*C*H$_2$), 55.2 (O*C*H$_3$), 60.4 (*C*H$_2$OH), 70.0 (O*C*H$_2$), 114.0 (2 × Ar*C*H), 114.9 (Ar*C*H), 115.0 (Ar*C*H), 120.3 (Ar*C*H), 128.1 (Ar*C*), 129.2 (2 × Ar*C*H), 130.6 (Ar*C*H), 140.5 (Ar*C*), 159.6 (Ar*C*), 159.7 (Ar*C*), 171.4 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 3433 (OH), 2953, 2928, 2856, 1654 (C=O), 1587, 1514; MS (ES$^+$): *m/z* (%) 394 ([M+Na]$^+$, 100); HRMS (ES$^+$): $C_{22}H_{30}NO_4$ ([M+H]$^+$) requires 372.2170, found 372.2167.

70 (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(4-methoxybenzyl)sulfide



Following general procedure *E*, using **68** (0.266 g, 0.716 mmol), oxalyl chloride (0.069 mL, 0.79 mmol), DMSO (0.10 mL, 1.4 mmol), and NEt_3 (0.50 mL, 3.6 mmol) in CH_2Cl_2 (5 mL), followed by R_FSH (0.18 mL, 0.63 mmol) and TFAA (0.20 mL, 1.4 mmol) in CH_2Cl_2 (9 mL) gave a complex mixture of products. Purification by FSPE followed by flash column chromatography on silica gel eluting with 10% EtOAc in petroleum ether, gave **70** (0.302 g, 0.503 mmol, 70%) as a white amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.20-2.36 (2 H, m; CF_2CH_2), 2.58-2.70 (2 H, m; SCH_2CH_2), 3.72 (2 H, s; $ArCH_2$), 3.81 (3 H, s; OCH_3), 6.88 (2 H, d, *J* = 8.5 Hz; 2 × Ar*H*), 7.23 (2 H, d, *J* = 8.5 Hz; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 21.8 (t, *J* = 4.1 Hz; SCH_2CH_2), 31.8 (t, *J* = 22.3 Hz; CF_2CH_2), 35.9 ($ArCCH_2$), 55.2 (OCH_3), 114.1 (2 × Ar*C*H), 129.4 (Ar*C*), 129.9 (2 × Ar*C*H), 158.9 (Ar*C*); MS (EI$^+$): *m/z* (%) 600 ([M]$^+$, 45), 120 (100); HRMS (EI$^+$): $C_{18}H_{13}OF_{17}S$ requires 600.0410, found 600.0421.

111a 3-Bromothiophene-2-carbaldehyde[203]

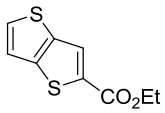


To a solution of diisopropylamine (3.29 mL, 23.5 mmol) in THF (43 mL) at -78 °C was added *n*BuLi (9.10 mL, 2.58 M in hexanes, 23.5 mmol) dropwise followed by stirring for 1 h at -78 °C. 3-Bromothiophene (3.83 g, 23.5 mmol) was then added dropwise at -78 °C and the reaction mixture warmed to 0 °C and stirred for 30 min. *N*-Formylpiperidine (2.61 mL, 23.5 mmol) was then added at 0 °C and the resulting solution was stirred for 3 h at 20 °C. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl (50 mL). The mixture was extracted with Et_2O (3 × 50 mL), and the combined organic fractions dried (Na_2SO_4), and concentrated *in vacuo* to yield **111a** (4.03 g, 21.1 mmol, 90%) as a pale yellow oil, which was used in the next step without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.13 (1 H, d, *J* = 5.1 Hz; Ar*H*), 7.71 (1 H, d, *J* = 5.1 Hz; Ar*H*), 9.96 (1 H, s; C*H*O); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 120.2 (Ar*C*), 131.9 (Ar*C*H), 134.8 (Ar*C*H), 136.8 (Ar*C*), 182.9 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 3101, 2843, 2816, 2774, 1657 (C=O); MS (ES$^+$): *m/z*

(%) 189 ([M+H]$^+$, 100), 413 (50); HRMS (ES$^+$): C_5H_3OSBr requires 189.9083, found 189.9086.

[Data consistent with literature]

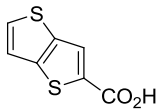
111b Ethyl thieno[3,2-*b*]thiophene-2-carboxylate[203]



To a solution of **111a** (4.03 g, 21.1 mmol) in DMF (40 mL) was added K_2CO_3 (3.94 g, 28.5 mmol) and ethyl 2-mercaptoacetate (2.3 mL, 21.0 mmol). The resulting suspension was stirred for 78 h at 20 ˚C under N_2. The reaction mixture was then poured into H_2O (100 mL) and extracted with CH_2Cl_2 (5 × 100 mL), dried (Na_2SO_4), and concentrated *in vacuo* to give the crude product. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in hexane yielded pure **111b** (4.04 g, 19.0 mmol, 90%) as an amorphous white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.39 (3 H, t, J = 7.2 Hz; CH_2CH_3), 4.38 (2 H, q, J = 7.2 Hz; CH_2CH_3), 7.25 (1 H, d, J = 5.3 Hz; Ar*H* next to ArC), 7.55 (1 H, d, J = 5.3 Hz; Ar*H* next to S), 7.97 (1 H, s; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.2 (CH_2CH_3), 61.2 (CH_2CH_3), 119.6 (Ar*C*H next to ArC), 125.4 (Ar*C*H next to ArCCO_2Et), 131.5 (Ar*C*H next to S), 135.0 (Ar*C*), 138.6 (Ar*C*), 143.7 (Ar*C*), 162.5 (*C*=O).

[Data consistent with literature]

111c Thieno[3,2-b]thiophene-2-carboxylic acid[203]

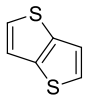


To a solution of **111b** (4.04 g, 19.0 mmol) in THF (40 mL) was added an aqueous solution of LiOH (40 mL, 1 M). The resulting mixture was heated for 3 h at reflux. After cooling to 20 °C, concentrated aqueous HCl (54 mL) was carefully added, resulting in the formation of a white precipitate, which was collected by filtration and washed with H_2O (2 × 10 mL) to give **111c** (3.36 g, 18.2 mmol, 96%) as a white solid, which was used in the next step without further purification; mp (H_2O) 218-220 °C [Lit (H_2O) 221-222 °C]; ^{1}H NMR (500

MHz, DMSO-d_6) δ ppm 7.50 (1 H, d, *J* = 5.4 Hz; Ar*H*), 7.91 (1 H, d, *J* = 5.4 Hz; Ar*H*), 8.11 (1 H, s; Ar*H*), 13.23 (1 H, br. s; CO_2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ ppm 120.3 (Ar*C*H), 126.1 (Ar*C*H), 133.0 (Ar*C*H), 135.7 (Ar*C*), 138.6 (Ar*C*), 143.3 (Ar*C*), 163.5 (*C*=O); MS (ES^-): *m/z* (%) 183 ([M-H]$^-$, 100), 139 (40); HRMS (ES^-): $C_7H_3O_2S_2$ requires 182.9579, found 182.9586.

[Data consistent with literature]

111 Thieno[3,2-b]thiophene[203,204]

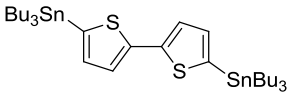


To a solution of **111c** (0.467 g, 2.53 mmol) in quinoline (3.7 mL) was added copper powder (93 mg, 1.46 mmol), the resulting suspension was then heated at 260 ˚C for 1 h. The mixture was cooled, Et_2O (5 mL) was added and the mixture washed with 5% HCl in H_2O (4 × 2 mL), H_2O (3 × 2 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product. Purification by flash column chromatography on silica gel eluting with petroleum ether yielded **111** (0.283 g, 2.02 mmol, 80%) as a white solid, mp (petroleum ether) 55-57 °C [Lit (CH_2Cl_2) 57 °C][277]; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.31 (2 H, d, *J* = 4.9 Hz; 2 × Ar*H*), 7.43 (2 H, d, *J* = 4.9 Hz; 2 × Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 119.3 (2 × Ar*C*H), 127.3 (2 × Ar*C*H), 139.4 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3099, 3084, 1564.

[Data consistent with literature]

General procedure I: Preparation of bis-organostannanes

114 5,5'-*bis*(Tributylstannyl)-2,2'-bithiophene[205]

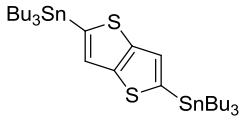


To a solution of 2,2'-bithiophene (0.22g, 1.32 mmol) in THF (5.5 mL) at -78 ˚C was added *n*BuLi (1.75 mL, 1.56 M in hexane, 2.73 mmol) dropwise over 5 min. The suspension was then allowed to warm to 0 ˚C and stirred for 1 h, cooled to -78 ˚C and Bu_3SnCl (0.74 mL, 2.73 mmol) added dropwise. The reaction mixture was warmed to rt and stirred for 16 h.

Hexane (5.5 mL) was added and the solution washed with a saturated aqueous solution of KF (3 × 3 mL), a saturated aqueous solution of $NaHCO_3$ (3 mL), and H_2O (3 mL), and concentrated *in vacuo*. The resulting crude product was purified by filtration through a small plug of neutral alumina eluting with petroleum ether 40-60 ˚C to yield **114** (0.72 g, 0.967 mmol, 73%) as a clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.91 (18 H, t, *J* = 7.3 Hz; 6 × C*H*$_3$), 1.07-1.16 (12 H, m; 6 × C*H*$_2$), 1.28-1.41 (12 H, m; 6 × C*H*$_2$), 1.48-1.65 (12 H, m; 6 × C*H*$_2$), 7.06 (2 H, d, *J* = 3.3 Hz; 2 × Ar*H*), 7.30 (2 H, d, *J* = 3.3 Hz; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 10.8 (6 × *C*H_3), 13.7 (6 × Sn*C*H_2), 27.3 (6 × *C*H_2), 28.9 (6 × *C*H_2), 124.7 (2 × Ar*C*H), 136.1 (2 × Ar*C*H and 2 × Ar*C*), 143.0 (2 × Ar*C*).

[Data consistent with literature]

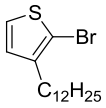
112 2,5-*bis*(Tributylstannyl)thieno[3,2-b]thiophene[206]



Following general procedure *I*, using **111** (0.205 g, 1.46 mmol), *n*BuLi (1.22 mL, 3.07 mmol, 2.52 M in hexanes) and Bu_3SnCl (0.83 mL, 3.1 mmol) in THF (6.0 mL) gave **112** (0.995 g, 1.39 mmol, 95%) as a colourless oil after purification by passing the crude product through a plug of alumina eluting with hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.92 (18 H, t, *J* = 7.3 Hz; 6 × C*H*$_3$), 1.14 (12 H, m; 6 × C*H*$_2$), 1.37 (12 H, m; 6 × C*H*$_2$), 1.61 (12 H, m; 6 × C*H*$_2$), 7.25 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 10.9 (6 × *C*H_3), 13.7 (6 × *C*H_2), 27.3 (6 × *C*H_2), 29.0 (6 × *C*H_2), 126.2 (2 × Ar*C*H), 140.1 (2 × Ar*C*), 147.6 (2 × Ar*C*).

[Data consistent with literature]

113a 2-Bromo-3-dodecylthiophene[207]

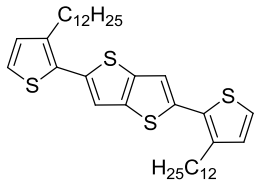


To a solution of 3-dodecylthiophene (1.80 g, 7.13 mmol) in THF (21 mL) at 0 °C was added NBS (1.34 g, 7.53 mmol). The resulting solution was stirred for 6 h at 0 °C and then concentrated *in vacuo*. Purification by flash column chromatography on silica gel eluting

with hexane gave pure **113a** (2.20 g, 6.64 mmol, 93%) as a clear oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.89 (3 H, t, *J* = 6.7 Hz; C*H*$_3$), 1.18-1.40 (18 H, m; 9 × C*H*$_2$), 1.50-1.65 (2 H, m; C*H*$_2$), 2.56 (2 H, t, *J* = 7.6 Hz; ArC*H*$_2$), 6.80 (1 H, d, *J* = 5.7 Hz; Ar*H*), 7.19 (1 H, d, *J* = 5.7 Hz; Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 14.1 (*C*H$_3$), 22.7 (*C*H$_2$), 29.2 (*C*H$_2$), 29.35 (*C*H$_2$), 29.38 (*C*H$_2$), 29.40 (*C*H$_2$), 29.56, 29.63, 29.66, 29.72 (5 × *C*H$_2$), 31.9 (*C*H$_2$), 108.8 (Ar*C*), 125.1 (Ar*C*H), 128.2 (Ar*C*H), 142.0 (Ar*C*); MS (GC/MS-EI$^+$): *m/z* (%) 330 ([M]$^+$, 15), 251 (35), 175 (30), 97 (100); HRMS (EI$^+$): $C_{16}H_{27}BrS$ requires 330.1011, found 330.1014.

[Data consistent with literature]

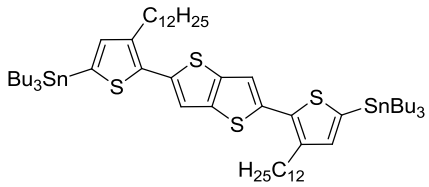
113b 2,5-*bis*(3-Dodecylthiophen-2-yl)thieno[3,2-b]thiophene[75]



To a sealed tube containing **112** (1.15 g, 1.60 mmol) was added $Pd(PPh_3)_4$ (37 mg, 0.032 mmol), and **113a** (1.06 g, 3.20 mmol). The tube was then subjected to 3 × flush-fill cycles with argon before adding toluene (16 mL). The reaction mixture was heated at 110 °C for 24 h, then cooled and poured into MeOH (~100 mL) and filtered to obtain the crude product. Purification by flash column chromatography on silica gel eluting with hexane gave pure **113b** (0.868 g, 1.36 mmol, 85%) as a cream coloured solid, m.p (hexane) 70-73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.90 (6 H, t, *J* = 6.8 Hz; 2 × C*H*$_3$), 1.20-1.44 (36 H, m; 18 × CH_2), 1.67 (4 H, app quin, *J* = 7.6 Hz; 2 × C*H*$_2$), 2.81 (4 H, t, *J* = 7.9 Hz; 2 × C*H*$_2$), 6.98 (2 H, d, *J* = 5.2 Hz; 2 × Ar*H*), 7.23 (2 H, d, *J* = 5.2 Hz; 2 × Ar*H*), 7.25 (2 H, s; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (2 × *C*H$_3$), 22.7, 29.2, 29.4, 29.5, 29.55, 29.60, 29.65, 29.69, 30.8, 31.9 (22 × *C*H$_2$), 118.0 (2 × Ar*C*H), 124.3 (2 × Ar*C*H), 130.0 (2 × Ar*C*H), 130.7 (2 × Ar*C*), 137.6 (2 × Ar*C*), 139.1 (2 × Ar*C*), 140.2 (2 × Ar*C*); MS (AP$^+$): *m/z* (%) 641 ([M+H]$^+$, 100); HRMS (ES$^+$) $C_{38}H_{56}S_4$ requires 640.3259, found 640.3244.

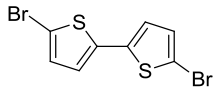
[Data consistent with literature]

113 2,5-*bis*(3-Dodecyl-5-(tributylstannyl)thiophen-2-yl)thieno[3,2-b]thiophene[75]



Following general procedure *I*, using **113b** (0.663 g, 0.994 mmol), *n*BuLi (1.31 mL, 2.08 mmol, 1.59 M in hexanes), and *n*Bu_3SnCl (0.62 mL, 2.29 mmol) in THF (5 mL) gave **113** (1.21 g, 0.992 mmol, 100%) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.75-0.92 (24 H, m; 8 × C*H*$_3$), 1.00-1.09 (12 H, m; 6 × C*H*$_2$), 1.13-1.66 (64 H, m; 34 × C*H*$_2$), 2.68-2.80 (4 H, m; 2 × C*H*$_2$), 6.90 (2 H, s; 2 × Ar*H*), 7.14 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 10.9 (6 × *C*H$_2$), 13.7 (6 × *C*H$_3$), 14.13 (2 × *C*H$_3$), 17.5, 22.7, 26.9, 27.3, 27.8, 29.0, 29.2, 29.4, 29.5, 29.66, 29.70, 30.9, 31.9 (34 × *C*H$_2$), 117.3 (2 × Ar*C*H), 136.3 (2 × Ar*C*), 136.5 (2 × Ar*C*), 137.9 (2 × Ar*C*), 138.6 (2 × Ar*C*H), 139.0 (2 × Ar*C*), 141.0 (2 × Ar*C*).

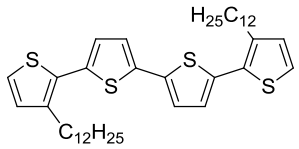
115 5,5'-Dibromo-2,2'-bithiophene[208]



To a solution of 2,2'-bithiophene (1.58 g, 9.50 mmol) in DMF (20 mL) at 0 °C was added NBS (3.47 g, 19.5 mmol). The solution was then allowed to warm to rt and stirred for 18 h. H_2O (20 mL) and CH_2Cl_2 (30 mL) were then added and the aqueous layer separated, the organic layer was washed further with H_2O (2 × 20 mL), then dried (Na_2SO_4) and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with hexane gave pure **115** (3.00 g, 9.23 mmol, 97%) as a white solid, mp (hexane) 140-142 °C [Lit ($CHCl_3$) 141 °C][278]; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 6.86 (2 H, d, *J* = 4.0 Hz; 2 × Ar*H*), 6.97 (2 H, d, *J* = 4.0 Hz; 2 × ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 111.5 (2 × Ar*C*), 124.1 (2 × Ar*C*H), 130.6 (2 × Ar*C*H), 137.8 (2 × Ar*C*).

[Data consistent with literature]

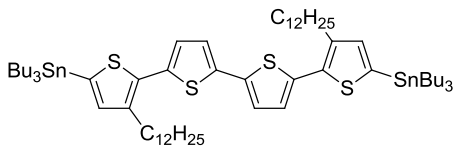
116a 3,3'''-Didodecyl-2,2':5',2'':5'',2'''-quaterthiophene[279]



To a solution of **113a** (5.82 g, 17.6 mmol) in THF (87 mL) was added magnesium turnings (0.449 g, 18.5 mmol) and a single crystal of iodine under N_2. The mixture was stirred vigourously and heated to reflux for 6 h. The solution was then cooled to 20 ˚C and **115** (2.28 g, 7.04 mmol) in THF (87 mL), and Pd(dppf)Cl_2 (0.643 g, 0.879 mmol) added under N_2. The solution was then heated to reflux for 16 h, cooled to rt, poured into MeOH (~200 mL) and filtered to obtain the crude product. Purification by flash column chromatography on silica gel eluting with hexane gave pure **116a** (3.75 g, 5.62 mmol, 80%) as a yellow solid, mp (hexane) 52-55 °C [Lit (MeOH/*i*PrOH) 59 °C][209]; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.95 (6 H, t, *J* = 6.8 Hz; 2 × CH_3), 1.28-1.47 (36 H, m; 18 × CH_2), 1.72 (4 H, quin, *J* = 7.7 Hz; 2 × CH_2), 2.84 (4 H, t, *J* = 7.7 Hz; 2 × CH_2), 6.98 (2 H, d, *J* = 5.2 Hz; 2 × Ar*H*), 7.07 (2 H, d, *J* = 3.7 Hz; 2 × Ar*H*), 7.17 (2 H, d, *J* = 5.2 Hz; 2 × Ar*H*), 7.21 (2 H, d, *J* = 3.7 Hz; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (2 × *C*H_3), 22.7 (2 × *C*H_2), 29.3 (2 × *C*H_2), 29.4 (2 × *C*H_2), 29.46 (2 × *C*H_2), 29.52 (2 × *C*H_2), 29.6 (2 × *C*H_2), 29.66 (2 × *C*H_2), 29.68 (2 × *C*H_2), 29.69 (2 × *C*H_2), 30.6 (2 × *C*H_2), 31.9 (2 × *C*H_2), 123.7 (4 × Ar*C*H), 126.4 (2 × Ar*C*H), 130.0 (2 × Ar*C*H), 130.3 (2 × Ar*C*), 135.3 (2 × Ar*C*), 136.8 (2 × Ar*C*), 139.8 (2 × Ar*C*). Elemental analysis: Expected, %: C, 72.01; H, 8.76; S, 19.23; Found, %: C, 71.78; H, 9.11; S, 19.10.

[Data consistent with literature]

116 (3,3'''-Didodecyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)*bis*(tributylstannane)[210]

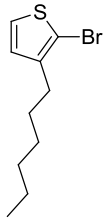


Following general procedure *I*, using **116a** (1.01 g, 1.51 mmol), *n*BuLi (2.08 mL, 3.18 mmol, 1.53 M in hexanes), and *n*Bu_3SnCl (0.90 mL, 3.32 mmol) in THF (6 mL) gave **116** (1.88 g, 1.51 mmol, 100%) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.10-1.22 (24

H, m; 8 × CH_3), 1.30-1.46 (12 H, m; 6 × CH_2), 1.47-1.70 (48 H, m; 24 × CH_2), 1.81-1.99 (16 H, m; 8 × CH_2), 3.01-3.11 (4 H, m; 2 × ArCCH_2), 7.28 (2 H, d, *J* = 3.7 Hz; 2 × Ar*H*), 7.37 (2 H, d, *J* = 3.7 Hz; 2 × Ar*H*), 7.52 (2 H, s; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 10.8 (6 × CH_2), 13.7 (6 × *C*H_3), 14.1 (2 × CH_3), 22.7, 27.3, 28.9, 29.2, 29.3, 29.4, 29.5, 29.6, 29.66, 29.69, 29.70, 30.7, 31.9 (34 × *C*H_2), 123.7 (2 × Ar*C*H), 125.8 (2 × Ar*C*H), 135.7 (2 × Ar*C*), 135.8 (2 × Ar*C*), 135.9 (2 × Ar*C*), 136.5 (2 × Ar*C*), 138.7 (2 × Ar*C*H), 140.7 (2 × Ar*C*).

[Data consistent with literature]

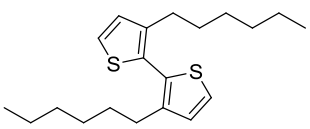
117 2-Bromo-3-hexylthiophene[211]



To a solution of 3-hexylthiophene (1.87 g, 11.1 mmol) in THF (50 mL) was added NBS (2.08 g, 11.7 mmol) at 0 ˚C. The solution was stirred for 6 h at 0 ˚C and then allowed to warm to rt and stirred overnight. The crude reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel eluting with hexane to give pure **117** (2.48 g, 10.0 mmol, 90%) as a clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.90 (3 H, t, *J* = 6.9 Hz; CH_3), 1.18-1.44 (6 H, m; 3 × CH_2), 1.46-1.66 (2 H, m; CH_2), 2.52-2.62 (2 H, m; ArCCH_2), 6.80 (1 H, d, *J* = 5.7 Hz; Ar*H*), 7.19 (1 H, d, *J* = 5.7 Hz; Ar*H*); IR (ATR): ν_{max}/cm^{-1} 2954, 2924, 2855; MS (GCMS-EI$^+$): *m/z* (%) 246 ([M]$^+$, 20) , 175 (80), 97 (100); HRMS (EI$^+$): $C_{10}H_{15}SBr$ requires 246.0072, found 246.0071.

[Data consistent with literature]

118a 3,3'-Dihexyl-2,2'-bithiophene[211]

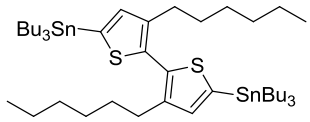


To a solution of **117** (1.16 g, 4.69 mmol) in THF (23 mL) was added magnesium turnings (0.120 g, 4.94 mmol) and a single crystal of iodine under N_2. The mixture was stirred

vigourously and heated to reflux for 6 h. The solution was then cooled to 20 ˚C and **117** (1.16 g, 4.69 mmol) in THF (6 mL), and Pd(dppf)Cl_2 (0.172 g, 0.235 mmol) were added under N_2. The solution was then heated to reflux for 16 h, before being quenched with aqueous HCl (5 mL, 1 M) and extracted with CH_2Cl_2 (3 × 30 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Purification by flash column chromatography eluting with petroleum ether yielded pure **118a** (1.45 g, 4.34 mmol, 92%) as a clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.86 (6 H, t, J = 6.9 Hz; 2 × CH_3), 1.08-1.41 (12 H, m; 6 × CH_2), 1.46-1.62 (4 H, m; 2 × CH_2), 2.37-2.57 (4 H, m; 2 × CH_2), 6.97 (2 H, d, J = 5.2 Hz; 2 × ArH), 7.29 (2 H, d, J = 5.2 Hz; 2 × ArH); ^{13}C NMR ($CDCl_3$) δ ppm 14.1 (2 × CH$_3$), 22.6 (2 × CH$_2$), 28.8 (2 × CH$_2$), 29.1 (2 × CH$_2$), 30.7 (2 × CH$_2$), 31.6 (2 × CH$_2$), 125.2 (2 × ArCH), 128.5 (2 × ArCH), 128.7 (2 × ArC), 142.3 (2 × ArC).

[Data consistent with literature]

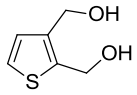
118 (3,3'-Dihexyl-[2,2'-bithiophene]-5,5'-diyl)*bis*(tributylstannane)[212]



Following general procedure *I*, using **118a** (0.465 g, 1.39 mmol), *n*BuLi (1.32 mL, 2.92 mmol, 2.21 M in hexanes) and Bu_3SnCl (0.79 mL, 2.91 mmol) in THF (11 mL) gave **118** (1.15 g, 1.26 mmol, 91%) as a colourless oil after purification by filtration of the crude product through alumina eluting with hexane; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.88 (6 H, t, J = 7.4 Hz; 2 × CH_3), 0.91-0.96 (18 H, m; 6 × CH_3), 1.13 (12 H, t, J = 8.2 Hz; 6 × SnCH_2), 1.22-1.44 (24 H, m; 12 × CH_2), 1.46-1.71 (16 H, m; 8 × CH_2), 2.57 (4 H, t, J = 7.9 Hz; 2 × ArCCH_2), 7.01 (2 H, s; 2 × ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 10.8 (6 × $SnCH_2$), 13.6 (6 × CH$_3$), 14.1 (2 × CH$_3$), 22.6 (2 × CH$_2$), 27.3 (6 × CH$_2$), 28.7 (2 × $ArCCH_2$), 29.0 (6 × CH$_2$), 29.2 (2 × CH$_2$), 30.9 (2 × CH$_2$), 31.7 (2 × CH$_2$), 136.1 (2 × ArC), 137.1 (2 × ArC), 137.2 (2 × ArCH), 142.6 (2 × ArC).

[Data consistent with literature]

50 Thiophene-2,3-diyldimethanol[186]

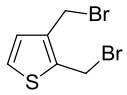


To a solution of thiophene-2,3-dicarbaldehyde (0.88 g, 6.27 mmol) in MeOH (20 mL) at 0 °C was added $NaBH_4$ (0.52 g, 13.7 mmol) portionwise over 10 min. The resulting mixture was allowed to warm to 20 °C and stirred for 15 min before quenching with H_2O (10 mL). The MeOH was then removed *in vacuo* and the aqueous solution washed with CH_2Cl_2 (5 × 30 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated *in vacuo* to yield 2,3-*bis*(hydroxymethyl)thiophene **50** (0.88 g, 6.10 mmol, 97%) as a colourless oil which was used immediately without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.79 (1 H, s; O*H*), 3.10 (1 H, s; O*H*), 4.66 (2 H, s; CH_2OH), 4.77 (2 H, s; CH_2OH), 7.00 (1 H, d, *J* = 5.0 Hz; Ar*H*), 7.19 (1 H, d, *J* = 5.0 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 57.3 (*C*H_2), 58.5 (*C*H_2), 124.0 (Ar*C*H), 128.9 (Ar*C*H), 139.1 (Ar*C*), 139.8 (Ar*C*).

[Data consistent with literature]

General procedure J: Bromination of alcohols using PBr_3

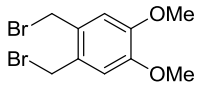
45 2,3-*bis*-Bromomethylthiophene[186]



To a solution of **50** (0.14 g, 0.97 mmol) in CH_2Cl_2 (10 mL), was added PBr_3 (0.18 mL, 1.96 mmol) dropwise at 0 °C. The solution was then warmed to rt and stirred for 16 h. A saturated aqueous solution of $NaHCO_3$ (10 mL) was then added at 0 °C and the solution stirred for 30 min at rt. The organic layer was separated, dried ($MgSO_4$), and concentrated *in vacuo* to give **45** (0.22 g, 0.81 mmol, 84%) as a pale green crystalline solid, which was used immediately without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.54 (2 H, s; CH_2Br), 4.76 (2 H, s; CH_2Br), 7.02 (1H, d, *J* = 5.3 Hz; Ar*H*), 7.28 (1H, d, *J* = 5.3 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 23.5 (*C*H_2Br), 24.0 (*C*H_2Br), 126.0 (Ar*C*H), 129.5 (Ar*C*H), 136.9 (Ar*C*), 137.3 (Ar*C*); MS (ES^-): *m/z* (%) 305 ($[M+Cl]^-$, 100).

[Data consistent with literature]

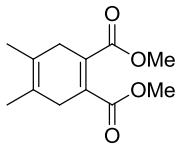
90 1,2-*bis*(Bromomethyl)-4,5-dimethoxybenzene[198]



To a solution of 1,2-dimethoxybenzene (9.2 mL, 72 mmol) and paraformaldehyde (4.35 g, 0.145 mol) in AcOH (100 mL) was carefully added a solution of HBr (28.2 mL, 33% AcOH) at 10 °C. The solution was then allowed to warm to 20 °C and was stirred for 20 h before heating at 64 °C for 1 h. The solution was then concentrated *in vacuo* to yield the crude product as green crystals. Recrystallisation from EtOAc yielded pure **90** (9.54 g, 29.4 mmol, 41%) as a white solid, mp (EtOAc) 117-120 °C [Lit (cyclohexane) 107-109 °C][280]; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 3.91 (6 H, s; 2 × OCH_3), 4.64 (4 H, s; 2 × CH_2Br), 6.85 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 30.6 (2 × *C*H_2Br), 56.0 (2 × O*C*H_3), 113.5 (2 × Ar*C*H), 129.0 (2 × Ar*C*), 149.4 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3005, 2954, 2926, 2828, 1604, 1521.

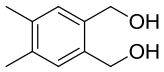
[Data consistent with literature]

79a Dimethyl 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate[192,281,282]



To butadiene (5.0 mL, 44 mmol) was added dimethyl but-2-ynedioate (5.2 mL, 42 mmol) and toluene (5 mL). The resulting mixture was then heated at 66 °C for 24 h in a sealed microwave vial. The mixture was then cooled to rt and concentrated *in vacuo* to yield the crude product **79a** which was used immediately in the next step; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.64 (6 H, s; 2 × CH_3), 2.90 (4 H, s; 2 × CH_2), 3.76 (6 H, s; 2 × OCH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 17.9 (2 × *C*H_3), 34.0 (2 × *C*H_2), 52.1 (2 × O*C*H_3), 121.4 (2 × *C*=C), 132.7 (2 × *C*=C), 168.3 (2 × *C*=O); IR (ATR): ν_{max}/cm^{-1} 2997, 2956, 2919, 2859, 2819, 1738 (C=O), 1710, 1658, 1529; MS (ES$^+$): *m/z* (%) 471 (80), 288 (30), 279 (35), 247 ([M+Na]$^+$, 100); HRMS (ES$^+$): $C_{12}H_{16}O_4Na_1$ requires 247.0941, found 247.0943.

