# Liquid crystalline properties of thioesters

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**Abstract**

An extension of the new method forming thioesters with mesomorphic properties has been described, whereby the treatment of aryl *tert*-butylthioethers with long chain acid chlorides in the presence of bismuth triflate afforded simple derivatives in good yields. This method in the case of 1-cyanoazulenes was however complicated by a competitive Friedel-Crafts type acylation side reaction at the 3-position. Long chain derivatives of cyanobiphenyl attached through a thioester linkage exhibited mesophases comparable with their ester analogues. The use of shorter chains to decorate the cyanobiphenyl moiety did not show mesophasic behaviour, unlike their ester analogues. The cyanobiphenyl derivatives showing mesophasic behaviour were studied by small angle X-ray diffraction, showing alignment for molecules possessing a smectic A phases. It was found that the layer spacing in the smectic A phase was approximately 1.5 times the length of the molecule, due to antiparallel pairing arising from π stacking between neighbouring units. Calculations suggest these derivatives should exhibit large dielectric anisotropy, however, instability made an exact value difficult to determine. For potential use in a liquid crystal display (LCD), the thioester holds some promise, although this may be limited by the relative stability of the thioester functionality.

## Introduction

Of the available data for mesomorphic properties of thioesters, it has been shown that the thioester moiety tends stabilise the nematic phase compared to the analogous carboxylate ester, resulting in a higher clearing point.1 It is believed that the decreased angle between C-S-C and the relative increased bond length between sulphur and carbon result in better packing in the mesophases, and therefore higher clearing points. In regard to synthesis of thioesters, we have recently shown that aryl *tert*-butylthioethers **1** are convenient precursors that can be directly transformed into the corresponding thioacetates **2** in a procedure, which avoids the use of boron tribromide, previously employed.2 This transformation which employs bismuth triflate and acetyl chloride was geared towards making materials for molecular electronics as sulphur can act as an electrode anchoring group (Scheme 1).2 This protocol was found to be tolerant of many functional groups, including protected alkynes, nitriles and the keto functionality and has in fact also been used to synthesize an undecanoate thioester, which was integrated into a redox active “H-cruciform” motif to improve its solubility.3



Scheme 1

To further the possible scope of this chemistry, it was of interest to investigate the possibility for using long chain acid chlorides with the aim of targeting derivatives with potential mesomorphic behaviour, specifically those with nematic properties, thus having linear structures with more than one aromatic ring capped with an aliphatic chain. Some simple linear structures can be seen in Figure 1, where the cyanobiphenyl is capped with an aliphatic ester of varying lengths (**3**), and likewise, two esters have been introduced to a 1,4-diphenylbuta-1,3-diyne core (**4**). In the field of liquid crystals, the cyanobiphenyl end group has been extensively studied.3 This end group is not only interesting for its ability to form liquid crystalline material, but also for its moderately large dipole moment. One of the largest uses for liquid crystals is in display devices, where a fast response time is required in order for the display to be useful. It is well known that a relationship between the response time and the dipole moment exists, thus measuring a molecule with a large electric dipole moment are desirable. Indeed, many 4-cyanobiphenyls bearing the ester group and having chains of differing lengths have already been synthesized and studied. Having a 1,4-diphenylbuta-1,3-diyne core capped on both ends with long aliphatic chains attached through ester linkages gave derivatives which possessed a nematic phase.5,6 On the other hand, these systems do potentially have some drawbacks as the transition temperatures are rather high. Many molecules in these linear arrangements were shown to exhibit a nematic phase.

The aim of this study was to prepare thioester analogues of materials such as **3** and **4**, giving **5** and **6** respectively (Figure 1). Assuming the thioesters retain the mesomorphic properties of the parent materials then any changes to the physical properties (transition temperatures, smectic layer spacings, dielectric anisotropies etc.) could be linked directly to the swapping of oxygen for sulphur. In addition, as research efforts in the group have been dedicated to 1-cyanoazulene derivatives, and as dyes possessing a nematic phase are of interest for LCDs, azulenes **7** were also targeted.7