79 (4,5-Dimethyl-1,2-phenylene)dimethanol[192]

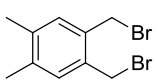


To a solution of crude **79a** in chlorobenzene (150 mL) was added DDQ (20.1 g, 88.5 mmol). The resulting solution was heated at 110 ° C for 48 h. The mixture was then concentrated *in vacuo* and passed through a plug of silica gel eluting with 30% EtOAc in hexane to yield the crude product dimethyl 4,5-dimethylphthalate (7.2 g) which was used immediately in the next step without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.32 (6 H, s; 2 × CH_3), 3.89 (6 H, s; 2 × OCH_3), 7.49 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 19.66 (2 × *C*H_3), 52.47 (2 × O*C*H_3), 129.34 (2 × Ar*C*), 130.02 (2 × Ar*C*H), 140.24 (2 × Ar*C*), 168.29 (2 × *C*=O); IR (ATR): ν_{max}/cm^{-1} 2949, 1721, 1611, 1564; MS (ES$^+$): 223 ([M+H]$^+$, 100%), 191 (60%).

To a solution of crude dimethyl 4,5-dimethylphthalate in THF (100 mL) was added $LiAlH_4$ (3.4 g, 90 mmol) portionwise at 0 ° C. The resulting solution was stirred at rt for 24 h then quenched with H_2O (100 mL). The resulting precipitate was removed by filtration and the product extracted with Et_2O (3 × 100 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel eluting with 60% EtOAc in hexane followed by recrystallisation from EtOAc/hexane gave **79** (2.75 g, 16.5 mmol, 39 % for 3 steps) as a pale pink solid, mp (EtOAc.Hexane) 102-105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.27 (6 H, s; 2 × CH_3), 2.77 (2 H, br. s; 2 × O*H*), 4.69 (4 H, s; 2 × CH_2O), 7.13 (2 H, s; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 19.3 (2 × *C*H_3), 64.1 (2 × *C*H_2O), 131.3 (2 × Ar*C*H), 136.8 (2 × Ar*C*), 136.9 (2 × Ar*C*); MS (ES$^+$): *m/z* 189 ([M+Na]$^+$, 100); HRMS (ES$^+$) $C_{10}H_{14}O_2Na_1$ requires 189.0886, found 189.0883.

[Data consistent with Literature]

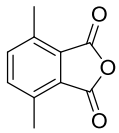
80 1,2-*bis*(Bromomethyl)-4,5-dimethylbenzene



Following general procedure *J*, using **79** (0.86 g, 5.17 mmol) and PBr_3 (0.97 mL, 10.3 mmol) in CH_2Cl_2 (26 mL), followed by purification by recrystallisation from MeCN gave **80** (1.35 g, 4.61 mmol, 89%) as a white solid, mp (MeCN) 116-120 °C; ^{1}H NMR (500 MHz,

$CDCl_3$) δ ppm 2.29 (6 H, s; 2 × CH_3), 4.68 (4 H, s; 2 × CH_2Br), 7.19 (2 H, s; 2 × ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 19.3 (2 × CH$_3$), 30.3 (2 × CH$_2$Br), 132.2 (2 × ArCH), 133.7 (2 × ArC), 138.1 (2 × ArC); IR (ATR): ν_{max}/cm^{-1} 2965, 2916, 2851, 1502; MS (GC/MS-EI+): *m/z* (%): 292 ([M]$^+$, 10), 211 (65), 132 (100); HRMS (EI$^+$): $C_{10}H_{12}Br_2$ requires 289.9300, found 289.9300.

81 4,7-Dimethylisobenzofuran-1,3-dione[193]

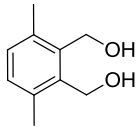


A solution of 2,5-dimethylfuran (4.52 g, 47.0 mmol) and furan-2,5-dione (4.61 g, 47.0 mmol) in Et_2O (9.4 mL) was strirred for 16 h at 20 °C. The resulting suspension was filtered and the filtrand washed with Et_2O (2 mL), to yield crude 5,6-dimethyl-4,7-epoxyisobenzofuran-1,3(4H,7H)-dione as a white solid which was used immediately in the next step without any further purification.

To concentrated H_2SO_4 (9.4 mL, 98%) at -10 °C was added in small portions crude 5,6-dimethyl-4,7-epoxyisobenzofuran-1,3(4H,7H)-dione maintaining the temperature below 0 °C. The solution was then allowed to slowly warm to 10 °C, poured slowly into an excess of crushed ice, and filtered to obtain crude **81** as a white solid. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in hexane yielded **81** (4.04 g, 22.9 mmol, 49% for two steps) as a white solid, mp (EtOAc/Hexane) 133-137 °C [Lit (Toluene) 143-144 °C]; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.67 (6 H, s; 2 × CH_3), 7.51 (2 H, s; 2 × ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 17.3 (2 x CH_3), 128.4 (2 × ArC), 137.7 (2 × ArCH and 2 × ArC), 163.2 (2 × C=O); IR (ATR): ν_{max}/cm^{-1} 2931, 1843 (C=O), 1776 (C=O), 1691.

[Data consistent with Literature]

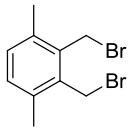
82 (3,6-Dimethyl-1,2-phenylene)dimethanol[193]



To a stirred suspension of $LiAlH_4$ (1.13 g, 29.8 mmol) in THF (40 mL) under N_2 was added dropwise a solution of **81** (4.04 g, 22.9 mmol) in THF (40 mL) over 30 min. The solution was then refluxed for 16 h. H_2O (2 mL), NaOH (2 mL, 15% aq.) and H_2O (4 mL) where then added, the mixture filtered and the filtrand washed with Et_2O (2 × 20 mL). The sample was then concentrated *in vacuo* to yield **82** (3.51 g, 21.1 mmol, 92%) as a white solid which was used without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.37 (6 H, s; 2 × CH_3), 3.38 (2 H, br. s; 2 × O*H*), 4.70 (4 H, s; 2 × CH_2), 7.05 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 19.5 (2 × *C*H_3), 59.1 (2 × *C*H_2), 130.2 (2 × Ar*C*H), 134.8 (2 × Ar*C*), 137.9 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3275 (OH), 2967, 2920, 2868, 1484; MS (ES$^+$): *m/z* (%) 189 ([M+Na]$^+$, 100); HRMS (ES$^+$): $C_{10}H_{14}O_2Na_1$ requires 189.0886, found 189.0885.

[Data consistent with literature]

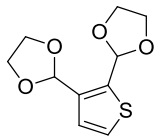
83 2,3-*bis*(Bromomethyl)-1,4-dimethylbenzene[193]



Following general procedure *J*, using **82** (0.892 g, 5.37 mmol), and PBr_3 (1.0 mL, 10.7 mmol) in CH_2Cl_2 (27 mL), followed by purification by recrystallisation from MeCN gave **83** (1.38 g, 4.74 mmol, 88%) as a white solid; (MeCN) 97-102 °C [Lit 100 °C (EtOH)][283]; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.41 (6 H, s; 2 × C*H*$_3$), 4.70 (4 H, s; 2 × C*H*$_2$), 7.09 (2 H, s; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 19.1 (2 × *C*H_3), 27.7 (2 × *C*H_2), 131.1 (2 × Ar*C*H), 134.8 (2 × Ar*C*), 135.9 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2954, 2926, 2857, 1612, 1587, 1514.

[Data consistent with literature]

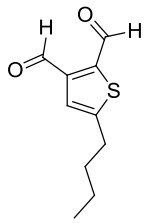
91 2,2'-(Thiophene-2,3-diyl)*bis*(1,3-dioxolane)[200]



To a solution of thiophene-2,3-dicarbaldehyde (2.97 g, 21.2 mmol) in benzene (37 mL) was added ethylene glycol (2.54 mL, 46.2 mmol) and *p*-toluenesulfonic acid monohydrate (3 mg, 0.02 mmol). The resulting solution was stirred for 18 h at reflux under Dean-Stark conditions. The solution was then cooled and concentrated *in vacuo*. The crude product was then purified by flash column chromatography on silica gel eluting with 20% EtOAc in hexane to yield **91** (3.89 g, 17.0 mmol, 80%) as a clear oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.92-4.04 (4 H, m; 2 × CH_2), 4.06-4.18 (4 H, m; 2 × CH_2), 6.03 (1 H, s; C*H*), 6.34 (1 H, s; C*H*), 7.10 (1 H, d, *J* = 5.2 Hz; Ar*H*), 7.23 (1 H, d, *J* = 5.2 Hz; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 65.2 (2 × *C*H_2), 65.4 (2 × *C*H_2), 98.7 (*C*H), 99.2 (*C*H), 125.2 (Ar*C*H), 126.8 (Ar*C*H), 137.5 (Ar*C*), 140.1 (Ar*C*).

[Data consistent with literature]

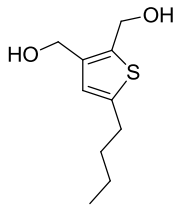
92 5-Butylthiophene-2,3-dicarbaldehyde[202]



To a solution of **91** (3.89 g, 17.0 mmol) in THF (50 mL) at -78 °C was added *n*BuLi (19.2 mL, 1.6 M, 30.7 mmol) dropwise. The resulting suspension was stirred at -78 °C for 1 h, then *n*BuI (3.88 mL, 34.1 mmol) was added dropwise. The mixture was then warmed to rt and stirred for 16 h. To the solution, HCl (3 M, 85 mL) and THF (85 mL) was then added and the solution refluxed for 2 h. The solution was then cooled, H_2O (100 mL) added and extracted with Et_2O (3 × 100 mL), washed with a saturated aqueous solution of $NaHCO_3$ (100 mL), dried ($MgSO_4$) and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography in silica gel eluting with 30% EtOAc in hexane yielded **92** (2.15 g, 11.0 mmol, 64%) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.96 (3 H, t, *J* = 7.3 Hz; CH_3), 1.37-1.47 (2 H, m; CH_2), 1.67-1.76 (2 H, m; CH_2), 2.89

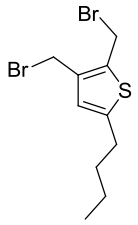
(2 H, t, *J* = 7.6 Hz; C*H*$_2$), 7.33 (1 H, s; Ar*H*), 10.34 (1 H, s; (CO)*H*), 10.4 (1 H, s; (CO)*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.7 (*C*H$_3$), 22.0 (*C*H$_2$), 30.2 (*C*H$_2$), 33.1 (*C*H$_2$), 126.9 (Ar*C*H), 143.9 (Ar*C*), 145.0 (Ar*C*), 156.3 (Ar*C*), 182.2 (*C*=O), 184.8 (*C*=O). IR (ATR): ν_{max}/cm^{-1} 2957, 2930, 2872, 1686 (C=O), 1662 (C=O), 1529, 1460, 1396, 1210, 1137, 1034;

93 (5-Butylthiophene-2,3-diyl)dimethanol



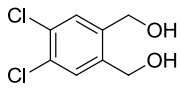
To a solution of **92** (2.15 g, 11.0 mmol) in MeOH (274 mL) at 0 °C was added $NaBH_4$ (0.912 g, 24.1 mmol) portionwise over 30 min. The solution was then warmed to rt and stirred for 20 min. H_2O (30 mL) was added and the MeOH was then removed *in vacuo* and the aqueous solution washed with CH_2Cl_2 (5 × 30 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 30% EtOAc in hexane yielded **93** (1.98 g, 9.89 mmol, 90%) as a white waxy solid which was used immediately without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.94 (3 H, t, *J* = 7.4 Hz; CH_3), 1.39 (2 H, dq, *J* = 15.1, 7.5 Hz; C*H*$_2$CH$_3$), 1.64 (2 H, dt, *J* = 15.1, 7.6 Hz; C*H*$_2$), 2.19 (1 H, br. s; O*H*), 2.45 (1 H, br. s; O*H*), 2.76 (2 H, t, *J* = 7.6 Hz; ArC*H*$_2$), 4.64 (2 H, s; C*H*$_2$OH), 4.74 (2 H, s; C*H*$_2$OH), 6.70 (1 H, s; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.8 (*C*H$_3$), 22.1 (*C*H$_2$), 29.6 (*C*H$_2$), 33.7 (*C*H$_2$), 57.6 (*C*H$_2$O), 58.9 (*C*H$_2$O), 125.8 (Ar*C*H), 137.0 (Ar*C*), 138.9 (Ar*C*), 144.7 (Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3372 (OH), 2955, 2927, 2856, 1665, 1464, 1378, 1352, 1255, 1161, 1140, 1055; MS (ES$^+$): *m/z* (%) 223 ([M+Na]$^+$, 60), 183 (100); HRMS (ES$^+$): $C_{10}H_{16}O_2S_1Na_1$ requires 223.0764, found 223.0764.

94 2,3-*bis*(Bromomethyl)-5-butylthiophene



Following general procedure *J*, using **93** (0.329 g, 1.64 mmol) and PBr_3 (0.31 mL, 3.3 mmol) in CH_2Cl_2 (8 mL) gave **94** (0.301 g, 0.923 mmol, 56%) as a pink oil, which was used without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.94 (3 H, t, *J* = 7.4 Hz; C*H*$_3$), 1.34-1.48 (2 H, m; C*H*$_2$CH$_3$), 1.55-1.73 (2 H, m; C*H*$_2$), 2.74 (2 H, t, *J* = 7.7 Hz; Ar*C*H$_2$), 4.47 (2 H, s; C*H*$_2$Br), 4.71 (2 H, s; C*H*$_2$Br), 6.69 (1 H, s; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.7 (*C*H$_3$), 22.2 (*C*H$_2$), 24.2 (*C*H$_2$), 24.3 (*C*H$_2$), 29.8 (*C*H$_2$Br), 33.3 (*C*H$_2$Br), 126.3 (Ar*C*H), 134.6 (Ar*C*), 136.6 (Ar*C*), 147.0 (Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2955, 2927, 2869, 2855, 1480, 1445; *Mass spectrometry was not informative*.

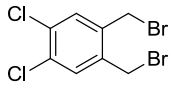
88a (4,5-Dichloro-1,2-phenylene)dimethanol[284]



To a solution of 4,5-dichlorophthalic acid (10.0 g, 42.5 mmol) in THF (10 mL) at -78 °C was added a suspension of $LiAlH_4$ (3.24 g, 85.4 mmol) in THF (40 mL) dropwise via cannula over 1 h. The suspension was then warmed to rt, stirred at rt for 2 h, then refluxed for 16 h. HCl (200 mL, 3 M) was added cautiously at 0 °C over 30 min, then the mixture extracted with Et_2O (3 × 200 mL), dried ($MgSO_4$), and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 60% EtOAc in hexane gave **88a** (6.48 g, 31.3 mmol, 73%) as a white solid, mp (EtOAc) 133-139 °C [Lit. 137-139 °C][284]; ^{1}H NMR (300 MHz, MeOD) δ ppm 4.62 (4 H, s; 2 × C*H*$_2$), 4.91 (2 H, s; 2 × O*H*), 7.55 (2 H, s; 2 × Ar*H*); ^{13}C NMR (75 MHz, MeOD) δ ppm 61.5 (2 × *C*H$_2$), 130.3 (2 × Ar*C*H), 131.9 (2 × Ar*C*), 140.9 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3273 (OH), 2905, 2851, 1483, 1442, 1382; MS (ES$^-$): *m/z* (%) 251 (100), 241 ([M+Cl]$^-$, 20), 205 ([M-H]$^-$, 20); HRMS (ES$^-$): $C_8H_7O_2Cl_2$ requires 204.9831, found 204.9828.

[Data consistent with literature]

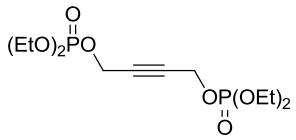
88 1,2-*bis*(Bromomethyl)-4,5-dichlorobenzene[284]



Following general procedure *J*, using **88a** (0.37 g, 1.8 mmol) and PBr_3 (0.30 mL, 3.2 mmol) in CH_2Cl_2 (5 mL) gave **88** (0.52 g, 1.6 mmol, 88%) as a white solid, mp (MeCN) 57-59 °C [Lit 63-64 °C (THF)][284]; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.56 (4 H, s; 2 × CH_2), 7.48 (2 H, s; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 28.0 (2 × *C*H_2), 132.6 (2 × Ar*C*H), 133.1 (2 × Ar*C*), 136.4 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 1472, 1459, 1226, 1206, 1135, 1099, 1050.

[Data consistent with literature]

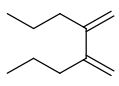
85a But-2-yne-1,4-diyl tetraethyl *bis*(phosphate)[285]



To a solution of but-2-yne-1,4-diol (0.893 g, 10.4 mmol) in pyridine (3.5 mL) at 0 °C, was added diethyl phosphorochloridate (3.28 mL, 22.8 mmol) dropwise. The resulting solution was stirred at 0 °C for 2 h, then brine (5 mL) was added. The mixture was extracted with Et_2O (5 × 5 mL), washed with 1M H_2SO_4 (5 mL), a saturated aqueous solution of $NaHCO_3$ (5 mL), brine (5 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield **85a** (2.28, 6.36 mmol, 67%) as a pale brown oil which was used immediately without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.35 (12 H, t, *J* = 7.1 Hz; 4 × CH_3), 4.10-4.20 (8 H, m; 4 × CH_2CH$_3$), 4.71 (4 H, d, *J* = 9.8 Hz; 2 × CH_2); IR (ATR): ν_{max}/cm^{-1} 2986, 2937, 1445, 1393, 1371, 1263, 1156, 1100, 1016, 986, 836.

[Data consistent with literature]

85 4,5-Dimethyleneoctane[286]

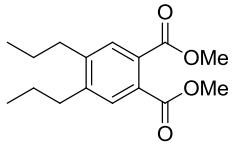


To a solution of propylmagnesium bromide (86 mL, 2 M in Et_2O, 172 mmol) and CuI (1.09 g, 5.72 mmol) in THF (57 mL) was added a solution of **85a** (20.6 g, 57.5 mmol) in THF (57 mL) dropwise at 0 °C. The solution was then allowed to warm to rt and stirred for 16 h.

H_2O (400 mL) was added and the resulting precipitate was removed by vacuum filtration. The solution was then extracted with pentane (3 × 100 mL), dried (Na_2SO_4), and concentrated *in vacuo* with the bath temperature set at 0 °C to give the crude product **85** (4.60 g, 33.2 mmol, 58%) as a colourless oil which was used immediately in the next step without further purification; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.92 (6 H, t, J = 7.3 Hz; 2 × CH_3), 1.41-1.54 (4 H, m; 2 × CH_2), 2.14-2.30 (4 H, m; 2 × CH_2), 4.92 (2 H, s; 2 × C=CH_aH$_b$), 5.06 (2 H, s; 2 × C=CH$_a$$H_b$);^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.9 (2 × CH$_3$), 21.7 (2 × CH$_2$), 36.4 (2 × CH$_2$), 111.4 (2 × C=CH$_2$), 147.7 (2 × C=CH$_2$).

[Data consistent with literature]

86a Dimethyl 4,5-dipropylphthalate[287]



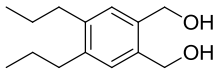
Dipropyl-1,3-butadiene **85** (3.20 g, 23.1 mmol), dimethyl but-2-ynedioate (2.85 mL, 23.1 mmol), and toluene (3 mL) were combined and heated at 110 °C for 16 h in a sealed tube. The mixture was then concentrated *in vacuo* to give crude dimethyl 4,5-dipropylcyclohexa-1,4-diene-1,2-dicarboxylate which was used immediately in the next step without further purification; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.90 (6 H, t, J = 7 Hz; 2 × CH_3), 1.31-1.47 (4 H, m; 2 × CH_2), 2.01-2.06 (4 H, m; 2 × CH_2), 2.96 (4 H, s; 2 × CH_2), 3.78 (6 H, s; 2 × OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (2 × CH$_3$), 21.2 (2 × CH$_2$), 32.1 (2 × CH$_2$), 34.1 (2 × CH$_2$), 52.1 (2 × OCH$_3$), 126.3 (2 × C=C), 132.8 (2 × C=C), 168.5 (2 × C=O).

To the crude dimethyl 4,5-dipropylcyclohexa-1,4-diene-1,2-dicarboxylate was added DDQ (10.5 g, 46. 3 mmol), and chlorobenzene (75 mL). The resulting solution was heated at 130 °C for 46 h. The crude reaction mixture was then concentrated *in vacuo* and purified by flash column chromatography on silica gel eluting with 20% EtOAc in petrol to yield **86a** (3.93 g, 14.1 mmol, 61%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.99 (6 H, t, J = 7.4 Hz; 2 × CH_3), 1.44-1.71 (4 H, m; 2 × CH_2), 2.49-2.73 (4 H, m; 2 × CH_2), 3.90 (6 H, s; 2 × OCH_3), 7.50 (2 H, s; 2 × ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 14.1 (2 × CH$_3$), 23.9 (2 × CH$_2$), 34.5 (2 × CH$_2$), 52.4 (2 × OCH$_3$), 129.3 (2 × ArC), 129.7 (2 × ArCH), 144.1 (2 × ArC),

168.4 (2 × *C*=O); MS (GC/MS-EI+): *m/z* (%) 278 ([M]$^+$, 44), 247 (100); HRMS (EI$^+$): $C_{16}H_{22}O_4$ requires 278.1513, found 278.1517.

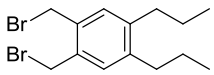
[Data consistent with literature]

86b (4,5-Dipropyl-1,2-phenylene)dimethanol



To a solution of dimethyl 4,5-dipropylphthalate **86a** (3.93 g, 14.1 mmol) in THF (150 mL) was added portionwise $LiAlH_4$ (1.28 g, 33.9 mmol) at 0 °C, the resulting suspension was then stirred for 12 h at rt before carefully quenching with an aqueous solution of NaOH (7.5% w/v). The resulting suspension was then filtered and the precipitate washed with EtOAc (200 mL). The filtrate was then washed with H_2O (100 mL), dried ($MgSO_4$), and concentrated *in vacuo* to yield **86b** (2.36 g, 10.6 mmol, 75%) as a white solid, mp (EtOAc) 58-61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.76-1.14 (6 H, m; 2 × C*H*$_3$), 1.55-1.65 (4 H, m; 2 × CH_2), 2.58 (4 H, t, *J* = 7.8 Hz; 2 × C*H*$_2$), 3.83 (2 H, br. s; 2 × O*H*), 4.59 (4 H, s; 2 × C*H*$_2$OH), 7.11 (2 H, s; 2 × Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 14.2 (2 × *C*H$_3$), 24.3 (2 × *C*H$_2$), 34.4 (2 × *C*H$_2$), 63.8 (2 × *C*H$_2$OH), 130.7 (2 × Ar*C*H), 136.6 (2 × Ar*C*), 140.6 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3395, 3300, 2957, 2928, 2870, 1489; MS (GC/MS-EI$^+$): *m/z* (%) 467 ([2M+Na]$^+$, 100), 245 ([M+Na]$^+$, 40); HRMS (EI$^+$): $C_{14}H_{22}O_2Na$ requires 245.1512, found 245.1514; Elemental analysis (**86b**:EtOAc 1:0.05) Expected, %: C, 75.22; H, 9.96; Found, %: C, 75.18; H, 9.68.

86 1,2-*bis*(Bromomethyl)-4,5-dipropylbenzene[288]

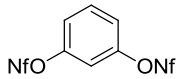


Following general procedure *J*, using (4,5-dipropyl-1,2-phenylene)dimethanol **86b** (0.447 g, 2.01 mmol), and PBr_3 (0.38 mL, 4.0 mmol) in CH_2Cl_2 (10 mL) gave **86** (0.701 g, 2.01 mmol, 100%) as a clear oil which was used immediately with no further purification; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.01 (6 H, t, *J* = 7.3 Hz; 2 × C*H*$_3$), 1.51-1.69 (4 H, m; 2 × C*H*$_2$), 2.46-2.63 (4 H, m; C*H*$_2$), 4.67 (4 H, s; 2 × C*H*$_2$Br), 7.16 (2 H, s; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.2 (2 × *C*H$_3$), 24.0 (2 × *C*H$_2$), 30.5 (2 × *C*H$_2$Br), 34.3 (2 × *C*H$_2$), 131.8 (2 × Ar*C*H), 133.6 (2 × Ar*C*), 142.0 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2956, 2928, 2869, 1455, 1441;

MS (EI^+): *m/z* (%) 267 ($[M\text{-}Br]^+$, 100); HRMS (EI^+): $C_{14}H_{20}Br_1$ requires 267.0743, found 267.0752.

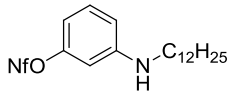
[Data consistent with literature]

72 1,3-Phenylene *bis*(1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate)



Nonafluorobutylsulfonyl fluoride (6.23 mL, 34.7 mmol) and triethylamine (6.91 mL, 49.6 mmol) were added to a stirred suspension of resorcinol **71** (1.82 g, 16.5 mmol) in CH_2Cl_2 (45 mL) at rt under nitrogen. The resulting suspension was stirred at rt for 16 h, then silica was added. The resulting mixture was concentrated *in vacuo* and purified by FSPE, eluting with 60% MeCN in H_2O, followed by THF (product) gave *bis*(sulfonate) **72** (10.8 g, 16.0 mmol, 97%) as a white solid, mp (Et_2O) 36-38 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 (1 H, t, *J* = 2.3 Hz; Ar*H*), 7.39 (2 H, dd, *J* = 8.3, 2.3 Hz; 2 × Ar*H*), 7.60 (1 H, t, *J* = 8.3 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 115.6 (Ar*C*H), 121.6 (2 × Ar*C*H), 131.4 (Ar*C*H), 149.8 (2 × Ar*C*); ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$) δ -[126.4-126.3] (2 F, m; C*F*$_2$), -[121.4-121.3] (2 F, m; C*F*$_2$), -[108.9-108.8] (2 F, m; C*F*$_2$), -[81.2-81.1] (3 F, m; C*F*$_3$); IR (ATR): ν_{max}/cm^{-1} 1481, 1438, 1421, 1352, 1226, 1187, 1140, 1106, 1031, 956, 880, 796, 772, 331, 679 cm^{-1}; MS (EI^+): *m/z* (%) 674 ($[M]^+$, 40), 546 (45), 391 (25), 311 (45), 219 (30), 131 (45), 108 (20), 92 (40), 69 (100); HRMS (ES^+): $C_{14}H_4O_6F_{18}S_2$ requires 673.9156, found 673.9151.

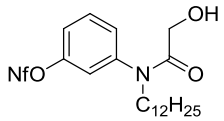
73 3-(Dodecylamino)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



To **72** (3.06 g, 4.54 mmol) in a microwave vial under N_2 was added $Pd(OAc)_2$ (41 mg, 0.18 mmol), xanthphos (0.210 g, 0.363 mmol), K_2PO_4 (1.92 g, 9.05 mmol), 4 Å MS (0.9 g), dodecylamine (0.924 g, 4.99 mmol), and toluene (12 mL, degassed for 1 h with N_2). The vial was then sealed and heated at 110 ˚C for 24 h. After cooling to 20 ˚C, the reaction mixture was filtered through celite and the celite washed with Et_2O before concentrating *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 5% CH_2Cl_2 in hexane yielded **73** (1.23 g, 2.20 mmol, 48%) as a

colourless oil and unconverted starting material **72** (0.440 g, 0.653 mmol, 14%); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.89 (3 H, t, J = 6.9 Hz; CH_3), 1.15-1.49 (18 H, m; 9 × CH_2), 1.62 (2 H, app. quin, J = 7.3 Hz; NCH$_2$CH_2), 2.98-3.18 (2 H, m; NCH_2), 3.87 (1 H, br. s; NH), 6.44 (1 H, t, J = 2.2 Hz; ArH), 6.56 (1 H, dd, J = 8.3, 2.2 Hz; 2 × ArH), 7.18 (1 H, t, J = 8.3 Hz; ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (*C*H$_3$), 22.7 (*C*H$_2$), 27.1 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.56 (*C*H$_2$), 29.58 (*C*H$_2$), 29.62 (*C*H$_2$), 29.64 (*C*H$_2$), 31.9 (*C*H$_2$), 43.7 (N*C*H$_2$), 104.6 (Ar*C*H), 108.7 (Ar*C*H), 112.4 (Ar*C*H), 130.4 (Ar*C*H), 150.0 (Ar*C*), 151.0 (Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2926, 2855, 1619, 1580, 1511; MS (ES$^+$): *m/z* (%) 560 ([M+H]$^+$, 100); HRMS (ES$^+$): $C_{22}H_{31}O_3F_9S_1N_1$ requires 560.1876, found 560.1888.

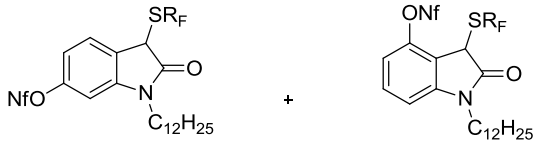
74 3-(*N*-Dodecyl-2-hydroxyacetamido)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Following general procedures *D* and *H,* using **73** (1.16 g, 2.07 mmol) in CH_2Cl_2 (20 mL), NEt_3 (0.35 mL, 2.5 mmol) and acetoxyacetyl chloride (0.27 mL, 2.5 mmol), followed by K_2CO_3 (1.14 g, 8.25 mmol) in MeOH (25 mL) and H_2O (5 mL), [N.B. reaction time of 40 min] gave the crude hydroxyamide. Purification by flash column chromatography on silica gel eluting with 20% EtOAc in hexane yielded **74** (1.06 g, 1.72 mmol, 83%) as a pale brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.87 (3 H, t, J = 6.8 Hz; CH_3), 1.12-1.37 (18 H, m; 9 × CH_2), 1.42-1.61 (2 H, m; CH_2), 3.37 (1 H, br. s; OH), 3.64-3.86 (4 H, m; CH_2OH and NCH_2), 7.13-7.18 (1 H, m; ArH), 7.25 (1 H, d, J = 7.8 Hz; ArH), 7.37 (1 H, d, J = 8.3 Hz; ArH), 7.48-7.63 (1 H, m; ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.0 (*C*H$_3$), 22.6 (*C*H$_2$), 26.6 (*C*H$_2$), 27.5 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (2 × *C*H$_2$), 31.9 (*C*H$_2$), 49.8 (N*C*H$_2$), 60.6 (HO*C*H$_2$), 121.8 (2 × Ar*C*H), 128.3 (Ar*C*H), 131.5 (Ar*C*H), 141.4 (Ar*C*), 150.0 (Ar*C*), 171.3 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 3447 (OH), 2925, 2855, 1665 (C=O), 1605, 1581; MS (APCI$^+$) *m/z* (%) 618 ([M+H]$^+$, 100); HRMS (APCI$^+$): $C_{24}H_{33}F_9NO_5S$ requires 618.1930, found 618.1923.

75 1-Dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate;

75a 1-Dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-4-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate

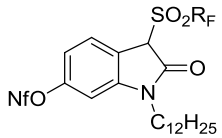


major minor

Following general procedure *E*, using **74** (1.53 g, 2.48 mmol), oxalyl chloride (0.24 mL, 2.8 mmol), DMSO (0.35 mL, 4.9 mmol) and NEt_3 (1.72 mL, 12.3 mmol) in CH_2Cl_2 (27 mL) gave the crude glyoxamide which was used immediately in the next step along with R_FSH (0.64 mL, 2.2 mmol), TFAA (3.1 mL, 22 mmol) and $BF_3{\cdot}OEt_2$ (1.6 mL, 13 mmol) in CH_2Cl_2 (100 mL) to give, after purification by FSPE eluting with 80% MeCN in H_2O, MeCN, and THF (product), the desired product as a mixture 4:1 mixture of regioisomers (by ^{1}H NMR) which were separated by flash column chromatography on silica gel eluting with 40% CH_2Cl_2 in hexane to give **75** (1.74 g, 1.62 mmol, 72%) and **75a** (0.46 g, 0.43 mmol, 19%) as white solids, mp **75** (CH_2Cl_2/hexane) 39-41 °C, **75a** (CH_2Cl_2/hexane) 45-48 °C; **75** : ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.88 (3 H, t, *J* = 6.9 Hz; C*H*$_3$), 1.14-1.47 (18 H, m; 9 × C*H*$_2$), 1.59-1.77 (2 H, m; C*H*$_2$), 2.27-2.53 (2 H, m, CF_2CH_2), 2.76-2.93 (1 H, m; SC*H*$_A$H$_B$), 2.93-3.09 (1 H, m; SCH$_A$*H*$_B$), 3.58-3.71 (1 H, m; NC*H*$_A$H$_B$), 3.71-3.84 (1 H, m; NCH$_A$*H*$_B$), 4.33 (1 H, s; SC*H*), 6.76 (1 H, d, *J* = 2.0 Hz; Ar*H*), 7.01 (1 H, dd, *J* = 8.1, 2.0 Hz; Ar*H*), 7.44 (1 H, d, *J* = 8.1 Hz; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (*C*H$_3$), 21.2 (t, J = 4 Hz; *C*H$_2$S), 22.7 (*C*H$_2$), 26.9 (*C*H$_2$), 27.2 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (2 × *C*H$_2$), 31.88 (*C*H$_2$), 31.92 (t, *J* = 22 Hz; CF_2CH_2), 40.7 (N*C*H$_2$), 44.2 (*C*H), 102.7 (Ar*C*H), 115.2 (Ar*C*H), 125.4 (Ar*C*), 126.5 (Ar*C*H), 145.2 (Ar*C*), 150.4 (Ar*C*), 174.6 (*C*=O); ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm –[126.3-126.1] (2 F, m; C*F*$_2$), -[126.0-125.8] (2 F, m; C*F*$_2$), -[124.0-124.3] (2 F, m; C*F*$_2$), -[123.3-123.1] (2 F, m; C*F*$_2$), -[122.7-122.1] (6 F, m; 3 × C*F*$_2$), -[121.6-121.2] (2 F, m; C*F*$_2$), -[115.3-114.8] (2 F, t, *J* = 12.8 Hz; C*F*$_2$), -[109.4-108.9] (2 F, m; C*F*$_2$), -81.3 (3 F, t, *J* = 10 Hz; C*F*$_3$), -[81.2-81.1] (3 F, m; C*F*$_3$); IR (ATR): ν_{max}/cm^{-1} 2959, 2923, 2857, 1719 (C=O), 1616.; MS (APCI+) *m/z* (%): 1078 ([M+H]$^+$, 15), 794 ([M-$SO_2(CF_2)_3CF_3$]$^+$, 100), 589 ([M-$SCH_2CH_2(CF_2)_7CF_3$]$^+$, 100); HRMS (APCI$^+$): $C_{34}H_{34}NO_4F_{26}S_2$ requires 1078.1509, found

1078.1509; **75a:** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.88 (3 H, t, J = 6.9 Hz; CH_3), 1.18-1.47 (18 H, m; 9 × CH_2), 1.67 (2 H, quin, J = 7.3 Hz; NCH$_2$CH_2), 2.32-2.63 (2 H, m; CF$_2$CH_2), 2.84 (1 H, ddd, J = 13.5, 10.9, 5.5 Hz; SCH_AH$_B$), 3.13 (1 H, ddd, J = 13.5, 10.7, 5.5 Hz; SCH$_A$$H_B$), 3.61-3.72 (1 H, m; NC$H_AH_B$), 3.72-3.82 (1 H, m; NCH$_A$$H_B$), 4.50 (1 H, s; C$H$), 6.88 (1 H, d, J = 8.2 Hz; ArH), 6.97 (1 H, d, J = 8.2 Hz; ArH), 7.42 (1 H, t, J = 8.2 Hz; ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.0 (CH$_3$), 21.4 (t, J = 4 Hz, SCH_2), 22.7 (CH$_2$), 26.9 (CH$_2$), 27.3 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.46 (CH$_2$), 29.54 (CH$_2$), 29.6 (2 × CH$_2$), 31.8 (t, J = 29 Hz, CF$_2$$CH_2$), 31.9 ($CH_2$), 40.9 (N$CH_2$), 43.2 ($C$H), 108.6 (Ar$C$H), 115.5 (Ar$C$H), 117.7 (Ar$C$), 131.5 (Ar$C$H), 145.9 (Ar$C$), 146.1 (Ar$C$), 174.0 ($C$=O); ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm –[126.2-126.0] (2 F, m; CF_2), -[125.9-125.7] (2 F, m; CF_2), -[123.6-123.5] (2 F, m; CF_2), -[122.9-122.6] (2 F; m; CF_2) (br. s), -[122.1-121.5] (6 F, m; 3 × CF_2), -[120.9-120.6] (2 F, m; CF_2), -[114.6-114.3] (2 F, m; CF_2), -109.0 (2 F, t, J = 14 Hz; CF_2), -80.7 (3 F, t, J = 10 Hz; CF_3), -80.6 (3 F, t, J = 10 Hz; CF_3); IR (ATR): ν_{max}/cm^{-1} 2928, 2856, 1724 (C=O), 1625.

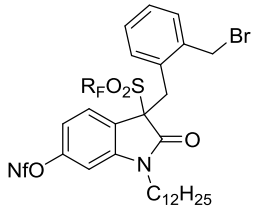
76 1-Dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Following general procedure *F* using **75** (5.22 g, 4.85 mmol) in CH_2Cl_2 (194 mL), and *m*CPBA (2.39 g, 10.7 mmol, 77% w/w) gave, after purification by FSPE, **76** (5.03 g, 4.53 mmol, 93%) as a white solid, mp (THF) 91–94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.88 (3 H, t, J = 6.9 Hz; CH_3), 1.20-1.39 (18 H, m; 9 × CH_2), 1.64-1.73 (2 H, m; CH_2), 2.69-2.88 (2 H, m; CF$_2$CH_2), 3.65-3.84 (3 H, m; NCH_2 and SO$_2$CH_AH$_B$), 3.87-3.96 (1 H, m; SO$_2$CH$_A$$H_B$), 4.86 (1 H, s; C$H$), 6.85 (1 H, s; Ar$H$), 7.08 (1 H, d, J = 8.2 Hz; ArH), 7.72 (1 H, d, J = 8.2 Hz; ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.0 (CH$_3$), 22.6 (CH$_2$), 24.2 (t, J = 23 Hz; CF$_2$$CH_2$), 26.7 ($CH_2$), 27.0 ($CH_2$), 29.1 ($CH_2$), 29.3 ($CH_2$), 29.4 ($CH_2$), 29.5 ($CH_2$), 29.6 (2 × CH$_2$), 31.9 (CH$_2$), 41.1 (NCH$_2$), 44.1 (SCH$_2$), 65.0 (CH), 103.6 (ArCH), 115.8 (ArCH), 116.4 (ArC), 128.7 (ArCH), 146.6 (ArC), 151.6 (ArC), 167.0 (C=O); IR (ATR): ν_{max}/cm^{-1}: 2934, 2863, 1723 (C=O), 1613, 1601; MS (APCI$^+$): *m/z* (%) 1132 ([M+Na]$^+$, 15) 849 (20), 826 ([M-SO$_2$(CF$_2$)$_3$CF$_3$]$^+$, 30) 598 ([M-SCH$_2$CH$_2$(CF$_2$)$_7$CF$_3$]$^+$, 70) 346 (70) 316 (100); HRMS (APCI$^+$): $C_{34}H_{34}F_{26}N_1O_6S_2$ requires

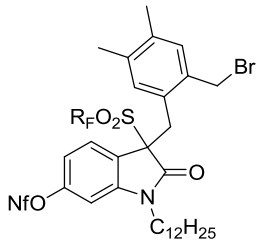
1110.1407, found 1110.1413; Elemental analysis: Expected, %: C, 36.80; H, 3.00; N, 1.26; Found, %: C, 36.87; H, 3.08; N, 1.30.

77 3-(2-(Bromomethyl)benzyl)-1-dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



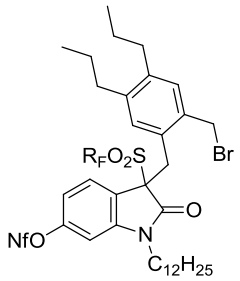
Using general procedure *G*, 1,2-*bis*(bromomethyl)benzene (0.398 g, 1.34 mmol), K_2CO_3 (0.185 g, 1.34 mmol) and sulfone **76** (0.298 g, 0.269 mmol) in DMF (8 mL) gave the crude product. Purification by FSPE gave alkylated oxindole **77** (0.276 g, 0.213 mmol, 80%) as a pale brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.89 (3 H, t, *J* = 6.8 Hz; CH_3), 0.94-1.05 (2 H, m; CH_2), 1.10-1.37 (18 H, m; 9 × CH_2), 2.51-2.89 (2 H, m; CF_2CH_2), 3.35-3.45 (1 H, m; NCH_AH_B), 3.57-3.69 (2 H, m; $SO_2CH_AH_B$ and NCH_AH_B), 3.74 (1 H, d, *J* = 14.0 Hz; ArCH_AH_B), 3.84-3.97 (1 H, m; $SO_2CH_AH_B$), 4.08 (1 H, d, *J* = 14.0 Hz; $ArCH_AH_B$), 4.40 (1 H, d, *J* = 10.7 Hz; ArCH_AH_B), 4.85 (1 H, d, *J* = 10.7 Hz; $ArCH_AH_B$), 6.55 (1 H, d, *J* = 7.4 Hz; Ar*H*), 6.67 (1 H, d, *J* = 2.3 Hz; Ar*H*), 6.94 (1 H, ddd, *J* = 7.4, 7.4, 1.2 Hz; Ar*H*), 7.07-7.18 (2 H, m; 2 × Ar*H*), 7.25 (1 H, dd, J = 8.0, 1.2 Hz; Ar*H*), 7.85 (1 H, d, *J* = 8.0 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (*C*H_3), 22.7 (*C*H_2), 24.1 (t, *J* = 22 Hz; CF_2CH_2), 26.4 (*C*H_2), 26.7 (*C*H_2), 29.0 (*C*H_2), 29.27 (*C*H_2), 29.31 (*C*H_2), 29.5 (*C*H_2), 29.6 (2 × *C*H_2), 31.6 (ArC*C*H_2), 31.9 (*C*H_2), 32.8 (ArC*C*H_2), 40.8 (SO_2CH_2), 40.9 (N*C*H_2), 74.4 (C_{quat}), 103.3 (Ar*C*H), 115.8 (Ar*C*H), 120.9 (Ar*C*), 128.3 (Ar*C*H), 128.6 (2 × Ar*C*H), 130.5 (Ar*C*H), 130.8 (Ar*C*), 131.1 (Ar*C*H), 137.0 (Ar*C*), 146.1 (Ar*C*), 151.6 (Ar*C*), 170.0 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2932, 2860, 1713 (C=O), 1612, 1494, 1198, 1143; MS (APCI$^-$): *m/z* (%) 1326 ([M+Cl]$^-$, 15), 849 (100), 511 (50); HRMS (APCI$^+$): $C_{42}H_{41}Br_1F_{26}N_1O_6S_2$ requires 1292.1138, found 1292.1139.

96 3-(2-(Bromomethyl)-4,5-dimethylbenzyl)-1-dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



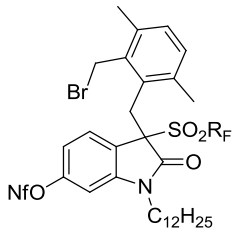
Using general procedure *G*, **80** (1.09 g, 3.73 mmol), K_2CO_3 (0.51 g, 3.7 mmol) and sulfone **76** (0.825 g, 0.744 mmol) in DMF (22 mL) gave the crude product. Purification by FSPE, followed by flash column chromatography on silica gel eluting with a gradient of 20-40% CH_2Cl_2 in hexane gave alkylated oxindole **96** (0.725 g, 0.549 mmol, 74%) as a pale brown amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.89 (3 H, t, *J* = 6.8 Hz; CH_2CH_3), 0.97-1.00 (2 H, m; CH_2), 1.06-1.45 (18 H, m, 9 × CH_2), 1.91 (3 H, s; CH_3), 2.10 (3 H, s; CH_3), 2.61-2.87 (2 H, m; CF_2CH_2), 3.30-3.41 (1 H, m; NCH_AH_B), 3.57-3.72 (3 H, m; NCH_AH_B and $ArCH_AH_B$ and $SO_2CH_AH_B$), 3.86-3.97 (1 H, m; $SO_2CH_AH_B$), 4.01 (1 H, d, *J* = 13.9 Hz; $ArCH_AH_B$), 4.35 (1 H, d, *J* = 10.6 Hz; $ArCH_AH_B$), 4.82 (1 H, d, *J* = 10.6 Hz; $ArCH_AH_B$), 6.25 (1 H, s; Ar*H*), 6.67 (1 H, s; Ar*H*), 7.00 (1 H, s; Ar*H*), 7.14 (1 H, d, *J* = 8.2 Hz; Ar*H*), 7.87 (1 H, d, *J* = 8.2 Hz; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.0 (CH_2CH_3), 18.9 (CH_3), 19.1 (CH_3), 22.7 (CH_2), 23.9 (CH_2), 24.1 (t, *J* = 23 Hz, CF_2CH_2), 26.4 (CH_2), 26.7 (CH_2), 29.2 (CH_2), 29.3 (2 × CH_2), 29.58 (CH_2), 29.60 (CH_2), 31.9 ($ArCCH_2$), 32.0 (CH_2), 32.7 ($ArCCH_2$), 40.9 (NCH_2 and SO_2CH_2), 74.4 (C_{quat}), 103.3 (Ar*C*H), 115.7 (Ar*C*H), 121.3 (Ar*C*), 127.9 (Ar*C*), 128.3 (Ar*C*H), 131.8 (Ar*C*H), 132.1 (Ar*C*H), 134.1 (Ar*C*), 137.0 (Ar*C*), 137.4 (Ar*C*), 146.1 (Ar*C*), 151.5 (Ar*C*), 170.1 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2930, 2860, 1714, 1609, 1199, 1142; MS (APCI$^-$): *m/z* (%) 1356 ([M+Cl]$^-$, 60), 511 (100), 444 (60); HRMS (APCI$^+$): $C_{44}H_{45}Br_1F_{26}N_1O_6S_2$ requires 1320.1451, found 1320.1449.

100 3-(2-(Bromomethyl)-4,5-dipropylbenzyl)-1-dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



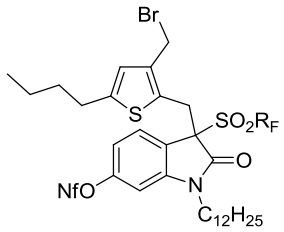
Using general procedure *G*, **86** (0.596 g, 1.71 mmol), K_2CO_3 (0.237 g, 1.71 mmol) and sulfone **76** (0.380 g, 0.342 mmol) in DMF (20 mL) gave the crude product. Purification by FSPE followed by flash column chromatography on silica gel eluting with a gradient of 20-40 % CH_2Cl_2 in hexane gave alkylated oxindole **100** (0.347 mg, 0.252 mmol, 74%) as a pale brown amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.78 (3 H, t, *J* = 7 Hz; CH_3), 0.85-0.95 (6 H, m; 2 × CH_3), 0.95-1.06 (2 H, m; CH_2), 1.12 -1.32 (20 H, m; 10 × CH_2), 1.41-1.54 (2 H, m; CH_2), 2.24 (2 H, t, *J* = 8 Hz; CH_2), 2.33-2.48 (2 H, m; CH_2), 2.64-2.85 (2 H, m; CF_2CH_2), 3.34-3.44 (1 H, m; NCH_AH$_B$), 3.55-3.70 (3 H, m; SO_2CH_AH$_B$, ArCH_AH$_B$ and NCH$_A$$H_B$), 3.86-3.97 (1 H, m; SO_2CH$_A$$H_B$), 4.04 (1 H, d, *J* = 14.2 Hz; ArCH$_A$$H_B$), 4.37 (1 H, d, *J* = 10.7 Hz; ArCH_AH$_B$), 4.89 (1 H, d, *J* = 10.7 Hz; ArCH$_A$$H_B$), 6.28 (1 H, s; Ar*H*), 6.66 (1 H, d, *J* = 1.9 Hz; Ar*H*), 7.00 (1 H, s; Ar*H*), 7.14 (1 H, dd, *J* = 8.2, 1.9 Hz; Ar*H*), 7.86 (1 H, d, *J* = 8.2 Hz; Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.8 (*C*H$_3$), 14.0 (*C*H$_3$), 14.0 (*C*H$_3$), 22.7 (*C*H$_2$), 23.8 (*C*H$_2$), 23.9 (*C*H$_2$), 24.1 (t, *J* = 22 Hz; CF_2CH_2), 26.3 (*C*H$_2$), 26.6 (*C*H$_2$), 29.0 (*C*H$_2$), 29.3 (2 × *C*H$_2$), 29.6 (2 × *C*H$_2$), 29.6 (*C*H$_2$), 31.9 (*C*H$_2$), 32.3 (ArC*C*H$_2$), 32.5 (ArC*C*H$_2$), 34.0 (ArC*C*H$_2$), 34.1 (ArC*C*H$_2$), 40.8 (N*C*H$_2$ and SO_2*C*H$_2$), 74.6 (*C*$_{quat}$), 103.3 (Ar*C*H), 115.7 (Ar*C*H), 121.2 (Ar*C*), 127.9 (Ar*C*), 128.4 (Ar*C*H), 131.3 (Ar*C*H), 131.7 (Ar*C*H), 133.9 (Ar*C*), 140.9 (Ar*C*), 141.3 (Ar*C*), 146.1 (Ar*C*), 151.5 (Ar*C*), 170.1 (*C*=O); IR (ATR): υ_{max}/cm^{-1} 2929, 2857, 1715 (C=O), 1608; MS (APCI$^-$): *m/z* (%) 1410 ([M+Cl]$^-$, 100); HRMS (APCI$^+$): $C_{48}H_{53}Br_1F_{26}N_1O_6S_2$ requires 1376.2077, found 1376.2085.

95 3-(2-(Bromomethyl)-3,6-dimethylbenzyl)-1-dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



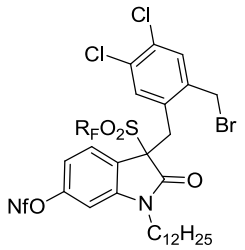
Using general procedure *G*, **83** (1.49 g, 5.10 mmol), K_2CO_3 (0.707 g, 5.12 mmol) and sulfone **76** (1.14 g, 1.03 mmol) in DMF (30 mL) gave the crude product. Purification by FSPE followed by flash column chromatography on silica gel eluting with 40% CH_2Cl_2 in hexane gave alkylated oxindole **95** (1.00 g, 0.757 mmol, 73%) as a pale yellow oil; ^{1}H NMR (400 MHz, 323 K, $CDCl_3$) δ ppm 0.90 (3 H, t, *J* = 6.8 Hz; CH_2CH_3), 1.29-1.37 (18 H, m; 9 × CH_2), 1.40-1.60 (2 H, m; CH_2), 1.87 (3 H, s; CH_3), 2.35 (3 H, s; CH_3), 2.56-2.88 (2 H, m; CF_2CH_2), 3.47-3.81 (4 H, m; SO_2CH_2 and NCH_2), 3.98 (1 H, d, *J* = 15.3 Hz; $ArCH_AH_B$), 4.03 (1 H, d, *J* = 15.3 Hz; $ArCH_AH_B$), 4.70 (1 H, d, *J* = 10.9 Hz; $ArCH_AH_B$), 4.77 (1 H, d, *J* = 10.9 Hz; $ArCH_AH_B$), 6.74 (1 H, d, *J* = 2.0 Hz; Ar*H*), 6.81-6.99 (3 H, m; 3 × Ar*H*), 7.31 (1 H, d, *J* = 8.0 Hz; Ar*H*); ^{13}C NMR (101 MHz, 323 K, $CDCl_3$) δ ppm 13.9 (CH_2CH_3), 19.5 (CH_3), 20.3 (CH_3), 22.6 (CH_2), 24.6 (t, *J* = 22 Hz, CF_2CH_2), 26.7 (CH_2), 26.9 (CH_2), 29.1, 29.3, 29.4, 29.5, 29.55, 29.60 (6 × CH_2 and $ArCCH_2$), 30.7 ($ArCCH_2$), 31.9 (CH_2), 40.9, 41.3 (SO_2CH_2 and NCH_2), 74.0 (C_{quat}), 102.9 (Ar*C*H), 115.3 (Ar*C*H), 121.1 (Ar*C*), 129.2 (Ar*C*H), 130.5 (Ar*C*H), 131.2 (Ar*C*H), 131.2 (Ar*C*), 136.0 (Ar*C*), 136.1 (Ar*C*), 136.2 (Ar*C*), 146.2 (Ar*C*), 151.5 (Ar*C*), 170.8 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2927, 2856, 1721 (C=O), 1610, 1492, 1429, 1352, 1330, 1303; MS ($APCI^-$): *m/z* (%) 1400 ($[M+Br]^-$, 90), 511 (100); HRMS ($APCI^+$): $C_{44}H_{45}Br_1F_{26}N_1O_6S_2$ requires 1320.1451, found 1320.1452.

98 3-((3-(Bromomethyl)-5-butylthiophen-2-yl)methyl)-1-dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



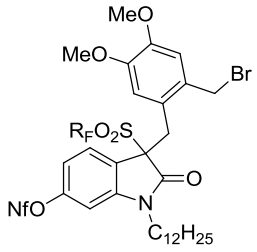
Using general procedure *G*, using **94** (1.84 g, 5.6 mmol), K_2CO_3 (0.78 g, 5.6 mmol) and sulfone **76** (1.25 g, 1.13 mmol) in DMF (40 mL) gave the crude product. Purification by FSPE followed by flash column chromatography on silica gel eluting with a gradient of 3-5% EtOAc in hexane gave alkylated oxindole **98** (0.235 g, 0.173 mmol, 15%) as a pale yellow waxy solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.85 (3 H, t, *J* = 7.3 Hz; CH_3), 0.89 (3 H, t, *J* = 6.9 Hz; CH_3), 1.05-1.16 (2 H, m; CH_2), 1.17-1.37 (18 H, m; 9 × CH_2), 1.38-1.48 (4 H, m; 2 × CH_2), 2.52 (2 H, t, *J* = 7.6 Hz; ArCH_2CH$_2$), 2.58-2.84 (2 H, m; CF_2CH_2), 3.43-3.59 (2 H, m; NCH_AH$_B$ and SO_2CH_AH$_B$), 3.68 (1 H, ddd, *J* = 14.4, 7.1, 7.1 Hz; NCH$_A$$H_B$), 3.76 (1 H, d, *J* = 14.5 Hz; ArCH_AH$_B$), 3.84 (1 H, ddd, *J* = 12.6, 12.3, 5.7 Hz; SO_2CH$_A$$H_B$), 4.04 (1 H, d, *J* = 14.5 Hz; ArCH$_A$$H_B$), 4.29 (1 H, d, *J* = 10.9 Hz; ArCH_AH$_B$), 4.49 (1 H, d, *J* = 10.9 Hz; ArCH$_A$$H_B$), 6.54 (1 H, s; Ar*H*), 6.73 (1 H, d, *J* = 2.1 Hz; Ar*H*), 7.14 (1 H, dd, *J* = 8.3, 2.1 Hz; Ar*H*), 7.78 (1 H, d, *J* = 8.3 Hz; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.5 (*C*H$_3$), 14.1 (*C*H$_3$), 22.0 (*C*H$_2$), 22.7 (*C*H$_2$), 24.0 (t, *J* = 21.8 Hz; CF_2*C*H$_2$), 25.2 (ArC*C*H$_2$), 26.5 (*C*H$_2$), 26.7 (*C*H$_2$), 29.1 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (2 × *C*H$_2$), 29.58 (*C*H$_2$), 29.61 (2 × *C*H$_2$), 29.9 (ArC*C*H$_2$), 31.9 (*C*H$_2$), 33.1 (*C*H$_2$), 41.0 (t, *J* = 3.6 Hz; SO_2*C*H$_2$), 41.1 (N*C*H$_2$), 73.7 (C_{quat}), 103.4 (Ar*C*H), 116.0 (Ar*C*H), 120.6 (Ar*C*), 125.5 (Ar*C*H), 127.7 (Ar*C*), 128.4 (Ar*C*H), 136.6 (Ar*C*), 146.0 (Ar*C*), 146.5 (Ar*C*), 151.9 (Ar*C*), 169.8 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2930, 2859, 1742 (C=O), 1613, 1494, 1442, 1426, 1368, 1351, 1332, 1368, 1310, 1235, 1200, 1143, 1096, 1031, 1007; MS (APCI$^-$): *m/z* (%) 1390 ([M+Cl]$^-$, 60), 511 ([$SO_2CH_2CH_2(CF_2)_7CF_3$]$^-$, 100); HRMS (ASAP): $C_{44}H_{47}Br_1F_{26}N_1O_6S_3$ requires 1354.1328, found 1354.1319.

97 3-(2-(Bromomethyl)-4,5-dichlorobenzyl)-1-dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Using general procedure *G*, using **88** (1.20 g, 3.61 mmol), K_2CO_3 (0.50 g, 3.6 mmol) and sulfone **76** (0.803 g, 0.723 mmol) in DMF (40 mL) gave the crude product. Purification by FSPE eluting with 80% MeCN in H_2O, MeCN, and THF (product) gave the product **97** (0.829 g, 0.609 mmol, 84%) as a waxy white solid. A small sample for full characterisation was purified by flash column chromatography on silica gel eluting with a gradient of 3-5% EtOAc in hexane for full characterisation; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.89 (3 H, t, *J* = 7.9 Hz; CH_3), 1.00-1.10 (2 H, m; CH_2), 1.13-1.42 (18 H, m; 9 × CH_2), 2.60-2.85 (2 H, m; CF_2CH_2), 3.43 (1 H, dt, *J* = 14.4, 7.1 Hz; NCH_AH_B), 3.49-3.61 (1 H, m; $SO_2CH_AH_B$), 3.63-3.74 (1 H, m; NCH_AH_B) 3.67 (1 H, d, *J* = 14.2 Hz; ArCH_AH_B), 3.78-3.90 (1 H, m; $SO_2CH_AH_B$), 3.99 (1 H, d, *J* = 14.2 Hz; $ArCH_AH_B$), 4.31 (1 H, d, *J* = 11.0 Hz; ArCH_AH_B), 4.73 (1 H, d, *J* = 11.0 Hz; $ArCH_AH_B$), 6.65 (1 H, s; Ar*H*), 6.76 (1 H, d, *J* = 2.1 Hz; Ar*H*), 7.18 (1 H, dd, *J* = 8.3, 2.1 Hz; Ar*H*), 7.35 (1 H, s; Ar*H*), 7.84 (1 H, d, *J* = 8.3 Hz; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (*C*H_3), 22.7 (*C*H_2), 24.1 (t, *J* = 23 Hz; CF_2CH_2) 26.5 (*C*H_2), 26.8 (*C*H_2), 29.1 (*C*H_2), 29.3 (*C*H_2 and ArC*C*H_2), 29.5 (*C*H_2), 29.55 (*C*H_2), 29.57 (*C*H_2), 29.60 (*C*H_2), 31.9 (*C*H_2), 32.0 (ArC*C*H_2), 40.9 (SO_2CH_2), 41.1 (NCH_2), 73.9 (C_{quat}), 103.7 (Ar*C*H), 116.2 (Ar*C*H), 120.3 (Ar*C*), 128.1 (Ar*C*H), 130.9 (Ar*C*), 132.1 (Ar*C*H), 132.5 (Ar*C*H), 132.6 (Ar*C*), 132.7 (Ar*C*), 137.1 (Ar*C*), 146.0 (Ar*C*), 151.9 (Ar*C*), 169.7 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2931, 2860, 1711 (C=O), 1611, 1479, 1457, 1428, 1415, 1352, 1331, 1300, 1236, 1200. 1142, 1094, 1033; MS (APCI$^-$): *m/z* (%) 1396 ([M+Cl]$^-$, 100).

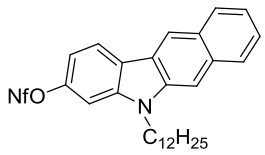
99 3-(2-(Bromomethyl)-4,5-dimethoxybenzyl)-1-dodecyl-3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Using general procedure *G*, using **90** (0.58 g, 1.8 mmol), K_2CO_3 (0.25 g, 1.8 mmol) and sulfone **76** (0.399 g, 0.360 g) in DMF (11 mL) gave the crude product. Purification by FSPE eluting with 80% MeCN in H_2O, MeCN, and THF gave the product **99** (0.427 g, 0.316 mmol, 88%) as a impure unstable yellow oil; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.86-0.98 (3 H, m; CH_3), 1.10-1.42 (20 H, m; 10 × CH_2), 2.62-2.79 (2 H, m; CF_2CH_2), 2.91 (1 H, dt, *J* = 14.2, 7.0 Hz; $SO_2CH_AH_B$), 3.04-3.17 (1 H, m; $SO_2CH_AH_B$), 3.21 (1 H, s; OCH_3), 3.21 (1 H, s; OCH_3), 3.55 (1 H, d, *J* = 14.1 Hz; ArCH_AHB), 3.63-3.78 (1 H, m; NCH_AH_B), 4.06-4.13 (1 H, m; NCH_AH_B), 4.17 (1 H, d, *J* = 14.1 Hz; $ArCH_AH_B$), 4.21 (1 H, d, *J* = 10.7 Hz; ArCH_AH_B), 5.07 (1 H, d, *J* = 10.7 Hz; $ArCH_AH_B$), 5.86 (1 H, s; Ar*H*), 6.34 (1 H, d, *J* = 2.2 Hz; Ar*H*), 6.39 (1 H, s; Ar*H*), 6.62 (1 H, dd, *J* = 8.3, 2.2 Hz; Ar*H*), 7.55 (1 H, d, *J* = 8.3 Hz; Ar*H*); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 14.6 (*C*H_3), 23.4, 25.0, 25.3, 26.9, 27.4, 29.8, 30.0, 30.2, 30.4, 30.4 (CF_2CH_2 and 10 × *C*H_2), 32.7 (2 × ArC*C*H_2), 41.0 (SO_2CH_2), 41.5 (N*C*H_2), 55.6 (O*C*H_3), 55.6 (O*C*H_3), 75.3 (C_{quat}), 104.0 (Ar*C*H), 114.4 (Ar*C*H), 114.4 (Ar*C*H), 116.1 (Ar*C*H), 122.4 (Ar*C*), 124.0 (Ar*C*), 128.9 (Ar*C*H), 129.8 (Ar*C*), 147.2 (Ar*C*), 149.8 (Ar*C*), 150.2 (Ar*C*), 151.9 (Ar*C*), 171.1 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2929, 2856, 1717 (C=O), 1608, 1520, 1492, 1429, 1352, 1238, 1200, 1143, 1033, 1009; MS (APCI$^+$): *m/z* (%) 1272 ([M-Br]$^+$, 40), 937 (40), 793 (80), 761 (80), 373 (100).

General procedure K: Preparation of nonaflyloxy benzo[b]carbazoles

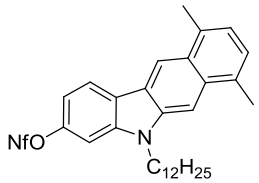
78 5-Dodecyl-5H-benzo[b]carbazol-3-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



To a stirred solution of **77** (89 mg, 0.069 mmol) and CF_3CH_2OH (0.36 mL of a 0.0192 g/ mL solution in degassed THF, 0.069 mmol) in THF (0.55 mL) at rt under nitrogen was added SmI_2 (2.88 mL of a 0.1 M solution in THF, 0.288 mmol) dropwise. The resulting dark blue/green suspension was stirred for 10 min at rt, then the flask was opened to the air. The resulting bright yellow suspension was concentrated *in vacuo* and the residue was partitioned between a saturated aqueous solution of $NaHCO_3$ (25 mL) and CH_2Cl_2 (15 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure to give the crude cyclohexadiene intermediate, which was then dissolved in CH_2Cl_2 (0.6 mL). *p*-Benzoquinone (30 mg, 0.28 mmol) was added, and the resulting mixture was stirred for 48 h at rt before CH_2Cl_2 (20 mL) and a 5% w/v aqueous solution of NaOH (10 mL) were added and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product. Purification by flash column chromatography on silica gel eluting with 5% toluene in hexane gave **78** (34 mg, 0.050 mmol, 72%) as a white solid, mp (toluene) 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (3 H, t, *J* = 6.8 Hz; C*H*$_3$), 1.10-1.50 (18 H, m; 9 × C*H*$_2$), 1.93 (2 H, quin, *J* = 7.3 Hz; C*H*$_2$), 4.33 (2 H, t, *J* = 7.3 Hz; NC*H*$_2$), 7.15 (1 H, dd, *J* = 8.5, 2.1 Hz; Ar*H*), 7.26 (2 H, d, *J* = 2.1 Hz; Ar*H*), 7.44 (1 H, ddd, *J* = 8.1, 6.9, 1.2 Hz; Ar*H*), 7.53 (1 H, ddd, *J* = 8.1, 6.9, 1.2 Hz; Ar*H*), 7.72 (1 H, s; Ar*H*), 8.00 (1 H, d, *J* = 8.1 Hz; Ar*H*), 8.06 (1 H, d, *J* = 8.1 Hz; Ar*H*), 8.21 (1 H, d, *J* = 8.5 Hz; Ar*H*), 8.57 (1 H, s; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (*C*H$_3$), 22.7 (*C*H$_2$), 27.3 (*C*H$_2$), 28.3 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.6 (3 × *C*H$_2$), 31.9 (*C*H$_2$), 43.5 (N*C*H$_2$), 101.6 (Ar*C*H), 103.9 (Ar*C*H), 111.5 (Ar*C*H), 119.3 (Ar*C*H), 121.8 (Ar*C*H), 122.6 (Ar*C*), 123.1 (Ar*C*H), 123.8 (Ar*C*H), 125.7 (Ar*C*H), 127.2 (Ar*C*), 128.3 (Ar*C*H), 128.5 (Ar*C*), 132.7 (Ar*C*), 140.9 (Ar*C*), 143.3 (Ar*C*), 149.0 (Ar*C*); ^{19}F NMR (471 MHz, $CDCl_3$/$CFCl_3$) δ ppm –[127.2-124.8] (2 F, m; C*F*$_2$), -[122.0-120.0] (2 F,

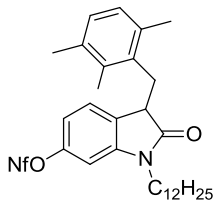
m; C*F*$_2$), -[110.3-107.6] (2 F, m; C*F*$_2$), -[84.2-78.0] (3 F, m; C*F*$_3$); IR (ATR): ν_{max}/cm^{-1} 2924, 2854, 1606; MS (APCI$^+$): *m/z* (%) 684 ([M+H]$^+$, 100), 391 (20); HRMS (APCI$^+$): $C_{32}H_{35}F_9NO_3S$ requires 684.2188, found 684.2177; Elemental analysis: Expected, %: C, 56.22; H, 5.01; N, 2.05; Found, %: C, 55.97; H, 4.86; N, 2.02.

101 5-Dodecyl-7,10-dimethyl-5H-benzo[b]carbazol-3-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



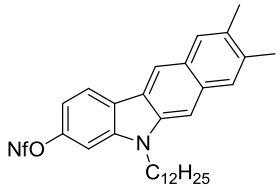
Using a slight modification of general procedure *K* (the SmI_2 addition step was carried out at 50 °C over 1 min), SmI_2 (14.7 mL of a 0.1 M solution in THF, 1.47 mmol), alkylated oxindole **95** (0.463 g, 0.351 mmol), and CF_3CH_2OH (0.32 mL of a 0.11 g/mL solution in THF, 0.35 mmol) in THF (3 mL), followed by *p*-benzoquinone (152 mg, 1.41 mmol) in CH_2Cl_2 (5 mL) gave **101** (0.124 g, 0.174 mmol, 50%) as a pale yellow solid, mp (toluene/hexane) 75-76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.92 (3 H, t, *J* = 6.9 Hz; CH_2CH_3), 1.19-1.49 (18 H, m; 9 × C*H*$_2$), 1.87-1.99 (2 H, m; C*H*$_2$), 2.80 (3 H, s; C*H*$_3$), 2.85 (3 H, s; C*H*$_3$), 4.29 (2 H, t, *J* = 6.9 Hz; NC*H*$_2$), 7.18 (1 H, d, *J* = 8.4 Hz; Ar*H*), 7.21 (1 H, d, *J* = 6.6 Hz; Ar*H*), 7. 27 (1 H, s; Ar*H*), 7.30 (1 H, d, *J* = 6.6 Hz; Ar*H*), 7.76 (1 H, s; Ar*H*), 8.22 (1 H, d, *J* = 8.4 Hz; Ar*H*), 8.68 (1 H, s; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (CH_2CH_3), 20.00 (*C*H$_3$), 20.04 (*C*H$_3$) 22.7 (*C*H$_2$), 27.3 (*C*H$_2$), 28.3 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 (*C*H$_2$), 29.55 (*C*H$_2$), 29.59 (2 × *C*H$_2$), 31.9 (*C*H$_2$), 43.2 (N*C*H$_2$), 101.0 (Ar*C*H), 101.6 (Ar*C*H), 111.4 (Ar*C*H), 116.1 (Ar*C*H), 121.7 (Ar*C*H), 122.8 (Ar*C*), 122.8 (Ar*C*H), 123.5 (Ar*C*H), 126.1 (Ar*C*), 127.6 (Ar*C*), 131.1 (Ar*C*), 132.2 (Ar*C*), 132.8 (Ar*C*), 140.4 (Ar*C*), 143.1 (Ar*C*), 148.8 (Ar*C*); ^{19}F NMR (471 MHz, $CDCl_3$/$CFCl_3$) δ ppm -[126.5-125.2] (2 F, m, C*F*$_2$), -[121.3-120.2] (2 F, m, C*F*$_2$), -[109.3-107.9] (2 F, m, C*F*$_2$), -[81.2-80.2] (3 F, m, C*F*$_3$); IR (ATR): ν_{max}/cm^{-1} 2925, 2854, 1511, 1489, 1422, 1350, 1339; MS (APCI$^+$): *m/z* (%) 712 ([M+H]$^+$, 100); HRMS (APCI$^+$): $C_{34}H_{39}F_9NO_3S$ requires 712.2501, found 712.2495; Elemental analysis: Expected, %: C, 57.38; H, 5.38; N, 1.97; Found, %: C, 57.10; H, 5.27; N, 1.91.

105 1-Dodecyl-2-oxo-3-(2,3,6-trimethylbenzyl)indolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Following general procedure *K*, using SmI_2 (19.3 mL of a 0.1 M solution in THF, 193 mmol), and alkylated oxindole **95** (0.607 g, 0.460 mmol) in THF (3.7 mL) gave, after purification by flash column chromatography on silica gel eluting with 20% EtOAc in hexane, **105** (0.215g, 0.294 mmol, 64 %) as a oily residue; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3 H, t, J = 7.0 Hz; CH_2CH_3), 1.15-1.44 (18 H, m; 9 × CH_2), 1.64-1.76 (2 H, m; CH_2), 2.07 (3 H, s; ArCH_3), 2.16 (3 H, s; ArCH_3), 2.28 (3 H, s; ArCH_3), 2.85 (1 H, dd, J = 14.0, 11.7 Hz; ArCH_AH_B), 3.53 (1 H, dd, J = 14.0, 5.6 Hz; ArCH_AH_B), 3.65 (1 H, dd, J = 11.7, 5.6 Hz; C*H*), 3.74 (2 H, t, J = 7.3 Hz; NCH_2), 6.22 (1 H, dd, J = 8.2, 0.8 Hz; Ar*H*), 6.68 (1 H, dd, J = 8.2, 2.2 Hz; Ar*H*), 6.74 (1 H, d, J = 2.2 Hz; Ar*H*), 6.95 (1 H, d, J = 7.7 Hz; Ar*H*), 7.04 (1 H, d, J = 7.7 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (CH_2CH_3), 15.9 (ArCCH_3), 20.6 (ArCCH_3), 20.8 (ArCCH_3), 22.7 (CH_2), 26.9 (CH_2), 27.3 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.47 (CH_2), 29.53 (CH_2), 29.6 (2 × CH_2), 31.0 (ArCCH_2), 31.9 (CH_2), 40.2 (NCH_2), 44.1 (C*H*), 102.0 (Ar*C*H), 113.8 (Ar*C*H), 125.9 (Ar*C*H), 127.8 (Ar*C*H), 128.3 (Ar*C*), 128.6 (Ar*C*H), 134.2 (Ar*C*), 134.6 (Ar*C*), 135.0 (Ar*C*), 135.4 (Ar*C*), 145.2 (Ar*C*), 149.5 (Ar*C*), 177.1 (*C*=O); ^{19}F NMR (376 MHz, $CDCl_3/CFCl_3$) δ ppm –[126.10-125.60] (2 F, m; CF_2), -[121.15-120.59] (2 F, m; CF_2), -[108.96-108.49] (2 F, m; CF_2), -[80.96-80.44] (3 F, m; CF_3).

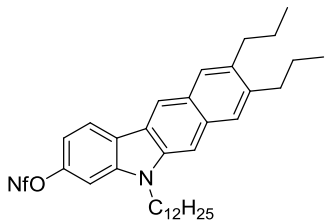
102 5-Dodecyl-8,9-dimethyl-5H-benzo[b]carbazol-3-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Following general procedure *K*, SmI_2 (5.29 mL of a 0.1 M solution in THF, 0.529 mmol), alkylated oxindole **96** (0.167 mg, 0.126 mmol), and CF_3CH_2OH (0.66 mL of a 0.0192 g/mL solution, 0.13 mmol) in THF (1 mL), followed by *p*-benzoquinone (55 mg, 0.509 mmol) in

CH_2Cl_2 (1 mL) gave **102** (71 mg, 0.100 mmol, 79%) as a white solid, mp (toluene/hexane) 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.90 (3 H, t, J = 6.8 Hz; CH_2CH_3), 1.23-1.45 (18 H, m; 9 × CH_2), 1.89 (2 H, quin, J = 7.3 Hz; CH_2), 2.49 (3 H, s, CH_3), 2.51 (3 H, s; CH_3) 4.24 (2 H, t, J = 7.3 Hz; NCH_2), 7.12 (1 H, dd, J = 8.5, 2.2 Hz; Ar*H*), 7.22 (1 H, d, J = 2.2 Hz; Ar*H*), 7.57 (1 H, s; Ar*H*), 7.78 (1 H, s; Ar*H*), 7.75 (1 H, s; Ar*H*), 8.13 (1 H, d, J = 8.5 Hz; Ar*H*), 8.39 (1 H, s; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (CH_2CH_3), 20.1 (CH_3), 20.4 (CH_3), 22.7 (CH_2), 27.3 (CH_2), 28.3 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.47 (CH_2), 29.56 (CH_2), 29.61 (2 × CH_2), 31.9 (CH_2), 43.3 (NCH_2), 101.4 (Ar*C*H), 102.8 (Ar*C*H), 111.1 (Ar*C*H), 118.1 (Ar*C*H), 121.5 (Ar*C*H), 122.8 (Ar*C*), 123.0 (Ar*C*), 126.5 (Ar*C*H), 127.4 (Ar*C*), 127.7 (Ar*C*H), 131.8 (Ar*C*), 132.7 (Ar*C*), 135.6 (Ar*C*), 140.5 (Ar*C*), 143.0 (Ar*C*), 148.7 (Ar*C*); ^{19}F NMR (471 MHz, $CDCl_3$/$CFCl_3$) δ ppm -[127.1-125.4] (2 F, m, CF_2), -[121.5-120.7] (2 F, m, CF_2), -[108.7-108.9] (2 F, m, CF_2), -[81.7-79.8] (3 F, m, CF_3); IR (ATR): ν_{max}/cm^{-1} 2925, 2856, 1609, 1486, 1470, 1422, 1350; MS (APCI$^+$): *m/z* (%) 712 ([M+H]$^+$, 100); HRMS (APCI$^+$): $C_{34}H_{39}F_9NO_3S$ requires 712.2501, found 712.2496.

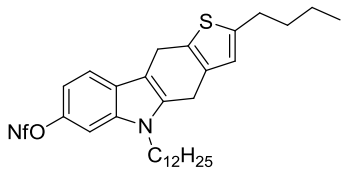
103 5-Dodecyl-8,9-dipropyl-5H-benzo[b]carbazol-3-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Following general procedure *K*, SmI_2 (3.66 mL of a 0.1 M solution in THF, 0.366 mmol), alkylated oxindole **100** (0.120 mg, 0.0871 mmol), and CF_3CH_2OH (0.80 mL of a 0.0110 g/mL solution, 0.088 mmol) in THF (0.7 mL), followed by *p*-benzoquinone (57 mg, 0.527 mmol) in CH_2Cl_2 (1 mL) gave **103** (45 mg, 0.060 mmol, 69%) as a pale yellow solid, mp (toluene/hexane) 78-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.89 (t, J = 6.9 Hz, 3 H; CH_3), 1.09 (3 H, t, J = 7.3; CH_3), 1.10 (3 H, t, J = 7.3 Hz; CH_3), 1.17-1.48 (18 H, m; 9 × CH_2), 1.70-1.85 (4 H, m; 2 × CH_2), 1.86-1.98 (2 H, m; CH_2), 2.74-2.89 (4 H, m; 2 × ArCCH_2), 4.29 (2 H, t, J = 7.1 Hz; NCH_2), 7.12 (1 H, dd, J = 8.4, 1.8 Hz; Ar*H*), 7.23 (1 H, d, J = 1.8 Hz; Ar*H*), 7.61 (1 H, s; Ar*H*), 7.76 (1 H, s; Ar*H*), 7.81 (1 H, s; Ar*H*), 8.16 (1 H, d, J = 8.4 Hz; Ar*H*), 8.45 (1 H, s; Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (CH_3), 14.29 (CH_3), 14.35 (CH_3), 22.7 (CH_2),

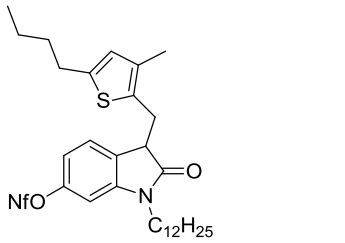
24.1 (*C*H_2), 24.2 (*C*H_2), 27.3 (*C*H_2), 28.3 (*C*H_2), 29.3 (*C*H_2), 29.40 (*C*H_2), 29.46 (*C*H_2), 29.55 (*C*H_2), 29.57 (2 × *C*H_2), 31.9 (*C*H_2), 34.9 (ArC*C*H_2), 35.2 (ArC*C*H_2), 43.5 (N*C*H_2), 101.4 (Ar*C*H), 103.0 (Ar*C*H), 111.2 (Ar*C*H), 118.3 (Ar*C*H), 121.5 (Ar*C*H), 122.8 (Ar*C*), 123.2 (Ar*C*), 126.1 (Ar*C*H), 127.2 (Ar*C*H), 127.3 (Ar*C*), 131.7 (Ar*C*), 136.7 (Ar*C*), 139.6 (Ar*C*), 140.6 (Ar*C*), 143.1 (Ar*C*), 148.8 (Ar*C*); ^{19}F NMR (471 MHz, $CDCl_3/CFCl_3$) δ ppm -[126.0-125.6] (2 F, m, C*F*$_2$), -[120.0-121.1] (2 F, m, C*F*$_2$), -[108.7-108.9] (2 F, m, C*F*$_2$), -[80.9-80.3] (3 F, m, C*F*$_3$); IR (ATR): ν_{max}/cm^{-1} 2960, 2923, 2855, 1608, 1483, 1468, 1407; MS (APCI$^+$): *m/z* (%) 768 ([M+H]$^+$, 100); HRMS (APCI$^+$): $C_{38}H_{47}F_9NO_3S$ requires 768.3127, found 768.3121; Elemental analysis: Expected, %: C, 59.44; H, 6.04; N, 1.82; Found, %: C, 59.07; H, 6.01; N, 1.78.

106 2-Butyl-5-dodecyl-5H-thieno[3,2-b]carbazol-7-yl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Following general procedure *K*, using premixed SmI_2 (1.98 mL of a 0.1 M solution, 0.198 mmol) and NiI_2 (1 mg, 0.003 mmol), alkylated oxindole **98** (0.045 g, 0.033 mmol), and CF_3CH_2OH (0.40 mL of a 0.0082 g/mL solution in THF, 0.033 mmol) in THF (0.5 mL) gave, after purification by flash column chromatography on silica gel eluting with 10% EtOAc in hexane, **107** (16 mg, 0.021 mmol, 64%) as a colourless oil, and **106** (3 mg, 0.004 mmol, 12 %) as a white amorphous solid; MS (APCI$^+$): *m/z* (%) 746 ([M-H_2+H]$^+$, 30), 463 (40), 445 (50), 413 (100). HRMS (EI$^+$): $C_{34}H_{40}O_3N_1F_9S_2$ requires 745.2300, found 745.2300.

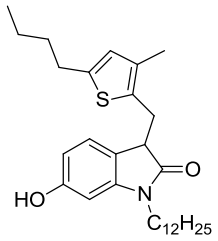
107 3-((5-Butyl-3-methylthiophen-2-yl)methyl)-1-dodecyl-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (3 H, t, *J* = 6.9 Hz; C*H*$_3$), 0.91 (3 H, t, *J* = 7.3 Hz; C*H*$_3$), 1.12-1.43 (20 H, m; 10 × C*H*$_2$), 1.46-1.64 (4 H, m; 2 × C*H*$_2$), 1.99 (3 H, s; ArC*H*$_3$), 2.66 (2 H, t,

J = 7.5 Hz; Ar*C*H$_2$CH$_2$), 3.14 (1 H, dd, *J* = 14.8, 8.8 Hz; ArCH$_A$*H*$_B$CH), 3.43 (1 H, dd, *J* = 14.8, 4.3 Hz; ArCH$_A$*H*$_B$CH), 3.57 (1 H, dt, *J* = 14.3, 7.2 Hz; NC*H*$_A$H$_B$), 3.64-3.77 (2 H, m; NCH$_A$*H*$_B$ and CH), 6.42 (1 H, s; Ar*H*), 6.68 (1 H, d, *J* = 2.3 Hz; Ar*H*), 6.87 (1 H, dd, *J* = 8.3, 2.3 Hz; Ar*H*), 6.93 (1 H, dd, *J* = 8.3, 1.0 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.7 (ArC*C*H$_3$), 13.9 (*C*H$_3$), 14.1 (*C*H$_3$), 22.1 (*C*H$_2$), 22.7 (*C*H$_2$), 26.8 (*C*H$_2$), 27.1 (*C*H$_2$), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.60 (*C*H$_2$), 29.64 (2 × *C*H$_2$), 29.7 (*C*H$_2$), 31.9 (*C*H$_2$), 33.6 (*C*H$_2$), 28.9 (ArC*C*H$_2$CH) 40.2 (N*C*H$_2$), 46.5 (*C*H), 102.1 (Ar*C*H), 114.1 (Ar*C*H), 125.6 (Ar*C*H), 126.8 (Ar*C*H), 128.4 (Ar*C*), 129.7 (Ar*C*), 134.5 (Ar*C*), 142.9 (Ar*C*), 145.7 (Ar*C*), 149.7 (Ar*C*), 176.4 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 2925, 2855, 1722 (C=O), 1618, 1603, 1455, 1426,1351, 1238, 1201; MS (APCI$^+$): *m/z* (%) 766 ([M+H]$^+$, 100); HRMS (APCI$^+$): $C_{34}H_{44}F_9N_1O_4S_2$ requires 765.2563, found 765.2537.

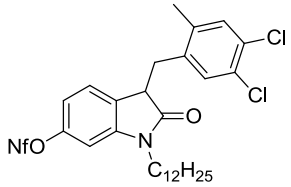
108 3-((5-Butyl-3-methylthiophen-2-yl)methyl)-1-dodecyl-6-hydroxyindolin-2-one



Following general procedure *K*, using premixed SmI_2 (1.92 mL of a 0.1 M, 0.192 mmol) and LiBr (0.20 g, 2.3 mmol), alkylated oxindole **98** (0.043 g, 0.032 mmol), and CF_3CH_2OH (0.39 mL of a 0.0082 g/mL solution in THF, 0.032 mmol) in THF (0.5 mL) gave after purification by flash column chromatography on silica gel eluting with 10% EtOAc in hexane, **108** (8 mg, 0.02 mmol, 63%) as a colourless oil; NMR (400 MHz, $CDCl_3$) δ ppm 0.89 (3 H, t, *J* = 6.8 Hz; C*H*$_3$), 0.91 (3 H, t, *J* = 7.3 Hz; C*H*$_3$), 1.12-1.41 (20 H, m; 10 × C*H*$_2$), 1.49-1.63 (4 H, m; 2 × C*H*$_2$), 2.00 (3 H, s; ArC*H*$_3$), 2.66 (2 H, t, *J* = 7.5 Hz; ArC*H*$_2$), 3.07 (1 H, dd, *J* = 14.8, 9.3 Hz; ArC*H*$_A$H$_B$), 3.39 (1 H, dd, *J* = 14.8, 4.5 Hz; ArCH$_A$*H*$_B$), 3.54 (1 H, dt, *J* = 14.4, 7.0 Hz; NC*H*$_A$H$_B$), 3.60 (1 H, dd, *J* = 9.3, 4.5 Hz; C*H*), 3.67 (1 H, ddd, *J* = 14.4, 7.0 Hz; NCH$_A$*H*$_B$), 6.36 (1 H, d, *J* = 1.9 Hz; Ar*H*), 6.39 (1 H, dd, *J* = 8.0, 1.9 Hz; Ar*H*), 6.41 (1 H, s; Ar*H*), 6.72 (1 H, dd, *J* = 8.0, 1.9 Hz; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.83 (*C*H$_3$), 14.0 (*C*H$_3$), 14.1 (*C*H$_3$), 22.1 (*C*H$_2$), 22.7 (*C*H$_2$), 26.8 (*C*H$_2$), 27.3 (*C*H$_2$), 29.28 (ArC*C*H$_2$), 29.34 (2 × *C*H$_2$), 29.5 (ArC*C*H$_2$CH$_2$), 29.6 (3 × *C*H$_2$), 29.7 (*C*H$_2$), 31.9 (*C*H$_2$), 33.7 (*C*H$_2$), 40.0 (N*C*H$_2$), 46.5 (*C*H), 96.9 (Ar*C*H), 108.0 (Ar*C*H), 120.2 (Ar*C*), 125.2 (Ar*C*H), 126.7 (Ar*C*H), 130.6 (Ar*C*),

134.1 (Ar*C*), 142.5 (Ar*C*), 145.3 (Ar*C*), 156.0 (Ar*C*OH), 177.4 (*C*=O); IR (ATR): ν_{max}/cm^{-1} 3194 (OH), 2955, 2919, 2851, 1682 (C=O), 1618, 1601, 1477, 1466, 1388; MS ($APCI^+$): *m/z* (%) 484 ($[M+H]^+$, 100); HRMS ($APCI^+$): $C_{30}H_{45}N_1O_2S_1$ requires 483.3166, found 483.3159.

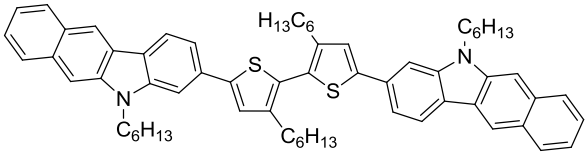
110 3-(4,5-Dichloro-2-methylbenzyl)-1-dodecyl-2-oxoindolin-6-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate



Using general procedure *K*, SmI_2 (3.46 mL of 0.1 M solution in THF, 0.346 mmol), alkylated oxindole **97** (0.112 g, 0.0823 mmol), and CF_3CH_2OH (0.20 mL of a 0.0412 g/ mL solution, 0.082 mmol) in THF (0.6 mL) gave a complex mixture of compounds. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in hexane yielded **110** (38 mg, 0.049 mmol, 60%) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (3 H, t, *J* = 6.6 Hz; CH_3), 1.16-1.41 (18 H, m; 9 × CH_2), 1.53-1.68 (2 H, m; CH_2), 2.25 (3 H, s; ArCH_3), 2.81 (1 H, dd, *J* = 14.3, 10.1 Hz; ArCH_AH$_B$), 3.40 (1 H, dd, *J* = 14.3, 4.8 Hz; ArCH$_A$$H_B$), 3.57-3.80 (3 H, m; NC$H_2$ and C*H*), 6.73 (1 H, d, *J* = 2.3 Hz; Ar*H*), 6.76 (1 H, dd, *J* = 8.3, 0.8 Hz; Ar*H*), 6.85 (2 H, dd, *J* = 8.3, 2.3 Hz; Ar*H*), 7.18 (1 H, s; Ar*H*), 7.28 (1 H, s; Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (*C*H$_3$), 19.0 (Ar*C*H$_3$), 22.7, 26.8, 27.2, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9 (10 × *C*H$_2$), 33.2 (Ar*C*H$_2$), 40.3 (N*C*H$_2$), 45.0 (*C*H), 102.4 (Ar*C*H), 114.2 (Ar*C*H), 125.5 (Ar*C*H), 128.0 (Ar*C*), 129.5 (Ar*C*), 130.7 (Ar*C*), 131.3 (Ar*C*H), 132.1 (Ar*C*H), 136.1 (Ar*C*), 136.9 (Ar*C*), 145.4 (Ar*C*), 149.8 (Ar*C*), 176.3 (*C*=O); ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -[125.87-125.74] (2 F, m; CF_2), -[120.91-120.75 (2 F, m; CF_2), -[108.79-108.62] (2 F, m; CF_2), -80.59 (3 F, t, *J* = 10.2 Hz; CF_3); IR (ATR): ν_{max}/cm^{-1} 2925, 2855, 1721 (C=O), 1616, 1603, 1492, 1470, 1425.

General procedure L: Preparation of carbazole end-capped oligothiophenes

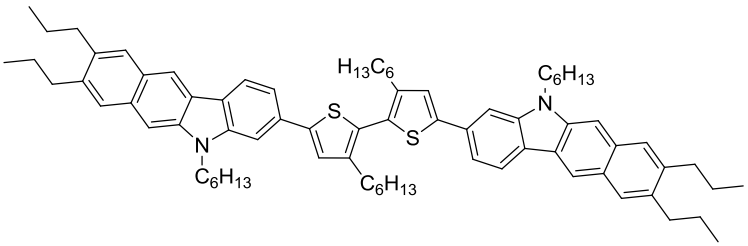
119 3,3'-(3,3'-Dihexyl-[2,2'-bithiophene]-5,5'-diyl)*bis*(5-hexyl-5H-benzo[*b*]carbazole)



To a microwave vial under N_2 was added **118** (0.017 g, 0.019 mmol), $Pd(PPh_3)_4$ (1 mg, 0.0009 mmol), 5-hexyl-5H-benzo[*b*]carbazol-3-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate[1] (0.021 g, 0.038 mmol), LiCl (1 mg, 0.02 mmol) and DMF (0.8 mL). The vial was then sealed and heated at 110 ˚C for 24 h. MeOH (4 mL) was then added and the crude product collected by filtration. Purification by flash column chromatography on silica gel eluting with 20% toluene in hexane followed by recrystallisation from toluene/hexane gave pure **119** (0.014 g, 0.015 mmol, 76%) as an orange solid, mp (toluene/hexane) 185-187 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.91 (12 H, t, *J* = 7.1 Hz, 4 × C*H*$_3$), 1.28-1.45 (20 H, m, 10 × C*H*$_2$), 1.45-1.54 (4 H, m, 2 × C*H*$_2$), 1.72 (4 H, app. quin, *J* = 7.8 Hz, 2 × C*H*$_2$), 1.98 (4 H, app. quin, *J* = 7.4 Hz, 2 × C*H*$_2$), 2.61-2.76 (4 H, t, *J* = 7.8 Hz , 2 × ArCC*H*$_2$), 4.38 (4 H, t, *J* = 7.4 Hz, 2 × NC*H*$_2$), 7.38 (2 H, s, 2 × thiophene Ar*H*), 7.39-7.45 (2 H, m, 2 × Ar*H*), 7.50 (2 H, t, *J* = 7.4 Hz, 2 × Ar*H*), 7.54-7.58 (2 H, m, 2 × Ar*H*), 7.59 (2 H, s, 2 × Ar*H*), 7.69 (2 H, s, 2 × Ar*H*), 7.99 (2 H, d, *J* = 8.2 Hz, 2 × Ar*H*), 8.06 (2 H, d, *J* = 8.2 Hz, 2 × Ar*H*), 8.21 (2 H, d, *J* = 8.2 Hz, 2 Ar*H*), 8.56 (2 H, s, 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.05 (2 × *C*H$_3$), 14.11 (2 × *C*H$_3$), 22.58 (2 × *C*H$_2$), 22.63 (2 × *C*H$_2$), 27.0 (2 × *C*H$_2$), 28.5 (2 × *C*H$_2$), 29.2 (2 × *C*H$_2$), 29.3 (2 × ArC*C*H$_2$), 30.8 (2 × *C*H$_2$), 31.6 (2 × *C*H$_2$), 31.7 (2 × *C*H$_2$), 43.2 (2 × N*C*H$_2$), 103.3 (2 × Ar*C*H), 105.1 (2 × Ar*C*H), 117.0 (2 × Ar*C*H), 118.6 (2 × Ar*C*H), 121.3 (2 × Ar*C*H), 122.3 (2 × Ar*C*), 122.7 (2 × Ar*C*H), 125.0 (2 × thiophene Ar*C*H and 2 × Ar*C*), 125.2 (2 × Ar*C*H), 127.1 (2 × Ar*C*H), 128.1 (2 × Ar*C*), 128.4 (2 × Ar*C*), 128.5 (2 × Ar*C*H), 132.6 (2 × Ar*C*), 133.4 (2 × Ar*C*), 141.0 (2 × Ar*C*), 143.5 (2 × Ar*C*), 143.6 (2 × Ar*C*), 144.8 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2953, 2926, 2855, 1605; MS (MALDI): *m/z* (%) 932 ([M+H]$^+$, 100); Elemental analysis: Expected, %: C, 82.35; H, 7.77; N, 3.00; S, 6.87; Found: C, 82.48; H, 8.15; N, 3.01; S, 6.94.

[1] Provided by Dr. S. Coote

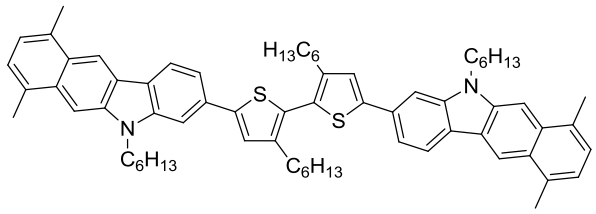
120 3,3'-(3,3'-Dihexyl-[2,2'-bithiophene]-5,5'-diyl)*bis*(5-hexyl-8,9-dipropyl-5H-benzo[*b*]carbazole)



Following general procedure *L*, using 5-hexyl-8,9-dipropyl-5H-benzo[*b*]carbazol-3-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate[2] (0.087 g, 0.13 mmol), **114** (0.058 g, 0.064 mmol), $Pd(PPh_3)_4$ (3 mg, 0.003 mmol), and LiCl (5 mg, 0.1 mmol) in DMF (2.5 mL), gave **120** (0.046 g, 0.042 mmol, 66%) as a yellow amorphous solid after purification by 2 × flash column chromatography on silica gel eluting with a gradient of 10-20% toluene in hexane; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.75-0.85 (6 H, m, 2 × C*H*$_3$), 0.90 (6 H, t, *J* = 6.3 Hz, 2 × C*H*$_3$), 0.99-1.25 (24 H, m, 4 × C*H*$_3$ and 6 × C*H*$_2$), 1.25-1.33 (8 H, m, 4 × C*H*$_2$), 1.33-1.46 (4 H, m, 2 × C*H*$_2$), 1.65 (4 H, quin, *J* = 7.2 Hz, 2 × C*H*$_2$), 1.72-1.89 (12 H, m, 6 × C*H*$_2$), 2.74-2.98 (12 H, m, 6 × CH_2), 3.92 (4 H, t, *J* = 6.9 Hz, 2 × NC*H*$_2$), 7.50 (2 H, s, 2 × Ar*H*), 7.59 (2 H, s, 2 × Ar*H*), 7.71 (2 H, d, *J* = 7.9 Hz, 2 × Ar*H*), 7.74 (2 H, s, 2 × Ar*H*), 7.83 (2 H, s, 2 × Ar*H*), 7.87 (2 H, s, 2 × Ar*H*), 8.15 (2 H, d, *J* = 7.9 Hz, 2 × Ar*H*), 8.46 (2 H, s, 2 × Ar*H*); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 14.8 (2 × *C*H_3), 15.0 (2 × *C*H_3), 15.1 (2 × *C*H_3), 15.1 (2 × *C*H_3), 23.4 (2 × *C*H_2), 23.6 (2 × *C*H_2), 25.2 (2 × *C*H_2), 25.3 (2 × *C*H_2), 27.8 (2 × *C*H_2), 29.2 (2 × *C*H_2), 30.3 (2 × *C*H_2), 30.5 (2 × *C*H_2), 32.0 (2 × *C*H_2), 32.4 (2 × *C*H_2), 32.7 (2 × *C*H_2), 36.0 (2 × *C*H_2), 36.2 (2 × *C*H_2), 43.7 (2 × N*C*H_2), 103.6 (2 × Ar*C*H), 106.3 (2 × Ar*C*H), 118.2 (2 × Ar*C*H), 119.2 (2 × Ar*C*H), 122.4 (2 × Ar*C*H), 123.9 (2 × Ar*C*), 125.5 (2 × Ar*C*), 126.1 (2 × Ar*C*H), 127.4 (2 × Ar*C*H), 128.6 (2 × Ar*C*H), 128.9 (2 × Ar*C*), 129.5 (2 × Ar*C*), 133.1 (2 × Ar*C*), 134.3 (2 × Ar*C*), 136.8 (2 × Ar*C*), 139.6 (2 × Ar*C*), 141.8 (2 × Ar*C*), 144.6 (2 × Ar*C*), 144.7 (2 × Ar*C*), 146.7 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2953, 2924, 2855, 1605, 1458; MS (MALDI$^+$): *m/z* (%) 1101 ([M]$^+$, 100).

[2] Provided by Dr S. Coote

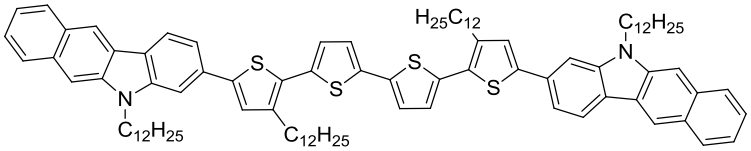
121 3,3'-(3,3'-Dihexyl-[2,2'-bithiophene]-5,5'-diyl)*bis*(5-hexyl-7,10-dimethyl-5H-benzo[*b*]carbazole)



Following general procedure *L*, using 5-hexyl-7,10-dimethyl-5H-benzo[*b*]carbazol-3-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate[3] (0.094 g, 0.15 mmol), **118** (0.062 g, 0.068 mmol), $Pd(PPh_3)_4$ (3 mg, 0.003 mmol), and LiCl (6 mg, 0.1 mmol) in DMF (3 mL), gave **121** (0.042 g, 0.042 mmol, 63%) as a yellow solid after purification by flash column chromatography on silica gel eluting with a gradient of 10-20% toluene in hexane followed by recrystallisation from hexane, mp (hexane) 145-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.78-1.03 (12 H, m; 4 × CH_3), 1.23-1.61 (24 H, m; 12 × CH_2), 1.74 (4 H, quin, *J* = 7.6 Hz; 2 × CH_2), 2.01 (4 H, quin, *J* = 7.3 Hz; 2 × CH_2), 2.68-2.72 (4 H, m; 2 × CH_2), 2.81 (6 H, s; 2 × CH_3), 2.87 (6 H, s; 2 × CH_3), 4.42 (4 H, t, *J* = 7.2 Hz; 2 × NCH_2), 7.08-7.32 (4 H, m; 4 × Ar*H*), 7.40 (2 H, s; 2 × Ar*H*), 7.53-7.65 (4 H, m; 4 × Ar*H*), 7.79 (2 H, s; 2 × Ar*H*), 8.26 (2 H, d, *J* = 7.8 Hz; 2 × Ar*H*), 8.73 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.05 (2 × *C*H_3), 14.13 (2 × *C*H_3), 20.1 (4 × *C*H_3), 22.57 (2 × *C*H_2), 22.64 (2 × *C*H_2), 27.0 (2 × *C*H_2), 28.4 (2 × *C*H_2), 29.2 (2 × *C*H_2), 29.3 (2 × *C*H_2), 30.8 (2 × *C*H_2), 31.6 (2 × *C*H_2), 31.7 (2 × *C*H_2), 43.0 (2 × N*C*H_2), 100.5 (2 × Ar*C*H), 105.1 (2 × Ar*C*H), 115.6 (2 × Ar*C*H), 116.9 (2 × Ar*C*H), 121.2 (2 × Ar*C*H), 122.5 (2 × Ar*C*), 123.1 (2 × Ar*C*H), 124.0 (2 × Ar*C*), 124.9 (2 × Ar*C*H), 125.6 (2 × Ar*C*H), 127.4 (2 × Ar*C*), 128.4 (2 × Ar*C*), 131.0 (2 × Ar*C*), 132.0 (2 × Ar*C*), 132.7 (2 × Ar*C*), 133.2 (2 × Ar*C*), 140.6 (2 × Ar*C*), 143.5 (2 × Ar*C*), 143.6 (2 × Ar*C*), 144.8 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2949, 2919, 2852, 1605, 1466; MS (MALDI$^+$): *m/z* (%) 989 ([M]$^+$, 100).

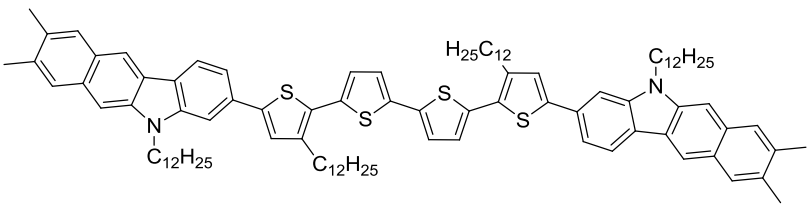
[3] Provided by Dr S. Coote

122 3,3'-(3,3'''-Didodecyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)*bis*(5-dodecyl-5H-benzo[*b*]carbazole)



Following general procedure *L*, using **78** (0.150 g, 0.219 mmol), **116** (0.125 g, 0.100 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol), and LiCl (8 mg, 0.2 mmol) in DMF (4.4 mL), gave **122** (0.103 mg, 0.0718 mmol, 72%) as an orange solid after purification by 3 × recrystallisation from toluene, mp (toluene) 200-201 °C; ^{1}H NMR (400 MHz, Tol-d_8) δ ppm 0.80-0.99 (12 H, m; 4 × CH_3), 1.12-1.56 (72 H, m; 36 × CH_2), 1.71-1.90 (8 H, m; 4 × CH_2), 2.90 (4 H, t, *J* = 7.7 Hz; 2 × CH_2), 4.08 (4 H, t, *J* = 6.7 Hz; 2 × NCH_2), 7.04 -7.12 (4 H, m; 4 × Ar*H*), 7.23-7.42 (6 H, m; 6 × Ar*H*), 7.48-7.60 (4 H, m; 4 × Ar*H*), 7.63 (2 H, s; 2 × Ar*H*), 7.87 (2 H, d, *J* = 8.3 Hz; 2 × Ar*H*), 7.92 (2 H, d, *J* = 8.3 Hz; 2 × Ar*H*), 8.05 (2 H, d, *J* = 7.8 Hz; 2 × Ar*H*), 8.38 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, Tol-d_8) δ ppm 14.2 (4 × *C*H_3), 23.15 (2 × *C*H_2), 23.16 (2 × *C*H_2), 27.8 (2 × *C*H_2), 29.0 (2 × *C*H_2), 29.86 (2 × *C*H_2), 29.91 (4 × *C*H_2), 30.07 (2 × *C*H_2), 30.14 (2 × *C*H_2), 30.16 (2 × *C*H_2), 30.20 (4 × *C*H_2), 30.24 (2 × *C*H_2), 30.27 (4 × *C*H_2), 30.32 (4 × *C*H_2), 30.4 (2 × *C*H_2), 31.2 (2 × *C*H_2), 32.46 (2 ×*C*H_2), 32.51 (2 × *C*H_2), 43.7 (2 × N*C*H_2), 104.0 (2 × Ar*C*H), 106.0 (2 × Ar*C*H), 117.9 (2 × Ar*C*H), 119.4 (2 × Ar*C*H), 121.9 (2 × Ar*C*H), 123.2 (2 × Ar*C*H), 123.6 (2 × Ar*C*), 124.6 (2 × Ar*C*H), 125.7 (2 × Ar*C*H), 125.9 (2 × Ar*C*), 126.8 (2 × Ar*C*H), 127.1 (2 × Ar*C*H), 127.7 (2 × Ar*C*H), 129.1 (2 × Ar*C*H), 129.5 (2 × Ar*C*), 131.0 (2 × Ar*C*), 133.9 (2 × Ar*C*), 134.2 (2 × Ar*C*), 136.6 (2 × Ar*C*), 137.4 (2 × Ar*C*), 141.6 (2 × Ar*C*), 142.0 (2 × Ar*C*), 144.60 (2 × Ar*C*), 144.64 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2949, 2916, 2848, 1604, 1467; MS (MALDI$^+$): *m/z* (%) 1434 ([M]$^+$, 100).

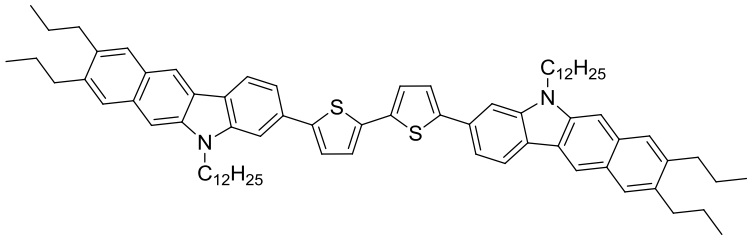
123 3,3'-(3,3'''-Didodecyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)*bis*(5-dodecyl-8,9-dimethyl-5H-benzo[*b*]carbazole)



Following general procedure *L*, using **102** (0.194 g, 0.273 mmol), **116** (0.154 g, 0.124 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), and LiCl (11 mg, 0.26 mmol) in DMF (10 mL), gave

123 (0.152 g, 0.102 mmol, 82%) as an orange solid after purification by 3 × recrystallisation from toluene, mp (toluene) 193-195 °C; ^{1}H NMR (400 MHz, Tol-d_8) δ ppm 0.82-0.99 (12 H, m; 4 × CH_2CH_3), 1.16-1.57 (72 H, m; 36 × CH_2), 1.73-1.92 (8 H, m; 4 × CH_2), 2.37 (12 H, s; 4 × CH_3), 2.92 (4 H, t, J = 7.8 Hz; 2 × $ArCCH_2$), 4.12 (4 H, t, J = 7.0 Hz; 2 × NCH_2), 6.97 -7.04 (4 H, m; 4 × Ar*H*), 7.34 (2 H, s; 2 × Ar*H*), 7.51 (2 H, s; 2 × Ar*H*), 7.58 (2 H, d, J = 8.0 Hz; 2 × Ar*H*), 7.65 (2 H, s; 2 × Ar*H*), 7.67 (2 H, s; 2 × Ar*H*), 7.71 (2 H, s; 2 × Ar*H*), 8.09 (2 H, d, J = 8.0 Hz; 2 × Ar*H*), 8.35 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, Tol-d_8) δ ppm 14.2 (4 × CH_3), 20.0 (4 × $ArCCH_3$) 23.2 (4 × CH_2), 27.9 (2 × CH_2), 29.0 (2 × CH_2), 29.8, 29.9, 30.1, 30.2, 30.26, 30.31 (28 × CH_2), 31.2 (2 × CH_2), 32.46 (2 × CH_2), 32.50 (2 × CH_2), 43.7 (2 × NCH_2), 103.1 (2 × Ar*C*H), 105.9 (2 × Ar*C*H), 117.8 (2 × Ar*C*H), 118.4 (2 × Ar*C*H), 121.7 (2 × Ar*C*H), 124.0 (2 × Ar*C*), 124.6 (2 × Ar*C*H), 126.7 (2 × Ar*C*H), 127.1 (2 × Ar*C*H), 127.4 (2 × Ar*C*H), 128.6 (2 × Ar*C*H), 130.8 (2 × Ar*C*), 132.4 (2 × Ar*C*), 133.1 (2 × ArC), 133.8 (2 × Ar*C*), 135.1 (2 × Ar*C*), 136.6 (2 × Ar*C*), 141.6 (2 × Ar*C*), 141.7 (2 × Ar*C*), 144.5 (2 × Ar*C*), 144.8 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2951, 2916, 2849, 1606, 1489; MS (MALDI$^+$): *m/z* (%) 1490 ([M]$^+$, 100).

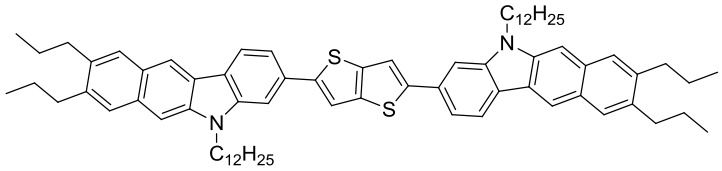
124 5,5'-*bis*(5-Dodecyl-8,9-dipropyl-5H-benzo[*b*]carbazol-3-yl)-2,2'-bithiophene



Following general procedure *L*, using **103** (0.168 g, 0.219 mmol), **114** (stannane) (0.078 g, 0.105 mmol) $Pd(PPh_3)_4$ (5 mg, 0.004 mmol), and LiCl (10 mg, 0.24 mmol) in DMF (4.4 mL), gave **124** (0.079 g, 0.072 mmol, 69%) after 3 × recrystallisation from toluene, mp (toluene) 211-212 °C; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.84-0.94 (6 H, m; 2 × CH_3), 1.01-1.05 (12 H, m; 4 × CH_3), 1.15-1.42 (36 H, m; 18 × CH_2), 1.71-1.88 (12 H, m; 6 × CH_2), 2.83 (8 H, td, J = 7.5, 4.6 Hz; 4 × CH_2), 4.05 (4 H, t, J = 7.2 Hz; 2 × NCH_2), 7.21 (2 H, d, J = 3.8 Hz; 2 × Ar*H*), 7.26 (2 H, d, J = 3.8 Hz; 2 × Ar*H*), 7.49-7.69 (6 H, m; 6 × Ar*H*), 7.81 (2 H, s; 2 × Ar*H*), 7.85 (2 H, s; 2 × Ar*H*), 8.11 (2 H, d, J = 7.8 Hz; 2 × Ar*H*), 8.44 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 14.5 (2 × CH_3), 14.6 (2 × CH_3), 14.7 (2 × CH_3), 23.4 (2 × CH_2), 24.92 (2 × CH_2), 24.94 (2 × CH_2), 28.0 (2 × CH_2), 29.1 (2 × CH_2), 30.07 (2 × CH_2), 30.10 (2 × CH_2),

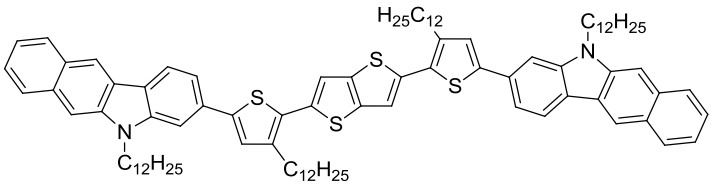
30.2 (2 × *C*H_2), 30.36 (2 × *C*H_2), 30.39 (4 × *C*H_2), 32.6 (2 × *C*H_2), 35.8 (2 × *C*H_2), 36.0 (2 × *C*H_2), 43.7 (2 × N*C*H_2), 103.5 (2 × Ar*C*H), 106.1 (2 × Ar*C*H), 118.0 (2 × Ar*C*H), 118.9 (2 × Ar*C*H), 122.1 (2 × Ar*C*H), 124.0 (2 × Ar*C*), 124.8 (2 × Ar*C*H), 125.45 (2 × Ar*C*H), 125.47 (2 × Ar*C*), 127.3 (2 × Ar*C*H), 128.27 (2 × Ar*C*H), 133.1 (2 × Ar*C*), 134.0 (2 × Ar*C*), 136.7 (2 × Ar*C*), 137.8 (2 × Ar*C*), 139.5 (2 × Ar*C*), 141.9 (2 × Ar*C*), 144.6 (2 × Ar*C*), 145.7 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2953, 2920, 2851, 1605, 1485; MS (MALDI$^+$): *m/z* (%) 1101 ([M]$^+$, 100).

125 2,5-*bis*(5-Dodecyl-8,9-dipropyl-5H-benzo[*b*]carbazol-3-yl)thieno[3,2-*b*]thiophene



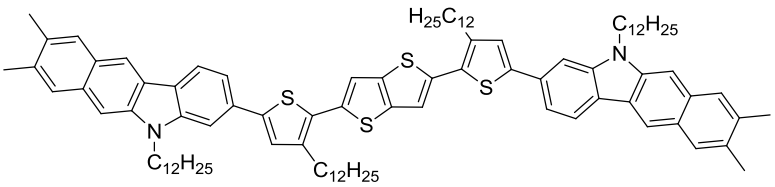
Following general procedure *L*, using **103** (0.165 g, 0.215 mmol), **112** (0.0735 g, 0.102 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol), and LiCl (10 mg, 0.24 mmol) in DMF (4.3 mL), gave **125** (0.083 g, 0.077 mmol, 75%) after 3 × recrystallisation from toluene, mp (toluene) 176-178 °C; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.90 (6 H, t, *J* = 6.7 Hz; 2 × C*H*$_3$), 1.01-1.12 (12 H, m; 4 × C*H*$_3$), 1.16-1.45 (36 H, m; 18 × C*H*$_2$), 1.69-1.88 (12 H, m; 6 × C*H*$_2$), 2.83 (8 H, q, *J* = 8.0 Hz; 4 × C*H*$_2$), 4.05 (4 H, t, *J* = 6.9 Hz; 2 × NC*H*$_2$), 7.41 (2 H, s; 2 × Ar*H*), 7.50-7.62 (4 H, m; 4 × Ar*H*), 7.65 (2 H, s; 2 × Ar*H*), 7.82 (4 H, d, *J* = 9.8 Hz; 4 × Ar*H*), 8.09 (2 H, d, *J* = 7.8 Hz; 2 × Ar*H*), 8.42 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 14.5 (2 × *C*H_3), 14.66 (2 × *C*H_3), 14.70 (2 × *C*H_3), 23.4 (2 × *C*H_2), 24.9 (2 × *C*H_2), 25.0 (2 × *C*H_2), 28.0 (2 × *C*H_2), 29.1 (2 × *C*H_2), 30.07 (2 × *C*H_2), 30.10 (2 × *C*H_2), 30.2 (2 × *C*H_2), 30.37 (2 × *C*H_2), 30.39 (4 × *C*H_2), 32.6 (2 × *C*H_2), 35.8 (2 × *C*H_2), 36.0 (2 × *C*H_2), 43.7 (2 × N*C*H_2), 103.5 (2 × Ar*C*H), 106.1 (2 × Ar*C*H), 116.5 (2 × Ar*C*H), 118.2 (2 × Ar*C*H), 118.9 (2 × Ar*C*H), 122.1 (2 × Ar*C*H), 124.1 (2 × Ar*C*), 125.5 (2 × Ar*C*), 127.2 (2 × Ar*C*H), 128.6 (2 × Ar*C*H), 133.1 (2 × Ar*C*), 134.6 (2 × Ar*C*), 136.7 (2 × Ar*C*), 139.5 (2 × Ar*C*), 140.5 (2 × Ar*C*), 141.9 (2 × Ar*C*), 144.6 (2 × Ar*C*), 148.2 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2916, 2849, 1609, 1466; MS (MALDI$^+$): *m/z* (%) 1075 ([M]$^+$, 100).

126 2,5-*bis*(3-Dodecyl-5-(5-dodecyl-5H-benzo[*b*]carbazol-3-yl)thiophen-2-yl)thieno[3,2-*b*]thiophene



Following general procedure *L*, using **78** (0.177 g, 0.259 mmol), **113** (0.144 g, 0.118 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol), and LiCl (0.010 mg, 0.24 mmol) in DMF (5 mL), gave **126** (0.127 g, 0.0902 mmol, 77%) as an orange solid after purification by 3 × recrystallisation from toluene, mp (toluene) 213-214 °C; ^{1}H NMR (400 MHz, Tol-d_8) δ ppm 0.84-0.96 (12 H, m; 4 × CH_3), 1.18-1.55 (72 H, m; 36 × CH_2), 1.76-1.89 (8 H, m; 4 × CH_2), 2.92 (4 H, t, *J* = 7.7 Hz; 2 × CH_2), 4.10 (4 H, t, *J* = 7.2 Hz; 2 × NCH_2), 7.24 (2 H, s; 2 × Ar*H*), 7.29 (2 H, t, *J* = 7.5 Hz; 2 × Ar*H*), 7.33-7.41 (4 H, m; 4 × Ar*H*), 7.54-7.63 (4 H, m; 4 × Ar*H*), 7.66 (2 H, s; 2 × Ar*H*), 7.88 (2 H, d, *J* = 8.0 Hz; 2 × Ar*H*), 7.93 (2 H, d, *J* = 8.0 Hz; 2 × Ar*H*), 8.08 (2 H, d, *J* = 8.0 Hz; 2 × Ar*H*), 8.40 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, Tol-d_8) δ ppm 14.2 (4 × *C*H_3), 23.1 (2 × *C*H_2), 23.2 (2 × *C*H_2), 27.9 (2 × *C*H_2), 29.0 (2 × *C*H_2), 29.86 (2 × *C*H_2), 29.92 (4 × *C*H_2), 30.07 (2 × *C*H_2), 30.14 (2 × *C*H_2), 30.16 (2 × *C*H_2), 30.19 (4 × *C*H_2), 30.25 (4 × *C*H_2), 30.27 (2 × *C*H_2), 30.31 (4 × *C*H_2), 30.34 (2 × *C*H_2), 31.3 (2 × *C*H_2), 32.46 (2 × *C*H_2), 32.51 (2 × *C*H_2), 43.7 (2 × N*C*H_2), 104.1 (2 × Ar*C*H), 106.1 (2 × Ar*C*H), 118.0 (2 × Ar*C*H), 118.6 (2 × Ar*C*H), 119.4 (2 × Ar*C*H), 122.0 (2 × Ar*C*H), 123.2 (2 × Ar*C*H), 123.7 (2 × Ar*C*), 125.7 (2 × Ar*C*), 125.9 (2 × Ar*C*H), 126.8 (2 × Ar*C*H), 127.7 (2 × Ar*C*H), 129.1 (2 × Ar*C*H), 129.5 (2 × Ar*C*), 131.4 (2 × Ar*C*), 133.9 (2 × Ar*C*), 134.2 (2 × Ar*C*), 138.9 (2 × Ar*C*), 140.3 (2 × Ar*C*), 141.9 (2 × Ar*C*), 142.0 (2 × Ar*C*), 144.6 (2 × Ar*C*), 145.1 (2 × Ar*C*); IR (ATR): ν_{max} /cm^{-1} 2948, 2917, 2850, 1604, 1468, 1445; MS (MALDI$^+$): *m/z* (%) 1408 ([M]$^+$, 100).

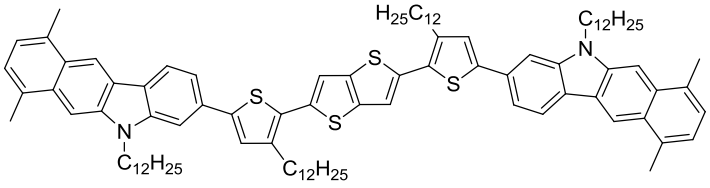
127 2,5-*bis*(3-Dodecyl-5-(5-dodecyl-8,9-dimethyl-5H-benzo[*b*]carbazol-3-yl)thiophen-2-yl)thieno[3,2-*b*]thiophene



Following general procedure *L*, using **102** (0.195g, 0.274 mmol), **113** (0.152 g, 0.125 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), and LiCl (11 mg, 0.26 mmol) in DMF (5.5 mL), gave

127 (0.135 g, 0.0922 mmol, 74%) as an orange solid after purification by 3 × recrystallisation from toluene, mp (toluene) 189-190 °C; ^{1}H NMR (400 MHz, Tol-d_8) δ ppm 0.77-1.03 (12 H, m; 4 × CH_3), 1.11-1.57 (72 H, m; 36 × CH_2), 1.69-1.98 (8 H, m; 4 × CH_2), 2.36 (12 H, s; 4 × CH_3), 2.92 (4 H, t, *J* = 7.8 Hz; 2 × CH_2), 4.11 (4 H, t, *J* = 7.2 Hz; 2 × NCH_2), 7.24 (2 H, s; 2 × Ar*H*), 7.34 (2 H, s; 2 × Ar*H*), 7.50 (2 H, s; 2 × Ar*H*), 7.57 (2 H, dd, *J* = 7.9, 1.1 Hz; 2 × Ar*H*), 7.65 (4 H, s; 4 × Ar*H*), 7.69 (2 H, s; 2 × Ar*H*), 8.08 (2 H, d, *J* = 7.9 Hz; 2 × Ar*H*), 8.33 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, Tol-d_8) δ ppm 13.8 (4 × *C*H_3), 19.9 (4 × *C*H_3), 22.7 (2 × *C*H_2), 22.8 (2 × *C*H_2), 27.5 (2 × *C*H_2), 28.6 (2 × *C*H_2), 29.46 (2 × *C*H_2), 29.53 (4 × *C*H_2), 29.67 (2 × *C*H_2), 29.74 (2 × *C*H_2), 29.77 (2 × *C*H_2), 29.79 (2 × *C*H_2), 29.80 (2 × *C*H_2), 29.86 (6 × *C*H_2), 29.91 (4 × *C*H_2), 29.94 (2 × *C*H_2), 30.9 (2 × *C*H_2), 32.06 (2 × *C*H_2), 32.10 (2 × *C*H_2), 43.3 (2 × N*C*H_2), 102.7 (2 × Ar*C*H), 105.5 (2 × Ar*C*H), 117.4 (2 × Ar*C*H), 118.0 (2 × Ar*C*H), 118.1 (2 × Ar*C*H), 121.3 (2 × Ar*C*H), 123.6 (2 × Ar*C*), 126.3 (2 × Ar*C*), 127.0 (2 × Ar*C*H), 128.2 (2 × Ar*C*H), 130.9 (2 × Ar*C*H), 132.0 (2 × Ar*C*), 132.7 (2 × Ar*C*), 133.3 (2 × Ar*C*), 134.7 (2 × Ar*C*), 138.5 (2 × Ar*C*), 139.8 (2 × Ar*C*), 141.3 (2 × Ar*C*), 141.5 (2 × Ar*C*), 144.0 (2 × Ar*C*), 144.8 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2916, 2849, 1606, 1467; MS (MALDI^{+}): *m/z* (%) 1465 ([M+H]$^{+}$, 100).

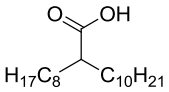
128 2,5-*bis*(3-Dodecyl-5-(5-dodecyl-7,10-dimethyl-5H-benzo[*b*]carbazol-3-yl)thiophen-2-yl)thieno[3,2-*b*]thiophene



Following general procedure *L*, using **101** (0.240 g, 0.337 mmol), **113** (0.187 g, 0.153 mmol), Pd(PPh$_3$)$_4$ (7 mg, 0.006 mmol), and LiCl (13 mg, 0.31 mmol) in DMF (7 mL), gave **128** (0.171 g, 0.117, 76%) as an orange solid after purification by 3 × recrystallisation from toluene, mp (toluene) 174-176 °C; ^{1}H NMR (400 MHz, Tol-d_8) δ ppm 0.82-0.94 (12 H, m; 4 × CH_3), 1.19-1.56 (72 H, m; 36 × CH_2), 1.75-1.95 (8 H, m; 4 × CH_2), 2.72 (6 H, s, 2 × CH_3), 2.75 (6 H, s; 2 × CH_3), 2.92 (4 H, t, *J* = 7.7 Hz; 2 × CH_2), 4.18 (4 H, t, *J* = 7.0 Hz; 2 × NCH_2), 7.07-7.13 (2 H, m; 2 × Ar*H*), 7.18 (2 H, d, *J* = 7.0 Hz; 2 × Ar*H*), 7.25 (2 H, s; 2 × Ar*H*), 7.35 (2 H, s; 2 × Ar*H*), 7.60 (2 H, dd, *J* = 8.0, 1.3 Hz; 2 × Ar*H*), 7.69 (s, , 2 × Ar*H*), 7.81 (s, 2 H, 2 × Ar*H*), 8.13 (d, *J* = 8.0 Hz, 2 H; 2 × Ar*H*), 8.75 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, Tol-d_8) δ

ppm 14.2 (4 × *C*H_3), 20.0 (2 × *C*H_3), 20.2 (2 × *C*H_3), 23.15 (2 × *C*H_2), 23.16 (2 × *C*H_2), 27.9 (2 × *C*H_2), 29.0 (2 × *C*H_2), 29.86 (2 × *C*H_2), 29.91 (4 × *C*H_2), 30.07 (2 × *C*H_2), 30.14 (2 × *C*H_2), 30.16 (2 × *C*H_2), 30.20 (4 × *C*H_2), 30.24 (2 × *C*H_2), 30.27 (4 × *C*H_2), 30.32 (4 × *C*H_2), 30.4 (2 × *C*H_2), 31.2 (2 × *C*H_2), 32.46 (2 × *C*H_2), 32.51 (2 × *C*H_2), 43.7 (2 × N*C*H_2), 104.0 (2 × Ar*C*H), 106.0 (2 × Ar*C*H), 117.9 (2 × Ar*C*H), 119.4 (2 × Ar*C*H), 122.0 (2 × Ar*C*H), 123.2 (2 × Ar*C*H), 123.7 (2 × Ar*C*), 124.6 (2 × Ar*C*H), 125.7 (2 × Ar*C*), 125.9 (2 × Ar*C*), 126.9 (2 × Ar*C*H), 127.1 (2 × Ar*C*H), 127.7 (2 × ArC), 129.1 (2 × Ar*C*), 129.5 (2 × Ar*C*), 131.0 (2 × Ar*C*), 133.9 (2 × Ar*C*), 134.2 (2 × Ar*C*), 136.6 (2 × Ar*C*), 141.6 (2 × Ar*C*), 142.0 (2 × Ar*C*), 144.60 (2 × Ar*C*), 144.64 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2918, 2849, 1609, 1465, 1439; MS (MALDI$^+$): *m/z* (%) 1463 ([M]$^+$, 100).

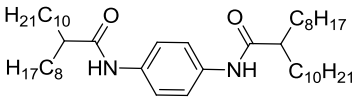
143 2-Octyldodecanoic acid



To a 3-necked flask fitted with an overhead stirrer was added H_5IO_4 (28.2 g, 0.124 mol) and MeCN (112 mL) followed by stirring at 0 °C for 15 min. 2-Octyldodecan-1-ol **142** (20.0 mL, 16.7 g, 55.9 mmol) was then added, followed immediately by pyridinium chlorochromate (240 mg, 1.12 mmol) at 0 °C. The solution was then allowed to warm to rt and stirred for 4 h. The reaction was then partially concentrated *in vacuo* to remove ~80 mL of MeCN before adding EtOAc (500 mL) and washing with brine / H_2O (1:1, 100 mL), a saturated aqueous solution of $NaHCO_3$ (100 mL), and brine (100 mL). The resulting solution was dried ($MgSO_4$), and concentrated *in vacuo* to yield pure **143** (16.9 g, 54.1 mmol, 97%) which was used immediately in the next step without any further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.89 (6 H, t, *J* = 6.7 Hz; 2 × C*H*$_3$), 1.20-1.39 (28 H, m, s; 14 × C*H*$_2$), 1.41-1.54 (2 H, m; C*H*$_2$), 1.56-1.70 (2 H, m; C*H*$_2$), 2.27-2.41 (1 H, m; C*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (2 × *C*H_3), 22.66 (*C*H_2), 22.69 (*C*H_2), 27.4 (2 × *C*H_2), 29.27 (*C*H_2), 29.34 (*C*H_2), 29.4 (*C*H_2), 29.5 (*C*H_2), 29.58 (2 × *C*H_2), 29.61 (2 × *C*H_2), 31.86 (*C*H_2), 31.92 (*C*H_2), 32.2 (2 × *C*H_2), 45.6 (1 × *C*H), 183.3 (1 × *C*=O); IR (ATR): ν_{max}/cm^{-1} 2914, 2850, 1694 (*C*=O), 1471, 1228; MS (ES$^+$): *m/z* (%) 335 ([M+Na]$^+$, 100), 349 (80), 392 (40), 648 (20); HRMS (ES$^+$): $C_{20}H_{40}O_2Na$ requires 335.2921, found 335.2917.

General Procedure M: Preparation of bis-amides

145 *N*,*N*'-(1,4-Phenylene)*bis*(2-octyldodecanamide)

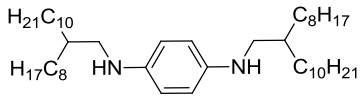


To a solution of **143** (16.9 g, 54.1 mmol) in CH_2Cl_2 (100 mL) was slowly added $SOCl_2$ (4.3 mL, 7.1 g, 59.3 mmol) at 0 °C. The resulting solution was allowed to warm to rt and stirred for 18 h, then concentrated *in vacuo* to yield crude 2-octyldodecanoyl chloride **144** which was used in the next step with no further purification.

The crude 2-octyldodecanoyl chloride **144** was dissolved in CH_2Cl_2 (20 mL) and then added by cannula to a solution of benzene-1,4-diamine (1.95 g, 18.0 mmol) and NEt_3 (7.54 mL, 5.47 g, 54.1 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The resulting mixture was allowed to warm to rt and then stirred for 18 h. The white precipitate was then collected by vacuum filtration and washed with EtOH (3 x 50 mL) to yield the poorly soluble crude *N*,*N*'-(1,4-phenylene)*bis*(2-octyldodecanamide) **145** (16.9 g) as an indistinguishable mixture of diastereoisomers which was used in the next step without further purification. A small sample for full characterisation was purified by recrystallisation from THF; mp (THF) 120-124° C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.79-1.01 (12 H, m; 4 × C*H*$_3$), 1.19-1.43 (56 H, m; 28 × C*H*$_2$), 1.44-1.58 (4 H, m; 2 × C*H*$_2$), 1.63-1.79 (4 H, m; 2 × C*H*$_2$), 2.10-2.25 (2 H, m; 2 × C*H*), 7.15 (2 H, s; 2 × N*H*), 7.45 (4 H, s; 4 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.98 (2 × *C*H$_3$), 14.01 (2 × *C*H$_3$), 22.62 (2 × *C*H$_2$), 22.64 (2 × *C*H$_2$), 27.7 (4 × *C*H$_2$), 29.25 (2 × *C*H$_2$), 29.30 (2 × *C*H$_2$), 29.47 (2 × *C*H$_2$) 29.52 (2 × *C*H$_2$), 29.59 (2 × *C*H$_2$), 29.62 (2 × *C*H$_2$), 29.8 (4 × *C*H$_2$), 31.86 (2 × *C*H$_2$), 31.91 (2 × *C*H$_2$), 33.2 (4 × *C*H$_2$), 49.1 (2 × *C*H), 120.8 (4 × Ar*C*H), 134.3 (2 × Ar*C*), 174.4 (2 × *C*=O); IR (ATR): ν_{max}/cm^{-1}: 3282 (NH), 2953, 2918, 2849, 1651 (C=O), 1538, 1518; MS (EI$^+$): *m/z* (%) 697 ([M]$^+$,100), 402 (70); HRMS (ES$^+$): $C_{46}H_{84}O_2N_2$ requires 696.6527, found 696.6506.

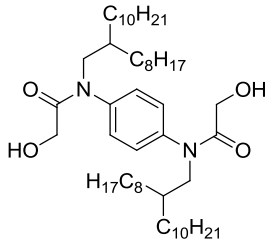
General procedure N: Preparation of bis-amines

146 *N*,*N*'-(1,4-Phenylene)*bis*(2-octyldodecanamide)



The crude *N*,*N*'-(1,4-phenylene)*bis*(2-octyldodecanamide) **145** (16.9 g) was suspended in THF (250 mL) and $LiAlH_4$ (3.8 g, 0.10 mol) was added portionwise at 0 °C (Caution!-Slow addition required to prevent formation of an expanding foam). The mixture was then heated at reflux for 18 h, then cooled and quenched carefully by addition of H_2O (5 mL) followed by aqueous NaOH (10 mL, 1 M) at 0 °C. The resulting precipitate was then removed by filtration, the filter cake washed with Et_2O (3 × 100 mL) and the solution concentrated *in vacuo.* The resulting oil was then redissolved in CH_2Cl_2 (50 mL) and washed with aqueous NaOH (50 mL, 0.1 M), dried (Na_2SO_4), and concentrated *in vacuo* to yield **146** (6.72 g, 10.0 mmol, 56% for three steps) as an unstable green oil which was immediately used without any further purification; ^{1}H NMR (500 MHz, C_6D_6) δ ppm 0.93 (12 H, t, *J* = 6.9 Hz; 4 × C*H*$_3$), 1.30–1.36 (64 H, m; 32 × C*H*$_2$), 1.57 (2 H, m; 2 × C*H*), 2.98 (4 H, d, *J* = 6.3 Hz; 2 × NC*H*$_2$), 6.62 (4 H, s; 4 × Ar*H*). ^{13}C NMR (125 MHz, C_6D_6) δ ppm 14.8 (4 × *C*H$_3$), 23.5, 27.6, 30.22, 30.57, 32.73, 32.99, 38.7 (32 × *C*H$_2$), 49.6 (2 × N*C*H$_2$), 115.3 (4 × Ar*C*H), 141.9 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2920, 2851, 1516, 1464, 1239; MS (MALDI$^+$): *m/z* (%) 669 ([M]$^+$, 100), 389 (60).

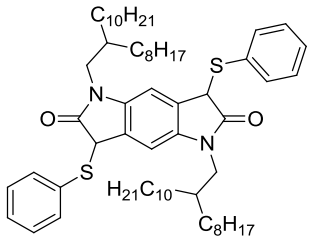
147 *N*,*N*'-(1,4-Phenylene)*bis*(2-hydroxy-*N*-(2-octyldodecyl)acetamide)



Following general procedures *D* and *H*, using **146** (6.72 g, 10.0 mmol), acetoxyacetyl chloride (2.59 mL, 24.1 mmol), and NEt_3 (3.22 mL, 23.1 mmol) in CH_2Cl_2 (100 mL), followed by K_2CO_3 (13.9 g, 101 mmol) in MeOH (90 mL), THF (100 mL), and H_2O (10 mL), stirring for 18 h gave crude **147**. Purification by flash column chromatography on silica gel eluting with a gradient of 5-60% EtOAc in hexane gave pure **147** (6.46 g, 8.23 mmol, 82%)

as a pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (12 H, t, J = 6.9 Hz; 4 × CH_3), 1.09-1.38 (64 H, m; 32 × CH_2), 1.48 (2 H, m; 2 × CH), 3.72 (4 H, d, J = 6.8 Hz; 2 × NCH_2), 3.78 (4 H, s; 2 × CH_2O), 7.25 (4 H, s; 4 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (4 × CH$_3$), 22.6, 26.2, 29.28, 29.33, 29.5, 29.57, 29.61, 30.0, 31.1, 31.86, 31.89 (32 × CH$_2$), 36.1 (2 × CH), 53.4 (2 × NCH$_2$), 60.6 (2 × CH$_2$O), 129.6 (4 × ArCH), 140.2 (2 × ArC), 171.8 (2 × C=O); IR (ATR): ν_{max}/cm^{-1} 3446 (OH), 2922, 2852, 1659 (C=O), 1510, 1457, 1385, 1289, 1094; MS (ES$^+$): *m/z* (%) 808 ([M+Na]$^+$, 100), 382 (40); HRMS (ES$^+$): $C_{50}H_{93}N_2O_4$ requires 785.7130, observed 785.7139.

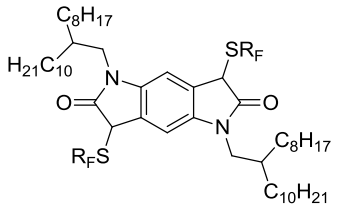
148 1,5-*bis*(2-Octyldodecyl)-3,7-*bis*(phenylthio)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione



Following general procedure *E*, using **147** (1.98 g, 2.52 mmol), oxalyl chloride (0.54 mL, 6.2 mmol), DMSO (0.80 mL, 11 mmol), and NEt_3 (3.93 mL, 28.2 mmol) in CH_2Cl_2 (60 mL), followed by thiophenol (0.58 mL, 5.6 mmol), $BF_3{\cdot}OEt_2$ (3.58 mL, 28.3 mmol), and TFAA (7.06 mL, 50.8 mmol), in CH_2Cl_2 (50 mL) gave crude **148** with >5:1 regioselectivity. Purification by flash column chromatography on silica gel eluting with a gradient of $CHCl_3$ gave pure **148** (1.12 g, 1.16 mmol, 46%) as a 1:1 mixture of diastereoisomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.80-0.96 (24 H, m; 8 × CH_3 [both diastereoisomers]), 1.11-1.38 (128 H, m; 64 × CH_2 [both diastereoisomers]), 1.64-1.80 (4 H, m; 4 × CH [both diastereoisomers]), 3.35-3.50 (8 H, m; 4 × NCH_2 [both diastereoisomers]), 4.56 (2 H, s; 2 × SCH [one diastereoisomer]), 4.57 (2 H, s; 2 × SCH [one diastereoisomer]), 6.69 (4 H, s; 4 × ArH [both diastereoisomers]), 7.09-7.32 (12 H, m; 12 × ArH [both diastereoisomers]), 7.40 (4 H, m, J = 8.5, 1.6 Hz; 4 × ArH [one diastereoisomer]), 7.42 (4 H, dd, J = 8.2, 1.3 Hz; 4 × ArH [one diastereoisomer]); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 13.99 (8 × CH$_3$ [both diastereoisomers]), 22.6, 26.1, 26.15, 26.18, 26.22, 29.47, 29.48, 29.53, 29.6, 29.90, 29.93, 31.13, 31.15, 31.23, 31.25, 31.8 (64 × CH$_2$ [both diastereoisomers]), 35.99 (2 × CH [one diastereoisomer]), 36.03 (2 × CH [one diastereoisomer]), 44.9 (4 × NCH$_2$ [both

diastereoisomers]), 49.3 (4 × S*C*H [both diastereoisomers]), 106.3 (4 × Ar*C*H [both diasteroeisomers]), 126.75 (2 × Ar*C* [one diastereoisomer]), 126.83 (2 × Ar*C* [one diastereoisomer]), 128.5 (2 × Ar*C*H [one diastereoisomer]), 128.57 (2 × Ar*C*H [one diastereoisomer]), 128.61 (4 × Ar*C*H [one diastereoisomer), 128.7 (4 × Ar*C*H [one diastereoisomer]), 131.0 (2 × Ar*C* [one diastereoisomer]), 131.1 (2 × Ar*C* [one diastereoisomer]), 133.9 (4 × Ar*C*H [one diastereoisomer]), 134.0 (4 × Ar*C*H [one diastereoisomer]), 139.1 (2 × Ar*C* [one diastereoisomer]), 139.2 (2 × Ar*C* [one diastereoisomer]), 173.4 (2 × *C*=O [one diastereoisomers]), 173.6 (2 × *C*=O [one diastereoisomer]); IR (ATR): ν_{max}/cm^{-1} 2922, 2853, 1699 (C=O), 1471, 1439, 1371,1346, 1337; *mass spectroscopy not informative*.

149 3,7-*bis*((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)thio)-1,5-*bis*(2-octyldodecyl)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione

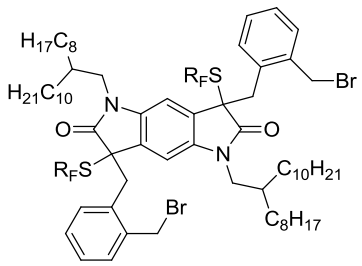


Following general procedure *E*, using **147** (0.544 g, 0.693 mmol), oxalyl chloride (0.13 mL, 1.49 mmol), DMSO (0.20 mL, 2.8 mmol), and NEt_3 (0.96 mL, 6.9 mmol) in CH_2Cl_2 (18 mL) followed by R_FSH (0.40 mL, 1.4 mmol), TFAA (0.87 mL, 6.26 mmol), $BF_3{\cdot}OEt_2$ (0.43 mL, 3.4 mmol) in CH_2Cl_2 (20 mL), and purification by FSPE eluting with 80% MeCN in H_2O, MeCN, and THF (product) gave **149** (crude mass = 1.07 g) as a waxy cream solid which was used immediately in the next step without any further purification. A small sample was purified for full characterisation by flash column chromatography on silica gel eluting with a gradient of 0-15% EtOAc in hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.78-0.95 (24 H, m; 8 × C*H*$_3$ [both diastereoisomers]), 1.08-1.53 (128 H, m; 64 × C*H*$_2$ [both diastereoisomers]), 1.80 -1.90 (4 H, m; 4 × C*H* [both diastereoisomers]), 2.32-2.58 (8 H, m; 4 × CF_2CH_2), 2.77-3.16 (8 H, m; 4 × SC*H*$_2$), 3.43-3.76 (8 H, m; 4 × NC*H*$_2$), 4.33 (2 H, s; 2 × C*H* [one diastereoisomer]), 4.34 (2 H, s; 2 × C*H* [one diastereoisomer]), 6.87 (2 H s; 2 × Ar*H* [one diastereoisomer]), 6.88 (2 H, s; 2 × Ar*H* [one diastereoisomer]); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.95 (4 × *C*H$_3$ [one diastereoisomer]), 13.99 (4 × *C*H$_3$ [one diastereoisomer]), 20.1 (2 × S*C*H$_2$ [one diastereoisomer]), 21.2 (2 × S*C*H$_2$ [one diastereoisomer]), 22.6, 26.2, 26.2,

26.3, 29.3, 29.3, 29.55, 29.60, 29.64, 29.97, 30.03, 31.89 (64 × CH_2 [both diastereoisomers]), 31.2-31.7 (m, 4 × CF_2CH_2 [both diastereoisomers]), 36.13 (2 × *C*H [one diastereoisomer]), 36.15 (2 × *C*H [one diastereoisomer]), 44.86 (4 × NCH_2 [both diastereoisomers]), 44.90 (2 × S*C*H [one diastereoisomer]), 45.11 (2 × S*C*H [one diastereoisomer]), 106.61 (2 × Ar*C*H [one diastereoisomer]) 106.64 (2 × Ar*C*H [one diastereoisomer]), 126.09 (2 × Ar*C* [one diastereoisomer]), 126.13 (2 × Ar*C* [one diastereoisomer]), 139.56 (2 × Ar*C* [one diastereoisomer]), 139.61 (2 × Ar*C*H [one diastereoisomer]), 174.50 (4 × *C*=O [both diastereoisomers]); IR (ATR): ν_{max} /cm^{-1} 2962, 2922, 2853, 1700, 1472, 1472, 1352, 1329; MS (AP^+): *m/z* (%) 1705 ($[M+H]^+$, 20) 1226 ($[M-SCH_2CH_2(CF_2)_7CF_3]^+$, 100).

General procedure O: Alkylation of bis-oxindoles

152 3-(2-(Bromomethyl)benzyl)-7-(2-(bromomethyl)phenethyl)-3,7-*bis*((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)-1,5-*bis*(2-octyldodecyl)-5,7-dihydropyrrolo[2,3-f]indole-2,6(1H,3H)-dione

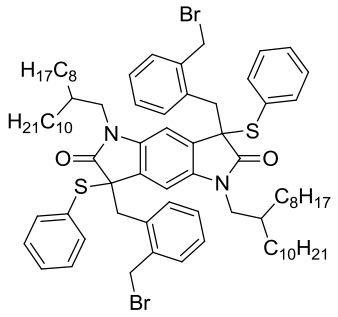


To a solution of **149** (crude mass = 1.07 g) in THF (20 mL) at -78 °C was added dropwise LDA (2.03 mL, 0.65 M, 1.3 mmol). The resulting suspension was stirred for 30 minutes at -78 °C then 1,2-*bis*(bromomethyl)benzene (1.66 g, 6.29 mmol) in THF (5 mL) was added rapidly via cannula. The solution was then stirred at -78 °C for a further three hours, allowed to warm and stirred for 16 h at rt. Hexane (50 mL) was added and the solution washed with H_2O (3 × 20 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield the crude product. Purification by FSPE eluting with 80% MeCN in H_2O, MeCN, and THF (product) gave crude **152** (crude mass = 1.14 g, ~1:1.6 mixture of diastereoisomers) as a brown oil which was used immediately in the next step without further purification. Purification of a small sample by flash column chromatography on silica gel eluting with 5% EtOAc in hexane, gave partial separation of the diastereoisomers for full

characterisation; Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (12 H, t, J = 6.7 Hz; 4 × CH_3), 0.96-1.40 (64 H, m; 32 × CH_2), 1.45-1.57 (2 H, m; 2 × CH), 2.36-2.50 (4 H, m; 2 × CF_2CH_2), 2.59-2.81 (4 H, m; 2 × SCH_2), 3.28 (2 H, dd, J = 14.1, 7.3 Hz; 2 × NC$H_A H_B$), 3.37 (2 H, d, J = 14.3 Hz; 2 × ArCH_AH$_B$), 3.49 (2 H, dd, J = 14.1, 7.3 Hz; 2 × NCH_AH$_B$), 3.65 (2 H, d, J = 14.3 Hz; 2 × ArC$H_A H_B$), 4.29 (2 H, d, J = 10.5 Hz; 2 × ArCH_AH$_B$), 4.71 (2 H, d, J = 10.5 Hz; 2 × ArC$H_A H_B$), 6.61 (2 H, s; 2 × ArH), 6.71 (2 H, d, J = 7.0 Hz; 2 × ArH), 6.90-6.98 (2 H, m; 2 × ArH), 7.07-7.14 (2 H, m; 2 × ArH), 7.19-7.25 (2 H, m; 2 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.00 (2 × CH$_3$), 14.04 (2 × CH$_3$), 19.7 (2 × SCH$_2$), 22.6, 26.0, 26.2, 29.3, 29.6, 29.7, 29.9, 30.1, 31.0, 31.2 (30 × CH$_2$), 31.0-31.4 (m, 2 × CF_2CH$_2$), 31.9 (2 × ArCH$_2$ and 2 × CH$_2$), 36.3 (2 × CH), 36.9 (2 × ArCH$_2$), 44.7 (2 × NCH$_2$), 55.3 (2 × C_{quat}), 106.0 (2 × ArCH), 128.0 (2 × ArCH), 128.1 (2 × ArCH), 129.5 (2 × ArC), 130.8 (2 × ArCH), 130.9 (2 × ArCH), 133.3 (2 × ArC), 137.1 (2 × ArC), 139.1 (2 × ArC), 175.7 (2 × C=O); IR (ATR): ν_{max}/cm^{-1} 2924, 2854, 1703 (C=O), 1473, 1347, 1238, 1205, 1147, 1134, 1114, 1086.

Minor diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (12 H, m; 4 × CH_3), 1.01-1.42 (64 H, m; 32 × CH_2), 1.53 (2 H, m; 2 × CH), 2.24 (4 H, m; CF_2CH_2), 2.65 (4 H, m; 2 × SCH_2), 3.29 (2 H, dd, J = 14.1, 6.5 Hz; 2 × ArCH_AH$_B$), 3.39 (2 H, d, J = 14.5 Hz; 2 × NCH_AH$_B$), 3.53 (2 H, dd, J = 14.1, 7.8 Hz; 2 × NC$H_A H_B$), 3.63 (2 H, d, J = 14.5 Hz; 2 × ArC$H_A H_B$), 4.14 (2 H, d, J = 10.5 Hz; 2 × ArCH_AH$_B$), 4.50 (2 H, d, J = 10.5 Hz; 2 × ArC$H_A H_B$), 6.57 (2 H, s; 2 × ArH), 6.86 (2 H, d, J = 7.3 Hz; 2 × ArH), 7.08-7.12 (2 H, m; 2 × ArH), 7.22 (4 H, m; 4 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 (2 × CH$_3$), 14.1 (2 × CH$_3$), 19.7-19.8 (m, 2 × SCH_2), 22.6, 26.0, 26.3, 29.4, 29.6, 29.7, 30.0, 30.2 (30 × CH$_2$), 30.8-31.4 (m, 2 × CF_2CH$_2$), 31.9 (2 × CH$_2$ and 2 × ArCH$_2$), 36.3 (2 × CH), 37.0 (2 × ArCH$_2$), 44.8 (2 × NCH$_2$), 55.4 (2 × C$_{quat}$), 106.1 (2 × ArCH), 128.1 (2 × ArCH), 128.2 (2 × ArCH), 129.6 (2 × ArC), 130.9 (2 × ArCH), 131.3 (2 × ArCH), 133.4 (2 × ArC), 137.1 (2 ×ArC), 138.9 (2 × ArC), 175.7 (2 × C=O).

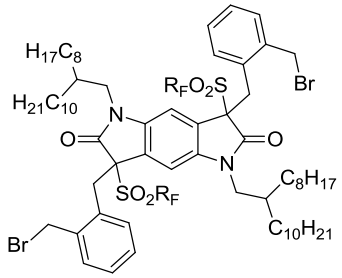
152a 3,7-*bis*(2-(Bromomethyl)benzyl)-1,5-*bis*(2-octyldodecyl)-3,7-*bis*(phenylthio)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione



Following general procedure *O*, using **148** (67 mg, 0.069 mmol), LDA (0.26 mL, 0.56 M, 0.15 mmol), 1,2-*bis*(bromomethyl)benzene (0.182 g, 0.689 mmol) in THF (0.5 mL), followed by purification by flash column chromatography on silica gel eluting with a gradient of 0-5% EtOAc in hexane gave **152a** (12 mg, 0.0090 mmol, 13%, ~1:1.4 mixture of diastereoisomers); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.79-0.94 (24 H, m; 8 × C*H*$_3$ [both diastereoisomers]), 1.05-1.37 (128 H, m; 64 × C*H*$_2$ [both diastereoisomers]), 1.39-1.52 (4 H, m; 4 × C*H* [both diastereoisomers]), 2.98 (2 H, dd, *J* = 13.9, 6.6 Hz; 2 × NC*H*$_A$H$_B$ [major diasteroisomer]), 2.97 (2 H, dd, *J* = 13.9, 6.4 Hz; 2 × NC*H*$_A$H$_B$ [minor diastereoisomer]), 3.32 (4 H, dd, *J* = 13.9, 7.8 Hz; 2 × NCH$_A$*H*$_B$ [major diastereoisomer]), 3.38-3.43 (2 H, m; 2 × NCH$_A$*H*$_B$ [minor diastereoisomer]), 3.40 (2 H, d, *J* = 14.5 Hz; 2 × ArC*H*$_A$H$_B$ [minor diastereoisomer]), 3.46 (2 H, d, *J* = 14.4 Hz; 2 × ArC*H*$_A$H$_B$ [major diastereoisomer]), 3.56 (2 H, d, *J* = 14.4 Hz; 2 × ArCH$_A$*H*$_B$ [major diastereoisomer]), 3.70 (2 H, d, *J* = 14.5 Hz; 2 × ArCH$_A$*H*$_B$ [minor diastereoisomer]), 4.11 (2 H, d, *J* = 10.6 Hz; 2 × ArC*H*$_A$H$_B$ [major diastereoisomer]), 4.13 (2 H, d, *J* = 10.3 Hz; 2 × ArC*H*$_A$H$_B$ [minor diastereoisomer]), 4.38 (2 H, d, *J* = 10.6 Hz; 2 × ArCH$_A$*H*$_B$ [major diastereoisomer]), 4.57 (2 H, d, *J* = 10.3 Hz; 2 × ArCH$_A$H$_B$ [minor diastereoisomer]), 6.30 (2 H, s; 2 × Ar*H* [major diastereoisomer]), 6.31 (2 H, s; 2 × Ar*H* [minor diastereoisomer]), 6.68 (2 H, d, *J* = 7.6 Hz; 2 × Ar*H* [minor diastereoisomer]), 6.76 (2 H, d, *J* = 7.3 Hz; 2 × Ar*H* [major diastereoisomer]), 6.95 (2 H, ddd, *J* = 7.6, 1.3 Hz; 2 × Ar*H* [minor diastereoisomer]), 7.04 (2 H, ddd, *J* = 7.5, 1.4 Hz; 2 × Ar*H* [major diastereoisomer]), 7.08-7.41 (28 H, m; 28 × Ar*H* [both diastereoisomers]); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (8 × *C*H$_3$ [both diastereoisomers]), 22.6, 25.9, 26.0, 26.3, 26.4, 29.29, 29.33, 29.59, 29.63, 29.7, 29.9, 29.98, 30.02, 30.1, 30.6, 30.9, 31.0, 31.1, 31.8 (64 × *C*H$_2$ [both diastereoisomers]), 32.1 (2 × Ar*C*H$_2$ [one diastereoisomer]), 32.2 (2 × Ar*C*H$_2$ [one diastereoisomer]), 36.0 (2 × *C*H [one diastereoisomer]), 36.2 (2 × *C*H [one diastereoisomer]), 36.6 (2 × Ar*C*H$_2$ [one diastereoisomer]), 37.1 (2 × Ar*C*H$_2$ [one

diastereoisomer]), 44.47 (2 × N*C*H_2 [one diastereoisomer]), 44.53 (2 × N*C*H_2 [one diastereoisomer]), 58.9 (2 × C_{quat} [one diastereoisomer]), 59.4 (2 × C_{quat} [one diastereoisomer]), 105.97 (2 × Ar*C*H [one diastereoisomer]), 106.00 (2 × Ar*C*H [one diastereoisomer]), 127.6 (2 × Ar*C*H [one diastereoisomer]), 127.7 (2 × Ar*C*H [one diastereoisomer]), 128.0 (2 × Ar*C*H [one diastereoisomer]), 128.1 (2 × Ar*C*H [one diastereoisomer]), 128.49 (8 × Ar*C*H [both diastereoisomers]), 128.51 (2 × Ar*C*H [one diastereoisomer]), 129.3 (2 × Ar*C* [one diastereoisomer]), 129.39 (2 × Ar*C* [one diasteroeisomer]), 129.42 (2 × Ar*C* [one diastereoisomer]), 129.6 (2 × Ar*C* [one diastereoisomer]), 129.7 (2 × Ar*C*H [one diastereoisomer]), 129.8 (2 × Ar*C*H [one diastereoisomer]), 130.6 (2 × Ar*C*H [both diastereoisomers]), 130.7 (4 × Ar*C*H [one diastereoisomers]), 130.9 (2 × Ar*C*H), 134.0 (2 × Ar*C* [one diastereoisomer]), 134.1 (2 × Ar*C* [one diastereoisomer]), 136.6 (4 × Ar*C*H [one diastereoisomer]), 137.09 (2 × Ar*C*H [one diastereoisomer]), 137.12 (2 × Ar*C* [one diastereoisomer]), 137.2 (2 × Ar*C* [one diastereoisomer]), 138.2 (2 × Ar*C* [one diastereoisomer]), 138.3 (2 × Ar*C* [one diastereoisomer]), 174.8 (2 × *C*=O [one diastereoisomer]), 175.0 (2 × *C*=O [one diastereoisomer]); IR (ATR): ν_{max}/cm^{-1} 2923, 2853 1699 (C=O), 1472, 1439, 1346, 1160, 1127; MS (ES^+): *m/z* (%) 1332 ($[M+H]^+$, 20), 1252 ($[M-Br]^+$, 40), 723 (60), 450 (50), 413 (50), 391 (50), 235 (100), 199 (60), 168 (70).

152b 3-(2-(Bromomethyl)benzyl)-7-(2-(bromomethyl)phenethyl)-3,7-*bis*((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)-1,5-*bis*(2-octyldodecyl)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione

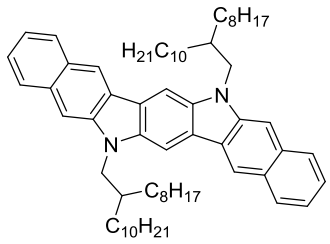


To a solution of **152** (major diastereoisomer from alkylation) (79 mg, 0.038 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added purified and dried *m*CPBA (33 mg, 0.19 mmol). The solution was then warmed to rt and stirred for 3 h. CH_2Cl_2 (10 mL) was added and the solution washed with a saturated aqueous solution of $NaHCO_3$ (3 × 5 mL), dried (Na_2SO_4), and concentrated *in vacuo* to give the crude product. Purification by FSPE yielded **152b** (81 mg, 0.038, 99%) as a pale brown oil; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (6 H, t, *J* =

6.8 Hz; 2 × CH_3), 0.89 (6 H, t, *J* = 6.5 Hz; 2 × CH_3), 1.16-1.29 (64 H, m; 32 × CH_2), 1.51-1.67 (2 H, m; 2 × C*H*), 2.61-2.88 (4 H, m; 2 × CF_2CH_2), 3.37-3.53 (4 H, m; 2 × NCH_2), 3.57-3.67 (2 H, m; 2 × $SO_2CH_AH_B$), 3.72 (2 H, d, *J* = 14.2 Hz; 2 × ArCH_AH_B), 3.90-4.01 (2 H, m; 2 × $SO_2CH_AH_B$), 4.06 (2 H, d, *J* = 14.2 Hz; 2 × ArCH_AH_B), 4.35 (2 H, d, *J* = 10.7 Hz; 2 × ArCH_AH_B), 4.85 (2 H, d, *J* = 10.7 Hz; 2 × ArCH_AH_B), 6.60 (2 H, d, *J* = 7.5 Hz; 2 × Ar*H*), 6.96 (2 H, ddd, *J* = 7.6, 7.6, 1.2 Hz; 2 × Ar*H*), 7.12 (2 H, ddd, *J* = 7.6, 7.6 1.2 Hz; 2 × Ar*H*), 7.15 (2 H, s; 2 × Ar*H*), 7.24 (2 H, dd, *J* = 7.6, 1.2 Hz; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0, 14.1 (4 × *C*H_3), 22.7 (4 × *C*H_2), 24.1 (t, *J* = 22 Hz; 2 × CF_2CH_2), 26.1, 26.3, 29.31, 29.34, 29.4, 29.56, 29.62, 29.7, 29.9, 30.0, 30.98, 31.04, 31.8, 31.87, 31.90, 32.7, 36.36 (28 × *C*H_2), 36.38 (2 × *C*H), 40.4 (2 × SO_2CH_2), 45.4 (2 × N*C*H_2), 74.9 (2 × C_{quat}), 108.6 (2 × ArCH), 123.6 (2 × Ar*C*), 128.6 (2 × Ar*C*H), 128.9 (2 × Ar*C*H), 130.7 (2 × Ar*C*H), 131.06 (2 × Ar*C*H), 131.09 (2 × ArC), 136.7 (2 × Ar*C*), 141.1 (2 × Ar*C*), 169.6 (2 × *C*=O); IR (ATR): ν_{max}/cm^{-1} 2925, 2855, 1703 (C=O), 1473, 1333, 1236, 1207, 1144; MS (AP$^+$): *m/z* (%): 2136 ([M+H]$^+$, 30), 1623 (50), 1399 (50), 114 (55), 954 (100).

General procedure P: Preparation of dibenzoindolo[3,2-b]carbazoles

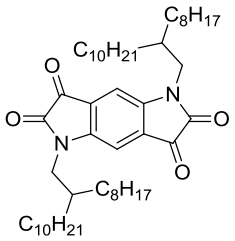
DBIC-1 6,14-*bis*(2-Octyldodecyl)-6,14-dihydrobenzo[*b*]benzo[5,6]indolo[2,3-*h*]carbazole



To a solution of **152** (crude mass = 1.14 g) in THF (14.9 mL, degassed by sparging with N_2) was added hexafluoroisopropanol (0.17 mL, 1.6 mmol), the solution was then heated to 60 °C and SmI_2 (55 mL, ~ 0.1 M in THF, 5.5 mmol) added immediately over 1 min. The mixture was then stirred for a further 1 min at 60 °C then allowed to cool to rt (5 min), the flask was then opened to air and the solution left to decolourise. A saturated solution of $NaHCO_3$ (100 mL) was then added and the mixture extracted with CH_2Cl_2 (5 × 50 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield the crude non-aromatised intermediate. The crude intermediate was dissolved in CH_2Cl_2 (15 mL) and *p*-

benzoquinone (0.48 g, 4.4 mmol) added, and the mixture was then stirred for 2 h at rt. Hexane (100 mL) was added and the mixture washed with an aqueous 1.0 M solution of NaOH (100 mL × 2), dried (Na_2SO_4), and concentrated *in vacuo* to yield the crude product. Purification by 2 × flash column chromatography on silica gel eluting with a gradient of 0-10% toluene in hexane and trituration of the product with MeCN gave **DBIC-1** (0.108 g, 0.118 mmol, 17% from hydroxyamide **147** [5 steps]) as a bright yellow solid and **161** (0.170 g, 0.177 mmol, 25% based on HSR_F used in Pummerer cyclisation) as a colourless solid; ^{1}H NMR (500 MHz, C_6D_6) δ ppm 0.84-0.98 (12 H, m; 4 × CH_3), 1.05-1.34 (52 H, m; 26 × CH_2), 1.37 -1.43 (12 H, m; 6 × CH_2), 2.31-2.39 (2 H, d, *J* = 5.4 Hz; 2 × *CH*), 3.99 (4 H d, *J* = 7.6 Hz; 2 × NCH_2), 7.43 (2 H, ddd, *J* = 7.4, 7.4, 0.9 Hz; 2 × Ar*H*), 7.50 (2 H, ddd, *J* = 7.4, 7.4, 0.9 Hz; 2 × Ar*H*), 7.73 (2 H, s; 2 × Ar*H*), 8.07 (2 H d, *J* = 7.9 Hz; 2 × Ar*H*), 8.07 (2 H, s; 2 × Ar*H*), 8.12 (2 H, d, J = 7.9 Hz; 2 × Ar*H*), 8.67 (2 H, s; 2 × Ar*H*); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 14.7 (2 × *C*H_3), 14.8 (2 × *C*H_3), 23.4, 23.5, 27.3, 30.16, 30.19, 30.4, 30.49, 30.52, 30.8, 32.67, 32.69 (32 × *C*H_2), 37.9 (2 × *C*H), 48.4 (2 × N*C*H_2), 100.4 (2 × Ar*C*H), 103.9 (2 × Ar*C*H), 119.4 (2 × Ar*C*H), 123.1 (2 × Ar*C*H), 124.2 (2 × Ar*C*), 125.9 (2 × Ar*C*H), 126.3 (2 × Ar*C*), 127.9 (2 × Ar*C*H), 128.7 (2 × Ar*C*), 129.3 (2 × Ar*C*H), 133.9 (2 × Ar*C*), 139.3 (2 × Ar*C*), 142.8 (2 × Ar*C*); IR (ATR): ν_{max} /cm^{-1} 2954, 2919, 2851, 1630, 1504, 1467, 1445, 1376, 1352; MS (MALDI$^+$): *m/z* (%) 918 ([M+H]$^+$, 100).

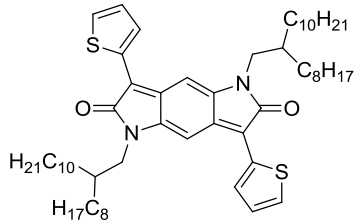
BPTa 1,5-*bis*(2-Octyldodecyl)pyrrolo[2,3-*f*]indole-2,3,6,7(1H,5H)-tetraone



Following general procedure *E*, using oxalyl chloride (0.85 mL, 9.76 mmol) in CH_2Cl_2 (30 mL), DMSO (1.26 mL, 5.1 mmol) in CH_2Cl_2 (10 mL), **147** (3.48 g, 4.43 mmol) in CH_2Cl_2 (10 mL), and NEt_3 (6.2 mL, mmol), followed by thiophenol (0.91 mL, 8.9 mmol), TFAA (5.5 mL, 40 mmol), and $BF_3{\cdot}OEt_2$ (2.8 mL, 22 mmol) in CH_2Cl_2 (50 mL) gave **148** as a deep red oil (crude mass, 4.13 g), which was used without further purification.

To a portion of crude **148** (1.66 g) was added THF (44 mL), H_2O (7.4 mL), and CAN (7.53 g, 13.7 mmol). The solution was stirred for 24 h at rt then concentrated *in vacuo*. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in hexane yielded the pure product **BPTa** (0.96 g, 1.2 mmol, 69% for 3 steps) as a blue oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.79-0.95 (12 H, m; 4 × C*H*$_3$), 1.15-1.45 (62 H, m; 30 × C*H*$_2$ and 2 × C*H*), 1.55-2.17 (4 H, m; 2 × C*H*$_2$), 3.62 (4 H, d, *J* = 7.6 Hz; 2 × NC*H*$_2$), 7.13 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (4 × *C*H$_3$), 22.6, 22.7, 26.2, 29.2, 29.3, 29.5, 29.6, 29.9, 31.3, 31.8, 31.9, 35.9 (32 × *C*H$_2$ and 2 × *C*H), 45.3 (2 × N*C*H$_2$), 106.9 (2 × Ar*C*H), 123.1 (2 × Ar*C*), 147.7 (2 × Ar*C*), 157.0 (2 × *C*=O), 183.2 (2 × *C*=O); IR (ATR): ν_{max}/cm^{-1} 2921, 2852, 1729 (C=O), 1465, 1159; MS (APCI$^+$): *m/z* (%) 778 ([M+H]$^+$, 100).

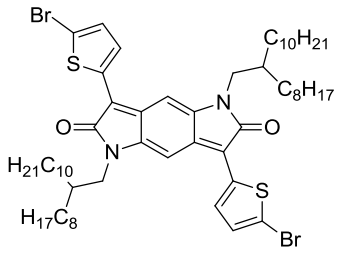
BPTb 1,5-*bis*(2-Octyldodecyl)-3,7-di(thiophen-2-yl)pyrrolo[2,3-*f*]indole-2,6(1H,5H)-dione



To a solution of **BPTa** (0.956 g, 1.23 mmol) in THF (26 mL) under N_2 at -78 °C was added dropwise thienyl magnesium bromide (3.69 mL, 1 M, 3.69 mmol). The resulting solution was stirred at -78 °C for 5 h, quenched with H_2O (10 mL), and the mixture was then allowed to warm to rt and hexane (50 mL) added. The solution was washed with a saturated aqueous solution of $NaHCO_3$ (3 × 20 mL), dried (Na_2SO_4), and concentrated *in vacuo*. To a suspension of the crude intermediate (1.05 g) in AcOH (100 mL) was added NaI (2.34 g, 15.6 mmol), and $NaPO_2H_2$ (1.65 g, 15.7 mmol), then the suspension refluxed for 3 h under N_2 in the absence of light. The solution was then cooled to rt and hexane (100 mL) added. The solution was washed with H_2O (5 × 100 mL), dried (Na_2SO_4), and concentrated *in vacuo*. To a solution of the crude intermediate (1.09 g) in CH_2Cl_2 (20 mL), was added DDQ (0.30 g, 1.3 mmol), followed by stirring at rt for 2 h. Hexane (100 mL) was then added and the solution washed with a saturated aqueous solution of $NaHCO_3$ (3 × 40 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 40% toluene in hexane gave pure **BPTb** (0.392 g, 0.430 mmol, 35% for 3 steps) as an amorphous magenta

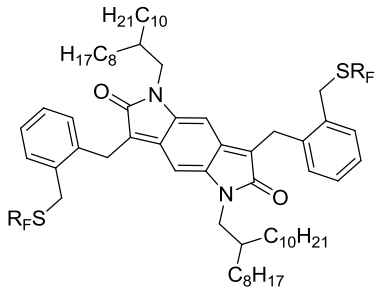
solid; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.84-1.01 (12 H, m; 4 × CH_3), 1.21-1.56 (64 H, m; 32 × CH_2), 1.87-2.07 (2 H, m; 2 × C*H*), 3.53 (4 H, d, *J* = 7.0 Hz; 2 × NCH_2), 6.61 (2 H, s; 2 × Ar*H*), 6.82 (2 H, dd, *J* = 5.1, 3.8 Hz; 2 × Ar*H*), 7.01 (2 H, dd, *J* = 5.1, 1.0 Hz; 2 × Ar*H*), 8.40 (2 H, dd, *J* = 3.8, 1.0 Hz; 2 × Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 14.1 (4 × *C*H_3), 22.7, 26.8, 29.3, 29.3, 29.6, 29.7, 29.7, 30.0, 31.8, 31.9 (32 × *C*H_2), 37.2 (2 × *C*H), 44.1 (2 × N*C*H_2), 98.4 (2 × Ar*C*H), 121.0 (2 × Ar*C*), 128.3 (2 × Ar*C*H), 128.9 (2 × Ar*C*H), 129.8 (2 × Ar*C*H), 129.9 (2 × Ar*C*), 134.5 (2 × Ar*C*), 143.6 (2 × Ar*C*), 169.1 (2 × *C*=O); IR (ATR): ν_{max}/cm^{-1} 2924, 2854, 1694 (C=O), 1424, 697; MS (APCI$^+$): *m/z* (%) 912 ([M+H]$^+$, 100%).

BPT 3,7-*bis*(5-Bromothiophen-2-yl)-1,5-*bis*(2-octyldodecyl)pyrrolo[2,3-*f*]indole-2,6(1H,5H)-dione



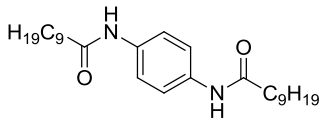
To a solution of **BPTb** (0.152 g, 0.167 mmol) in THF (2 mL) at 0 °C, in the absence of light, was added NBS (0.065 g, 0.367 mmol). After stirring for 16 h at rt, the solvent was removed *in vacuo*. Purification by flash column chromatography on silica gel eluting with 30-50% toluene in hexane gave the desired product (0.170 g, 0.159 mmol, 95%) as an amorphous purple solid; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.90-0.94 (12 H, m; 4 × CH_3), 1.36 (64 H, m; 32 × CH_2), 1.90 (2 H, m; 2 × C*H*), 3.48 (4 H, d, *J* = 7.3 Hz; 2 × NCH_2), 6.37 (2 H, s; 2 × Ar*H*), 6.75 (2 H, d, *J* = 4.2 Hz; 2 × Ar*H*), 7.92 (2 H, d, *J* = 4.2 Hz; 2 × Ar*H*); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 14.8 (4 × *C*H_3), 23.5, 27.6, 30.2, 30.46, 30.51, 30.52, 30.6, 30.9, 32.70, 32.73 (32 × *C*H_2), 38.0 (2 × *C*H), 44.2 (2 × N*C*H_2), 98.4 (2 × Ar*C*H), 118.1 (2 × Ar*C*), 120.4 (2 × Ar*C*), 130.6 (2 × Ar*C*H), 131.1 (2 × Ar*C*H), 132.0 (2 × Ar*C*), 137.5 (2 × Ar*C*), 144.6 (2 × Ar*C*), 169.1 (2 × *C*=O); IR (ATR): ν_{max}/cm^{-1} 2922, 2852, 1694 (C=O), 1411; MS (MALDI$^+$): m/z (%) 1071 ([M]$^+$, 100).

153 3,7-*bis*(2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)thio)methyl)benzyl)-1,5-*bis*(2-octyldodecyl)pyrrolo[2,3-*f*]indole-2,6(1H,5H)-dione



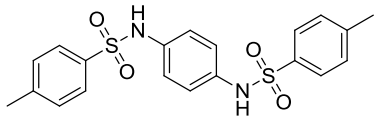
To a solution of **152** (47 mg, 0.023 mmol) in degassed THF (0.6 mL) was added trifluoroethanol (0.50 mL of a 0.01373 g/mL solution in degassed THF, 0.069 mmol). The solution was then cooled to -78 °C and SmI_2 (2.3 mL, 0.1 M solution in THF, 0.23 mmol) added dropwise over 5 min. The solution was stirred at -78 °C for a further 3 h, then quenched at -78 °C by passing compressed air through the reaction mixture. The suspension was then warmed to rt and a saturated aqueous solution of $NaHCO_3$ (20 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried (Na_2SO_4), and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with a gradient of 50-70% toluene in hexane gave the pure product **153** (29 mg, 0.015 mmol, 67%) as a dark brown amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (12 H, t, J = 6.7 Hz; 4 × CH_3), 0.97-1.49 (64 H, m; 32 × CH_2), 1.59 (2 H, s; 2 × CH), 2.19-2.41 (4 H, m; 2 × CF_2CH_2), 2.61-2.74 (4 H, m; 2 × $CH_2CH_2CF_2$), 3.24 (4 H, d, J = 7.5 Hz; 2 × NCH_2), 3.79 (4 H, s; 2 × ArCH_2), 3.93 (4 H, s; 2 × ArCH_2), 5.44 (2 H, s; 2 × C=CH), 7.22 (8 H, s; 8 × ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (4 × CH$_3$), 22.5 (t, J = 4 Hz, 2 × SCH$_2$), 28.0 (2 × ArCH$_2$), 22.7, 26.3, 29.4, 29.6, 29.7, 30.1, 31.3, 31.9 (32 × CH$_2$ and 2 × CF_2CH_2), 34.4 (2 × ArCH$_2$), 36.6 (2 × CH), 44.0 (2 × NCH$_2$), 96.1 (2 × C=CH), 127.1 (2 × ArCH), 127.9 (2 × ArCH), 129.0 (2 × C=C), 130.5 (2 × ArCH), 130.7 (2 × ArCH), 135.4 (2 × C=C), 135.9 (2 × C=C), 137.0 (2 × C=C), 143.0 (2 × C=C), 170.8 (2 × C=O); IR (ATR): ν_{max}/cm^{-1} 2923, 2853, 1694 (C=O), 1591, 1469; MS (APCI$^+$): *m/z* (%) 1912 ([M+H]$^+$, 100), 936 (85), 342 (75), 219 (90).

155a *N*,*N*'-(1,4-Phenylene)*bis*(decanamide)



Following general procedure *M*, using *p*-phenylenediamine (0.530 g, 4.90 mmol), decanoyl chloride (3.03 mL, 14.7 mmol), and NEt_3 (2.1 mL, 15 mmol) in CH_2Cl_2 (30 mL) gave the poorly soluble crude material **155a** (2.04 g) which was used immediately in the next step without any further purification. A small sample was purified by recrystallisation from THF for characterisation, mp (THF) 202-204 °C; ; IR (ATR): ν_{max}/cm^{-1}: 3320 (NH), 2954, 2917, 2872, 2847, 1650 (C=O), 1565, 1547, 1520, 1471, 1405, 1311, 1328, 1257, 1237, 1194, 1114; MS (ES^+): *m/z* (%) 440 ($[M+Na]^+$, 100), 411 (20), 256 (60); HRMS (ES^+): $C_{26}H_{44}N_2O_2Na_1$ requires 439.3295, found 439.3298.

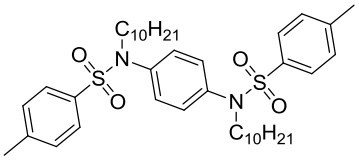
155b *N*,*N*'-(1,4-Phenylene)*bis*(4-methylbenzenesulfonamide)[289,290]



To a mixture of *p*-phenylenediamine (0.858 g, 7.94 mmol) in pyridine (10 mL) was added tosyl chloride (3.02 g, 15.8 mmol). The mixture was then heated at reflux for 1 h, the reaction cooled to rt, and ice added to precipitate the desired product. The product was isolated by vacuum filtration, washed with H_2O, and further dried under high vacuum to give the crude product **155b** (3.51 g) as a grey solid which was used immediately in the next step without further purification, mp (H_2O) 274-276 °C [Lit 276 °C][291]; ^1H NMR (500 MHz, Acetone-d_6) δ ppm 2.33 (6 H, s; 2 × CH_3), 7.03 (4 H, s; 4 × Ar*H*), 7.26 (4 H, d, *J* = 8.2 Hz; 4 × Ar*H*), 7.55 (4 H, d, *J* = 8.2 Hz; 4 × Ar*H*), 8.78 (2 H, s; 2 × N*H*); ^{13}C NMR (126 MHz, Acetone-d_6) δ ppm 21.9 (2 × *C*H_3), 123.4 (4 × Ar*C*H), 128.5 (4 × Ar*C*H), 130.8 (4 × Ar*C*H), 136.0 (2 × Ar*C*), 138.4 (2 × Ar*C*), 144.9 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3215(NH), 1598, 1504, 1451, 1376, 1391, 1307, 1272, 1211, 1187, 1153, 1091, 1016.

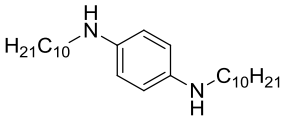
[Data consistent with literature]

155c *N*,*N*'-(1,4-Phenylene)*bis*(*N*-decyl-4-methylbenzenesulfonamide)[290]



To a solution of **155b** (3.09 g) in DMF (100 mL) was added iododecane (6.3 mL, 30 mmol) and K_2CO_3 (4.10 g, 29.7 mmol). The resulting suspension was stirred for 18 h, then EtOAc (100 mL) added and the solution washed with H_2O (100 mL) and brine (4 × 100mL), dried ($MgSO_4$), and concentrated *in vacuo* to give the crude product **155c** as a yellow solid which was used immediately in the next step without further purification. A small sample was purified by trituration with pentane, mp (pentane) 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.88 (6 H, t, *J* = 6.6 Hz; 2 × C*H*$_3$), 1.18-1.34 (28 H, m; 14 × C*H*$_2$), 1.36-1.45 (4 H, m; 2 × C*H*$_2$), 2.43 (6 H, s; 2 × C*H*$_3$), 3.50 (4 H, t, *J* = 6.9 Hz; 2 × NC*H*$_2$), 6.98 (4 H, s; 4 × Ar*H*), 7.25 (4 H, d, *J* = 8.1 Hz; 4 × Ar*H*), 7.44 (4 H, d, *J* = 8.1 Hz; 4 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.1 (2 × CH_2CH_3), 21.6 (2 × *C*H$_3$), 22.7 (2 × *C*H$_2$), 26.4 (2 × *C*H$_2$), 28.2 (2 × *C*H$_2$), 29.1 (2 × *C*H$_2$), 29.3 (2 × *C*H$_2$), 29.5 (4 × *C*H$_2$), 31.9 (2 × *C*H$_2$), 50.3 (2 × N*C*H$_2$), 127.6 (4 × Ar*C*H), 129.0 (4 × Ar*C*H), 129.4 (4 × Ar*C*H), 135.0 (2 × Ar*C*), 138.4 (2 × Ar*C*), 143.5 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2953, 2918, 2849, 1506, 1468, 1342, 1308, 1285, 1274, 1186, 1162, 1146, 1092, 1072; MS (ES$^-$): *m/z* (%) 731 ([M+Cl]$^-$, 80), 241 (100); HRMS (ES$^+$): $C_{40}H_{60}N_2O_4S_2Na$ requires 719.3887, found 719.3884.

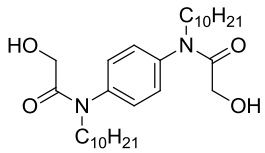
155 *N*1,*N*4-Didecylbenzene-1,4-diamine



Following general procedure *O*, using crude **155a** (2.04 g), and $LiAlH_4$ (1.1 g, 29 mmol) in THF (100 mL) gave crude diamine **155** (1.61 g) which was used immediately in the next step without any further purification, mp (THF) 65-69 °C; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.93 (6 H, t, *J* = 6.9 Hz; 2 × C*H*$_3$), 1.17-1.47 (32 H, m 16 × C*H*$_2$), 2.95 (4 H, t, *J* = 7.0 Hz; 2 × NC*H*$_2$), 6.60 (4 H, s; 4 × Ar*H*); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 14.7 (2 × *C*H$_3$), 23.5 (2 × *C*H$_2$), 28.0 (2 × *C*H$_2$), 30.2 (2 × *C*H$_2$), 30.3 (2 × *C*H$_2$), 30.40 (2 × *C*H$_2$), 30.44 (2 × *C*H$_2$), 30.6 (2 × *C*H$_2$), 32.7 (2 × *C*H$_2$), 45.8 (2 × N*C*H$_2$), 115.3 (4 × Ar*C*H), 141.8 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 3362 (NH), 2954, 2916, 2848, 1525, 1498, 1486, 1470, 1458, 1404, 1296, 1279, 1248, 1228, 1138, 1095, 1073.

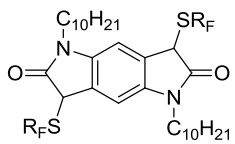
Alternative procedure starting from **155c**: A suspension of **155c** in H_2SO_4 (10 mL) and acetic acid (20 mL) was refluxed for 3 h. The solution was cooled to rt then carefully poured onto ice and basified (pH 8-10) by the addition of 10 M NaOH. The mixture was then extracted with Et_2O (3 × 300 ml), dried (Na_2SO_4) and concentrated *in vacuo* to yield the product **155** (1.57 g, 4.04 mmol, 58% for three steps) which was used immediately in the next step without further purification.

156 *N*,*N*'-(1,4-Phenylene)*bis*(*N*-decyl-2-hydroxyacetamide)



Following general procedures *D* and *H*, using crude diamine **155** (1.61 g), acetoxyl acetyl chloride (1.07 mL, 9.95 mmol), and NEt_3 (1.4 mL, 10 mmol) in CH_2Cl_2 (50 mL), followed by K_2CO_3 (5.7 g, 41 mmol) in MeOH (18 mL), H_2O (2 mL) and THF (20 mL) gave the crude hydroxyamide **156**. Purification by flash column chromatography on silica gel eluting with 50% EtOAc in hexane gave pure **156** (1.71 g, 3.39 mmol, 69% for 4 steps) as a colourless solid, mp (hexane) 105-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.81 (6 H, t, J = 6.7 Hz; 2 × CH_3), 1.05-1.33 (28 H, m; 14 × CH_2), 1.47 (4 H, s; 2 × CH_2), 3.40 (2 H, br. s; 2 × O*H*), 3.65-3.76 (8 H, m; 2 × NCH_2 and 2 × OCH_2), 7.21 (4 H, s; 4 × Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.9 (2 × *C*H_3), 22.4, 26.5, 27.5, 29.0, 29.26, 29.27, 31.6 (16 × *C*H_2), 49.5 (2 × N*C*H_2), 60.4 (2 × O*C*H_2), 129.6 (4 × Ar*C*H), 139.9 (2 × Ar*C*), 171.2 (2 × *C*=O); IR (ATR): ν_{max}/cm^{-1} 3338 (OH), 2957, 2917, 2850, 1648 (C=O), 1507, 1449, 1288; MS (ES$^-$): *m/z* (%) 539 ([M+Cl]$^-$, 100); HRMS (EI$^+$): $C_{30}H_{52}N_2O_4$ requires 504.3922, found 504.3917; Elemental analysis: Expected, %: C, 71.39; H, 10.38; N, 5.55; Found, %: C, 71.45; H, 10.36; N, 5.55.

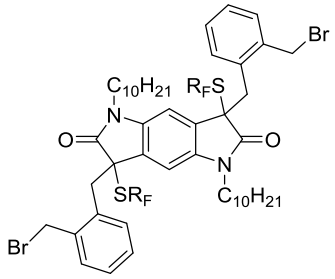
157 1,5-Didecyl-3,7-*bis*((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione



Following general procedure *E*, using **156** (0.442 g, 0.876 mmol), oxalyl chloride (0.17 mL, 1.9 mmol), DMSO (0.25 mL, 3.5 mmol), and NEt_3 (1.22 mL, 8.75 mmol) in CH_2Cl_2 (22 mL),

followed by R_FSH (0.50 mL, 1.7 mmol), TFAA (1.10 mL, 7.91 mmol), $BF_3{\cdot}OEt_2$ (0.55 mL, 4.4 mmol) in CH_2Cl_2 (25 mL) gave **157** (Crude mass = 1.06 g, >5:1 regioselectivity as a 1:1 mixture of diastereoisomers) after purification by FSPE eluting with 80% MeCN in H_2O, MeCN, and THF (product). A small sample was further purified by flash column chromatography on silica gel eluting with 80% CH_2Cl_2 in hexane to provide material as a 1:1 mixture of diastereoisomers for full characterisation; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.87 (12 H, t, *J* = 6.9 Hz; 4 × C*H*$_3$ [both diastereoisomers]), 1.16-1.43 (56 H, m; 28 × C*H*$_2$ [both diastereoisomers]), 1.60-1.72 (8 H, m; 4 × C*H*$_2$ [both diastereoisomers]), 2.31-2.54 (8 H, m; 4 × CF_2C*H*$_2$ [both diastereoisomers]), 2.75-3.06 (8 H, m; 4 × SC*H*$_2$ [both diastereoisomers]), 3.64 (2 H, dt, *J* = 14.2, 7.3 Hz; NC*H*$_A$H$_B$ [one diastereoisomer]), 3.71 (4 H, t, *J* = 7.4 Hz; 2 × NC*H*$_2$ [one diastereoisomer]), 3.79 (2 H, dt, *J* = 14.5, 7.3 Hz; 2 × NCH$_A$*H*$_B$ [one diastereoisomer]), 4.33 (2 H, s; SC*H* [one diastereoisomer]), 4.34 (2 H, s; SC*H* [one diastereoisomer]), 6.92 (2 H, s; 2 × Ar*H* [one diastereoisomer]), 6.92 (2 H, s; 2 × Ar*H* [one diastereoisomer]); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 14.0 (4 × *C*H$_3$ [both diastereoisomers]), 20.8 (m, 2 × S*C*H$_2$ [one diastereoisomer), 21.0 (m, 2 × S*C*H$_2$ [one diastereoisomer]), 22.6 (4 × *C*H$_2$ [both diastereoisomers]), 26.89 (2 × *C*H$_2$ [one diastereoisomer]), 26.91 (2 × *C*H$_2$ [one diastereoisomer), 27.4 (4 × *C*H$_2$ both diastereoisomers]), 29.2 (4 × *C*H$_2$ [both diastereoisomers]), 29.3 (4 × *C*H$_2$ [both diastereoisomers]), 29.48 (4 × *C*H$_2$ [both diastereoisomers]), 29.50 (4 × *C*H$_2$ [both diastereoisomers]), 31.7 (t, *J* = 22 Hz, 2 × CF_2*C*H$_2$ [one diastereoisomer]), 33.8 (t, *J* = 22 Hz, 2 × CF_2*C*H$_2$ [one diastereoisomer]), 31.8 (4 × *C*H$_2$ [both diastereoisomers]), 40.5 (2 × N*C*H$_2$ [one diastereoisomer]), 40.6 (2 × N*C*H$_2$ [one diastereoisomer]), 45.1 (2 × S*C*H [one diastereoisomer]), 45.3 (2 × S*C*H [one diastereoisomer]), 106.47 (2 × Ar*C*H [one diastereoisomer]), 106.52 (2 × Ar*C*H [one diastereoisomer]), 126.4 (4 × Ar*C* [both diastereoisomers]), 139.2 (2 × Ar*C* [one diastereoisomer]), 139.3 (2 × Ar*C* [one diastereoisomer]), 174.1 (4 × *C*=O [both diastereoisomers]); IR (ATR): ν_{max} /cm^{-1} 2961, 2927, 1699 (C=O), 1657, 1492, 1474, 1349, 1201; MS (APCI$^+$): *m/z* (%) 1425 ([M+H]$^+$, 100), 455.

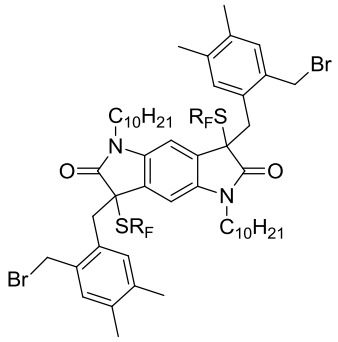
159 3,7-*bis*(2-(Bromomethyl)benzyl)-1,5-didecyl-3,7-*bis*((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione



Following general procedure *O*, using **157** (0.528 g of 1.06 g), LDA (1.16 mL, 0.67 M solution in THF, 0.78 mmol), and 1,2-*bis*(bromomethyl)benzene **158** (0.98 g, 3.7 mmol) in THF (10 mL) gave **159** (crude mass = 0.493 g, 1:1 mixture of diastereoisomers) as a brown oily solid after purification by FSPE eluting with 80% MeCN in H_2O, MeCN and THF (product). The product was used immediately in the next step without any further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.81-0.93 (12 H, m; 4 × CH_3 [both diastereoisomers]), 0.98-1.43 (64 H, m; 32 × CH_2 [both diastereoisomers]), 2.11-2.45 (8 H; m; 4 × CF_2CH_2 [both diastereoisomers]), 2.47-2.72 (8 H, m; 4 × SCH_2 [both diastereoisomers]), 3.29-3.47 (2 H, m; 2 × NCH_AH_B [diastereoisomer A]), 3.35 (2 H, d, *J* = 14.1 Hz; 2 × ArCH_AH_B [diastereoisomer A]), 3.39 (2 H, d, *J* = 14.1 Hz; 2 × ArCH_AH_B [diastereoisomer B]), 3.51-3.82 (6 H, m; 6 × NCH_AH_B [two from diastereoisomer A and four from diastereoisomer B]), 3.59 (2 H, d, *J* = 14.1 Hz; 2 × ArCH_AH_B [one diastereoisomer B]), 3.64 (2 H, *J* = 14.1 Hz; 2 × ArCH_AH_B [one diastereoisomer A]), 4.17 (2 H, d, *J* = 10.5 Hz; 2 × ArCH_AH_B [one diastereoisomer B]), 4.31 (2 H, d, *J* = 10.4 Hz; 2 × ArCH_AH_B [one diastereoisomer A]), 4.47 (2 H, d, *J* = 10.5 Hz; 2 × ArCH_AH_B [one diastereoisomer B]), 4.74 (2 H, d, *J* = 10.4 Hz; 2 × ArCH_AH_B [one diastereoisomer A]), 6.63 (2 H, d, *J* = 9.0 Hz; 2 × Ar*H* [diastereoisomer B), 6.64 (2 H, s; 2 × Ar*H* [diastereoisomer B]), 6.68 (2 H, s; 2 × Ar*H* [diastereoisomer A]), 6.84 (2 H, d, *J* = 7.8 Hz; 2 × Ar*H* [diastereoisomer A]), 6.90 (2 H, t, *J* = 7.2 Hz; 2 × Ar*H* [diastereoisomer B]), 7.09 (4 H, t, *J* = 7.3 Hz; 4 × Ar*H* [both diastereoisomers]), 7.17-7.27 (6 H, m; 6 × Ar*H* [two from diastereoisomer B and four from diastereoisomer A]); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.95 (2 × CH_3 [one diastereoisomer]), 13.99 (2 × CH_3 [one diastereoisomer]), 19.9 (m, 4 × SO_2CH_2 [both diastereoisomers]), 22.61, 22.62, 26.6, 26.7, 27.2, 29.2, 29.4, 29.36, 29.43, 29.45, 29.52, 29.6, 29.7 (32 × CH_2 [both diastereoisomers]), 31.0 (t, *J* = 22.0 Hz; 2 × CF_2CH_2 [one

diastereoisomer]), 31.5 (t, *J* = 22.0 Hz; 2 × CF_2CH_2 [one diastereoisomer]), 31.8 (2 × ArCH_2 [one diastereoisomer]), 31.9 (2 × ArCH_2 [one diastereoisomer]), 37.32 (2 × ArCH_2 [one diastereoisomer]), 37.34 (2 × ArCH_2 [one diastereoisomer]), 40.28 (2 × NCH_2 [one daistereoisomer]), 40.31 (2 × NCH_2 [one diastereoisomer]), 55.9 (4 × C_{quat} [both diastereoisomers]), 105.8 (2 × Ar*C*H [one diastereoisomer]), 105.9 (2 × Ar*C*H [one diastereoisomer]), 127.98 (2 × Ar*C*H [one diastereoisomer]), 128.01 (2 × Ar*C*H [one diastereoisomer]), 128.03 (2 × Ar*C*H [one diastereoisomer]), 128.2 (2 × Ar*C*H [one diastereoisomer]), 129.8 (2 × Ar*C* [one diastereoisomer]), 129.9 (2 × Ar*C* [one diastereoisomer]), 130.67 (2 × Ar*C*H [one diastereoisomer]), 130.73 (2 × Ar*C*H [one diastereoisomer]), 130.8 (2 × Ar*C*H [one diasteroisomer]), 131.2 (2 ×Ar*C*H [one diastereoisomer]), 133.1 (2 × Ar*C* [one diastereoisomers]), 133.3 (2 × Ar*C* [one diastereoisomer]), 137.08 (2 × Ar*C* [one diasteroisomers]), 137.10 (2 × Ar*C* [one diastereoisomer]), 138.6 (2 × Ar*C* [one diastereoisomer]), 138.8 (2 × Ar*C* [one diasteroeisomer]), 175.36 (2 × *C*=O [one diastereoisomer]), 175.40 (2 × *C*=O [one diastereoisomer]); IR (ATR): ν_{max}/cm^{-1} 2930, 2857, 1693 (C=O), 1491, 1471, 1348; MS ($APCI^-$): *m/z* (%) 1825 ($[M+Cl]^-$, 100).

160 3,7-*bis*(2-(Bromomethyl)-4,5-dimethylbenzyl)-1,5-didecyl-3,7-*bis*((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione

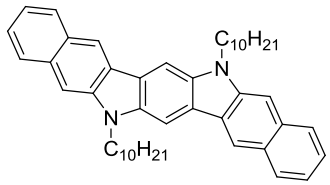


Following general procedure *O*, using **157** (0.531g of 1.06 g), LDA (1.17 mL, 0.67 M solution in THF, 0.78 mmol), and **80** (1.09 g, 3.73 mmol) in THF (10 mL) gave **160** (crude mass = 0.434 g, 1:1 mixture of diastereoisomers) as a brown waxy solid after purification by FSPE eluting with 80% MeCN in H_2O, MeCN, and THF (product). The product was used immediately in the next step without any further purification; ^1H NMR (400 MHz, $CDCl_3$) δ

ppm 0.78-0.94 (12 H, m; 4 × CH_3 [both diastereoisomers]), 1.00-1.46 (64 H, m; 32 × CH_2 [both diastereoisomers]), 1.96 (6 H, s; 2 × C*H*$_3$ [one diastereoisomer]), 2.09 (6 H, s; 2 × C*H*$_3$ [one diastereoisomer]), 2.14 (6 H, s; 2 × C*H*$_3$ [one diastereoisomer]), 2.20 -2.25 (4 H, m; 2 × CF_2CH_2 [one diastereoisomer]), 2.21 (6 H, s; 2 × C*H*$_3$ [one diastereoisomer]), 2.32-2.60 (8 H, m; 2 × S*CH*$_2$ [one diastereoisomer] and 2 × CF_2CH_2 [one diastereoisomer]), 2.64-2.75 (2 H, m; 2 × S*CH*$_A$H$_B$ [one diastereoisomer]), 2.77-2.95 (2 H, m; 2 × SCH$_A$*H*$_B$ [one diastereoisomer]), 3.25-3.49 (4 H, m; 4 × NC*H*$_A$H$_B$ [both diastereoisomers]), 3.32 (2 H, d, *J* = 14.3 Hz; 2 × ArC*H*$_A$H$_B$ [one diastereoisomer]), 3.39 (4 H, br. s; 2 × ArC*H*$_2$ [one diastereoisomer]), 3.50-3.65 (2 H, m; 2 × NCH$_A$*H*$_B$ [one diastereoisomer]), 3.58 (2 H, d, *J* = 14.3 Hz; 2 × ArCH$_A$*H*$_B$ [one diastereoisomer]), 3.75 (2 H, dt, *J* = 14.2, 7.3 Hz; 2 × NCH$_A$*H*$_B$ [one diastereoisomer]), 3.89 (2 H, d, *J* = 10.3 Hz; 2 × ArC*H*$_A$H$_B$), 3.96 (2 H, d, *J* = 10.3 Hz; 2 × ArCH$_A$*H*$_B$), 4.25 (2 H, d, *J* = 10.3 Hz; 2 × ArC*H*$_A$H$_B$), 4.60 (2 H, d, *J* = 10.3 Hz; 2 × ArCH$_A$*H*$_B$ [one diastereoisomer]), 6.45 (2 H, s; 2 × Ar*H* [one diastereoisomer]), 6.52 (2 H, s; 2 × Ar*H* [one diastereoisomer]), 6.66 (2 H, s; 2 × Ar*H* [one diastereoisomer]), 6.90 (2 H, s; 2 × Ar*H* [one diastereoisomer]), 6.94 (2 H, s; 2 × Ar*H* [one diastereoisomer]), 6.96 (2 H, s; 2 × Ar*H* [one diastereoisomer]); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 13.8 (2 × CH_2CH_3 [one diastereoisomer]), 13.9 (2 × CH_2CH_3 [one diastereoisomer]), 18.9 (2 × *C*H$_3$ [one diastereoisomer]), 19.1 (2 × *C*H$_3$ [one diastereoisomer]), 19.2 (2 × *C*H$_3$ [one diastereoisomer]), 19.5 (2 × *C*H$_3$ [one diastereoisomer]), 19.6 (m, 2 × SCH_2 [one diastereoisomer]), 19.9 (m, S*C*H$_2$ [one diastereoisomer]), 22.6 (2 × *C*H$_2$ [one diastereoisomer]), 22.6 (2 × *C*H$_2$ [one diastereoisomer]), 26.6 (2 × *C*H$_2$ [one diasteroisomer]), 26.7 (2 × *C*H$_2$ [one diastereoisomer]), 27.1 (2 × *C*H$_2$ [one diastereoisomer]), 27.3 (2 × *C*H$_2$ [one diastereoisomer]), 29.2, 29.26, 29.33, 29.4, 29.5, 29.6 (16 × *C*H$_2$ [both diastereoisomers]), 30.9 (t, *J* = 23 Hz; 2 × CF_2CH_2 [one diastereoisomer]), 31.2 (t, *J* = 21 Hz; 2 × CF_2CH_2 [one diastereoisomer]), 31.6 (2 × Ar*C*H$_2$ [one diastereoisomer]), 31.8 (4 × *C*H$_2$ [both diastereoisomers]), 32.2 (2 × Ar*C*H$_2$ [one diastereoisomer]), 36.7 (2 × Ar*C*H$_2$ [one diastereoisomer]), 37.1 (2 × Ar*C*H$_2$ [one diastereoisomer]), 40.15 (2 × N*C*H$_2$ [one diasteroisomer]), 40.24 (2 × N*C*H$_2$ [one diastereoisomer]), 55.3 (2 × C_{quat} [one diastereoisomer]), 56.0 (2 × C_{quat} [one diastereoisomer]), 105.7 (2 × Ar*C*H [one diastereoisomer]), 106.0 (2 × Ar*C*H [one diastereoisomer]), 129.7 (2 × Ar*C* [one diastereoisomer]), 129.9 (2 × Ar*C* [one diastereoisomer]), 130.4 (2 × Ar*C* [one diastereoisomer]), 130.5 (2 × Ar*C* [one

diastereoisomer]), 131.7 (2 × Ar*C*H [one diastereoisomer]), 131.7 (2 × Ar*C*H [one diastereoisomer]), 132.1 (2 × Ar*C*H [one diastereoisomer]), 133.2 (2 × Ar*C*H [one diastereoisomer]), 133.9 (2 × Ar*C* [one diastereoisomer]), 134.2 (2 × Ar*C* [one diastereoisomer]), 136.2 (2 × Ar*C* [one diastereoisomer]), 136.4 (2 × Ar*C* [one diastereoisomer]), 136.9 (2 × Ar*C* [one diasteroeisomer]), 137.3 (2 × Ar*C* [one diastereoisomer]), 138.1 (2 × Ar*C* [one diastereoisomer]), 138.4 (2 × Ar*C* [one diastereoisomer]), 175.3 (2 × *C*=O [one diastereoisomer]), 175.5 (2 × *C*=O [one diastereoisomer]); IR (ATR): ν_{max}/cm^{-1} 2927, 2856, 1702 (C=O), 1473, 1349, 1237, 1202, 1146, 1133, 1115, 1086, 1022.

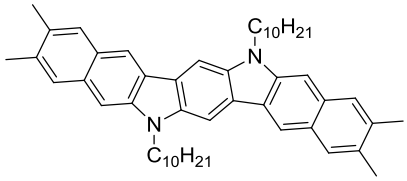
DBIC-2 6,14-Didecyl-6,14-dihydrobenzo[*b*]benzo[5,6]indolo[2,3-*h*]carbazole



Following general procedure *P*, using crude **159** (0.493 g), SmI_2 (27.5 mL, 2.75 mmol, 0.1 M in THF), and hexafluoroisopropanol (87 μL, 0.83 mmol) in degassed THF (7.4 mL) followed by *p*-benzoquinone (0.238 g, 2.20 mmol) in CH_2Cl_2 (7.4 mL) gave pure **DBIC-2** (0.043 g, 0.068 mmol, 16% from hydroxyamide **156** [5 steps]) as a yellow solid and **161** (0.150 g, 0.157 mmol, 37% recovery of HSR_F used in Pummerer cyclisation) as a white solid after purification by flash column chromatography on silica gel eluting with a gradient of 0-30% toluene in hexane; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.87 (6 H, t, *J* = 6.5 Hz; 2 × C*H*$_3$), 1.11-1.42 (28 H, m; 14 × C*H*$_2$), 1.81-1.89 (4 H, m; 2 × C*H*$_2$), 4.15 (4 H, t, *J* = 7.3 Hz; 2 × NC*H*$_2$), 7.40 (2 H, ddd, *J* = 8.0, 6.8, 1.0 Hz; 2 × Ar*H*), 7.48 (2 H, ddd, *J* = 8.3, 6.8, 1.3 Hz; 2 × Ar*H*), 7.67 (2 H, s; 2 × Ar*H*), 8.01 (2 H, d, *J* = 8.0 Hz; 2 × Ar*H*), 8.09 (2 H, d, *J* = 8.3 Hz; 2 × Ar*H*), 8.11 (2 H, s; 2 × Ar*H*), 8.63 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, C_6D_6) δ ppm 14.6 (2 × *C*H$_3$), 23.4 (2 × *C*H$_2$), 28.1 (2 × *C*H$_2$), 29.0 (2 × *C*H$_2$), 30.0 (2 × *C*H$_2$), 30.2 (2 × *C*H$_2$), 30.25 (2 × *C*H$_2$), 30.30 (2 × *C*H$_2$), 32.6 (2 × *C*H$_2$), 44.0 (2 × N*C*H$_2$), 100.5 (2 × Ar*C*H), 103.8 (2 × Ar*C*H), 119.6 (2 × Ar*C*H), 123.2 (2 × Ar*C*H), 124.6 (2 × Ar*C*), 125.9 (2 × Ar*C*H), 126.5 (2 × Ar*C*), 127.9 (2 × Ar*C*H), 128.9 (2 × Ar*C*) 129.3 (2 × Ar*C*H), 134.1 (2 × Ar*C*), 139.2 (2 × Ar*C*), 142.6 (2 × Ar*C*); IR (ATR): ν_{max} /cm^{-1} 2919, 2851, 1630, 1505, 1469, 1435, 1406, 1371,

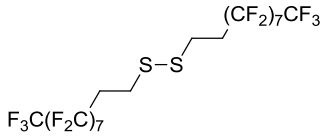
1352, 1300; MS (APCI$^+$): *m/z* (%) 637 ([M+H]$^+$, 100); HRMS (EI$^+$): $C_{46}H_{56}N_2$ requires 636.4438, found 636.4436.

DBIC-3 6,14-Didecyl-2,3,10,11-tetramethyl-6,14-dihydrobenzo[*b*]benzo[5,6]indolo[2,3-*h*]carbazole



Following general procedure *P*, using crude **160** (0.434 g), SmI_2 (23.5 mL, 2.35 mmmol, 0.1 M in THF), and hexafluoroisopropanol (74 μL, 0.70 mmol) in degassed THF (6.3 mL) followed by *p*-benzoquinone (0.203 g, 1.88 mmol) in CH_2Cl_2 (6.3 mL) gave pure **DBIC-3** (0.029 g, 0.042 mmol, 10% from hydroxyamide **156**) as a yellow solid and **161** (0.057 g, 0.059 mmol, 14% recovery of HSR_F used in Pummerer cyclisation) as a white solid after purification by flash column chromatography on silica gel eluting with a gradient of 0-30% toluene in hexane; ^{1}H NMR (400 MHz, C_6D_6) δ ppm 0.87 (6 H, t, *J* = 6.8 Hz; 2 × C*H*$_3$), 1.14-1.44 (28 H, m; 14 × C*H*$_2$), 1.85-1.93 (4 H, m, 2 × C*H*$_2$), 2.38 (6H, s; 2 × C*H*$_3$), 2.39 (6 H, s; 2 × C*H*$_3$), 4.19 (4 H, t, *J* = 7.2 Hz; 2 × NC*H*$_2$), 7.63 (2 H, s; 2 × Ar*H*), 7.79 (2 H, s; 2 × Ar*H*), 7.87 (2 H, s; 2 × Ar*H*), 8.15 (2 H, s; 2 × Ar*H*), 8.62 (2 H, s; 2 × Ar*H*); ^{13}C NMR (101 MHz, C_6D_6) *δ* ppm 14.6 (2 × CH$_2$*C*H$_3$), 20.5 (2 × *C*H$_3$), 20.8 (2 × *C*H$_3$), 23.4 (2 × *C*H$_2$), 28.1 (2 × *C*H$_2$), 29.1 (2 × *C*H$_2$), 30.1 (2 × *C*H$_2$), 30.2 (2 × *C*H$_2$), 30.29 (2 × *C*H$_2$), 30.34 (2 × *C*H$_2$), 32.6 (2 × *C*H$_2$), 44.0 (2 × N*C*H$_2$), 100.2 (2 × Ar*C*H), 102.9 (2 × Ar*C*H), 118.5 (2 × Ar*C*H), 124.6 (2 × Ar*C*), 126.0 (2 × Ar*C*), 127.6 (2 × Ar*C*H), 128.5 (2 × Ar*C*), 128.8 (2 × Ar*C*H), 132.2 (2 × Ar*C*), 133.3 (2 × Ar*C*), 135.3 (2 × Ar*C*), 139.1 (2 × Ar*C*), 142.4 (2 × Ar*C*); IR (ATR): ν_{max}/cm^{-1} 2921, 2850, 1634, 1505, 1471, 1443, 1428, 1404; MS (APCI$^+$): *m/z* (%) 694 ([M+H]$^+$, 100); HRMS (EI+): $C_{50}H_{64}N_2$ requires 692.5064, found 692.5045.

161 1,2-*bis*(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)disulfane



Data for **161**: mp (THF) 77-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.55 (4 H, tt, *J* = 17.6, 8.5 Hz; 2 × CF_2CH_2), 2.86-2.96 (4 H, m; 2 × SCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 28.8 (2 × SCH_2), 31.8 (2 × CF_2CH_2, t, *J* = 21.3 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ ppm –[126.27-126.04] (4 F, m; 2 × CF_2), -[123.53-123.15] (4 F, m; 2 × CF_2), -[122.92-122.57] (4 F, m; 2 × CF_2), -[122.10-121.8] (8 F, m; 4 × CF_2), -[121.8-121.66] (4 F, m; 2 × CF_2), -[113.88-113.52] (4 F, m; 2 × CF_2), -80.78 (6 F, t, *J* = 10 Hz; 2 × CF_3); IR (ATR): v_{max}/cm^{-1} 1441, 1364, 1333, 1197, 1145, 1116, 1080; MS (ASAP): *m/z* (%) 958 ($[M]^+$, 15), 490 (10), 411 (10), 391 (30), 321 (95), 295 (80), 224 (100), 158 (50); HRMS (ASAP): $C_{20}H_8F_{34}S_2$ requires 957.9525, found 957.9511.

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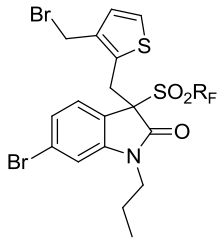
6 Apendices

Appendix A - Crystal structure of 47

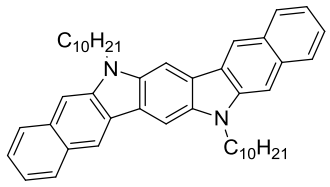


Identification code	s3326na
Empirical formula	$C_{27}H_{20}Br_2F_{17}NO_3S_2$
Formula weight	953.38
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 29.9639(18) A alpha = 90 deg. b = 11.7444(7) A beta = 92.3050(10) deg. c = 9.2236(6) A gamma = 90 deg.
Volume	3243.2(3) A^3
Z, Calculated density	4, 1.953 Mg/m^3
Absorption coefficient	2.760 mm^{-1}
F(000)	1872
Crystal size	0.30 x 0.20 x 0.04 mm
Theta range for data collection	1.36 to 28.28 deg.
Limiting indices	-39<=h<=38, -15<=k<=15, -12<=l<=12
Reflections collected / unique	27553 / 7672 [R(int) = 0.0406]
Completeness to theta = 25.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8976 and 0.715623
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7672 / 0 / 470
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.0987
R indices (all data)	R1 = 0.0727, wR2 = 0.1096
Largest diff. peak and hole	0.618 and -0.667 $e.A^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **47**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U (eq)
Br(1)	2311(1)	627(1)	2511(1)	36(1)
Br(2)	373(1)	8391(1)	3272(1)	52(1)
C(1)	1975(1)	5771(3)	2453(3)	20(1)
C(2)	2108(1)	4551(3)	2679(3)	21(1)
C(3)	2404(1)	4037(3)	3659(4)	24(1)
C(4)	2464(1)	2860(3)	3598(4)	28(1)
C(5)	2225(1)	2233(3)	2576(4)	25(1)
C(6)	1924(1)	2723(3)	1585(4)	24(1)
C(7)	1876(1)	3886(3)	1643(3)	20(1)
C(8)	1668(1)	5721(3)	1069(3)	20(1)
C(9)	1723(1)	6331(3)	3722(4)	25(1)
C(10)	1263(1)	5869(3)	3861(4)	24(1)
C(11)	614(1)	4671(4)	4410(5)	48(1)
C(12)	492(1)	5590(3)	3648(4)	35(1)
C(13)	867(1)	6298(3)	3324(4)	29(1)
C(14)	819(1)	7380(4)	2469(5)	40(1)
C(15)	1310(1)	4194(3)	-451(4)	24(1)
C(16)	862(1)	3810(3)	79(4)	32(1)
C(17)	565(1)	3409(4)	-1192(5)	45(1)
C(18)	2716(1)	6126(3)	656(3)	24(1)
C(19)	3186(1)	6615(3)	600(4)	22(1)
C(20)	3450(1)	6025(3)	-537(4)	23(1)
C(21)	3928(1)	6509(3)	-608(3)	21(1)
C(22)	4241(1)	5962(3)	-1708(3)	21(1)
C(23)	4721(1)	6476(3)	-1689(3)	21(1)
C(24)	5035(1)	5957(3)	-2821(3)	21(1)
C(25)	5514(1)	6462(3)	-2777(4)	24(1)
C(26)	5825(1)	5964(3)	-3920(4)	27(1)
C(27)	6309(1)	6424(4)	-3845(5)	38(1)
F(1)	3480(1)	4893(2)	-263(2)	36(1)
F(2)	3248(1)	6128(2)	-1869(2)	34(1)
F(3)	3887(1)	7623(2)	-932(3)	38(1)
F(4)	4122(1)	6419(2)	724(2)	38(1)
F(5)	4274(1)	4845(2)	-1424(3)	39(1)
F(6)	4055(1)	6088(2)	-3042(2)	36(1)
F(7)	4911(1)	6318(2)	-363(2)	38(1)
F(8)	4688(1)	7592(2)	-1939(3)	37(1)
F(9)	5065(1)	4834(2)	-2591(3)	38(1)
F(10)	4853(1)	6132(2)	-4148(2)	36(1)
F(11)	5708(1)	6270(2)	-1464(2)	38(1)
F(12)	5489(1)	7586(2)	-2993(2)	36(1)
F(13)	5846(1)	4835(2)	-3781(3)	50(1)
F(14)	5654(1)	6203(2)	-5250(2)	48(1)
F(15)	6516(1)	6101(4)	-2651(3)	85(1)
F(16)	6528(1)	5991(3)	-4922(3)	60(1)
F(17)	6320(1)	7516(2)	-3957(5)	88(1)
N(1)	1614(1)	4592(2)	723(3)	22(1)
O(1)	2751(1)	6491(2)	3454(3)	29(1)
O(2)	2309(1)	7821(2)	1911(3)	31(1)
O(3)	1495(1)	6513(2)	427(2)	26(1)
S(1)	1176(1)	4610(1)	4768(1)	41(1)
S(2)	2459(1)	6682(1)	2210(1)	22(1)

Appendix B - Crystal structure of DBIC-2

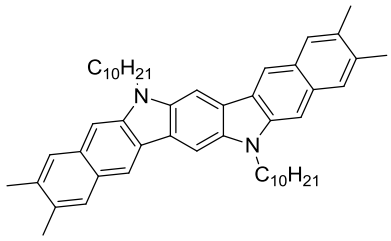


Identification code	s3720ma
Empirical formula	$C_{46}H_{56}N_2$
Formula weight	636.93
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 15.6742(10) A alpha = 90 deg.
	b = 5.4689(4) A beta = 90.055(6) deg.
	c = 21.5676(15) A gamma = 90 deg.
Volume	1848.8(2) A^3
Z, Calculated density	2, 1.144 Mg/m^3
Absorption coefficient	0.489 mm^{-1}
F(000)	692
Crystal size	0.80 x 0.20 x 0.02 mm
Theta range for data collection	4.98 to 66.57 deg.
Limiting indices	-18<=h<=18, -6<=k<=5, -25<=l<=25
Reflections collected / unique	7624 / 3263 [R(int) = 0.0717]
Completeness to theta = 66.57	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9903 and 0.6958
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3263 / 0 / 219
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1390
R indices (all data)	R1 = 0.0927, wR2 = 0.1601
Extinction coefficient	0.0017(3)
Largest diff. peak and hole	0.207 and -0.205 $e.A^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **DBIC-2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	1126(1)	7012(4)	5630(1)	31(1)
C(1)	574(2)	8393(4)	5256(1)	30(1)
C(2)	231(1)	10322(4)	5616(1)	29(1)
C(3)	618(1)	10163(4)	6224(1)	29(1)
C(4)	1163(1)	8065(4)	6214(1)	30(1)
C(5)	1612(1)	7333(4)	6728(1)	32(1)
C(6)	1543(2)	8740(5)	7278(1)	32(1)
C(7)	1986(2)	8067(5)	7826(1)	37(1)
C(8)	1927(2)	9449(5)	8353(1)	40(1)
C(9)	1421(2)	11583(5)	8363(1)	40(1)
C(10)	982(2)	12268(5)	7845(1)	35(1)
C(11)	1022(2)	10879(5)	7285(1)	31(1)
C(12)	560(1)	11571(4)	6751(1)	30(1)
C(13)	358(1)	8023(4)	4641(1)	30(1)
C(14)	1623(2)	4940(4)	5423(1)	31(1)
C(15)	2499(2)	5593(4)	5153(1)	30(1)
C(16)	2927(2)	3299(4)	4901(1)	32(1)
C(17)	3790(2)	3731(4)	4595(1)	33(1)
C(18)	4170(2)	1383(5)	4327(1)	34(1)
C(19)	5038(2)	1726(5)	4020(1)	35(1)
C(20)	5388(2)	-626(5)	3737(1)	34(1)
C(21)	6245(2)	-293(5)	3415(1)	36(1)
C(22)	6575(2)	-2607(5)	3101(1)	36(1)
C(23)	6063(2)	-3325(6)	2530(1)	52(1)

Appendix C - Crystal structure of DBIC-3

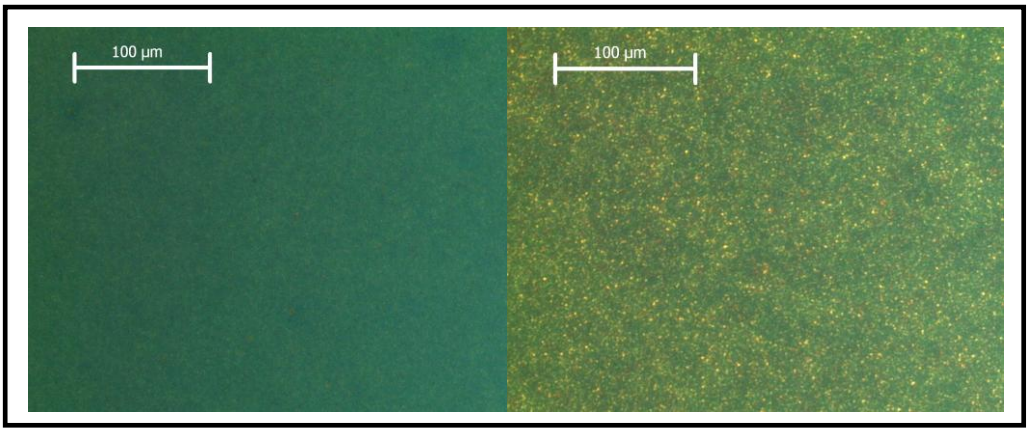


Chemical formula	$C_{50}H_{64}N_2$
Mr	693.03
Crystal system, space group	Triclinic, P
Temperature (K)	100
a, b, c (Å)	5.9862 (5), 16.452 (2), 20.7760 (18)
α, β, γ (°)	95.482 (9), 94.572 (7), 97.856 (9)
V ($Å^3$)	2008.7 (3)
Z	2
Radiation type	Cu Kα
μ (mm^{-1})	0.49
Crystal size (mm)	0.09 × 0.02 × 0.02
Diffractometer	Bruker APEX-II CCD diffractometer
Absorption correction	Multi-scan, CrysAlis PRO, Agilent Technologies, Version 1.171.36.20 (release 27-06-2012 CrysAlis171 .NET) (compiled Jul 11 2012,15:38:31) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Tmin, Tmax	0.622, 1.000
No. of measured, independent and observed [I > 2σ(I)] reflections	21331, 6838, 2923
Rint	0.215
(sin θ/λ)max ($Å^{-1}$)	0.595
R[F^2 > 2σ(F^2)], wR(F^2), S	0.089, 0.225, 1.03
No. of reflections	6838
No. of parameters	475
No. of restraints	0
H-atom treatment	H-atom parameters constrained
Δρmax, Δρmin (e $Å^{-3}$)	0.25, −0.23

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **DBIC-3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

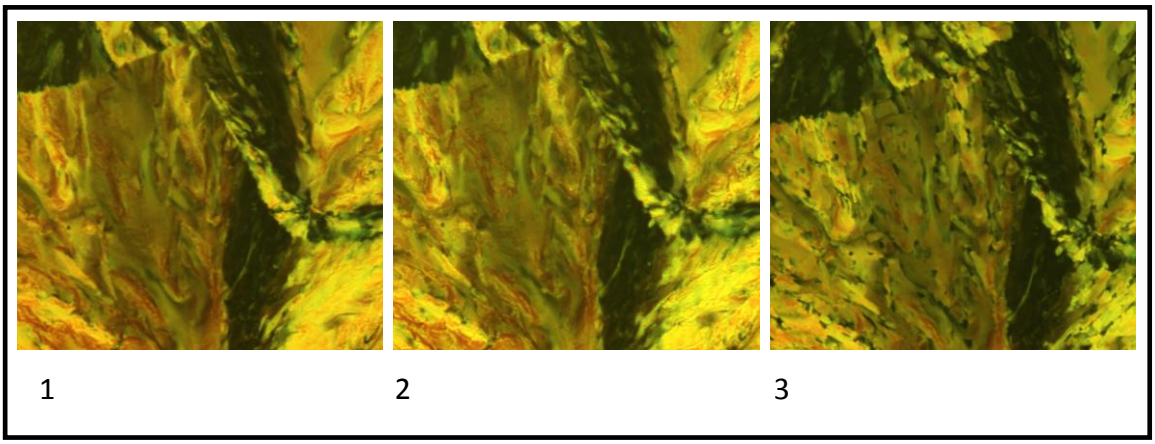
	x	y	z	U(eq)
C(1)	1886(9)	1105(3)	5912(2)	30(1)
C(2)	597(9)	1526(3)	6316(3)	33(1)
C(3)	1196(10)	1618(3)	6987(3)	33(1)
C(4)	-82(9)	2032(3)	7431(3)	33(1)
C(5)	508(9)	2147(3)	8087(3)	33(1)
C(6)	2458(10)	1827(4)	8349(3)	38(1)
C(7)	3675(10)	1409(4)	7936(3)	38(1)
C(8)	3086(9)	1286(3)	7253(3)	32(1)
C(9)	4376(9)	845(3)	6827(3)	33(1)
C(10)	3752(9)	759(3)	6170(2)	31(1)
C(11)	4666(1)	344(3)	5617(3)	30(1)
C(12)	3322(9)	486(3)	5050(2)	30(1)
C(13)	-67(9)	1199(3)	4794(2)	32(1)
C(14)	700(10)	1982(3)	4506(3)	36(1)
C(15)	-1153(11)	2188(4)	4015(3)	45(2)
C(16)	-1668(11)	1559(4)	3405(3)	42(2)
C(17)	247(13)	1545(4)	2973(3)	54(2)
C(18)	-272(13)	893(4)	2392(3)	56(2)
C(19)	1621(14)	884(5)	1951(3)	65(2)
C(20)	1146(14)	199(5)	1389(3)	59(2)
C(21)	2975(18)	182(5)	925(4)	81(3)
C(22)	2445(17)	-521(5)	389(4)	84(3)
C(23)	-910(10)	2608(4)	8532(3)	41(1)
C(24)	3164(11)	1969(4)	9066(3)	51(2)
C(25)	6350(9)	-151(3)	5566(2)	33(1)
C(26)	11710(9)	4970(3)	1233(2)	32(1)
C(27)	10388(9)	5003(3)	1748(2)	32(1)
C(28)	11274(9)	5506(3)	2327(2)	30(1)
C(29)	10026(9)	5577(3)	2880(2)	30(1)
C(30)	10869(10)	6049(3)	3445 (2)	34 (1)
C(31)	13097(9)	6491(3)	3495(2)	34(1)
C(32)	14354(9)	6450(3)	2965(2)	30(1)
C(33)	13503(9)	5963(3)	2376(2)	27(1)
C(34)	14792(9)	5940(3)	1834(2)	30(1)
C(35)	13899(9)	5450(3)	1265(2)	29(1)
C(36)	14747(10)	5281(3)	636(2)	27(1)
C(37)	13041(9)	4698(3)	265(2)	28(1)
C(38)	9280(9)	3885(3)	449(2)	30(1)
C(39)	9653(9)	3069(3)	687(2)	33(1)
C(40)	7466(10)	2460(3)	650(3)	38(1)
C(41)	5675(10)	2753(4)	1071(3)	44(2)
C(42)	6363(11)	2893(4)	1803(3)	42(1)
C(43)	4797(11)	3345(4)	2183(3)	42(1)
C(44)	5393(12)	3434(4)	2907(3)	48(2)
C(45)	3878(12)	3935(4)	3293(3)	47(2)
C(46)	4359(11)	3954(4)	4025(3)	45(2)
C(47)	2851(13)	4433(5)	4410(3)	56(2)
C(48)	9417(10)	6096(4)	4010(3)	40(1)
C(49)	14067(10)	7003(4)	4127(3)	37(1)
C(50)	16715(9)	5601(3)	368(2)	32(1)
N(1)	1649(8)	949(3)	5241(2)	34(1)
N(2)	11215(8)	4530(3)	627(2)	33(1)

Appendix D-POM images of 124



Polarised optical microscopy images of thin films of **124** on SiO_2 wafers at ×20 magnification observed under identical conditions. Image on the **right** shows a film which has been annealed at **100 °C** (Table 15, Entry 1); image on the **left** show a film annealed at **140 °C** (Table 15, Entry 2).

Appendix E - POM images of DBIC-1



Polarised optical microscopy images provided by Nicholas Kasch (School of Physics and Astronomy-The University of Manchester). Images show a sample of **DBIC-1** at 95 °C (1), 101 °C (2), and 105 °C. The images were captured during the second heating cycle.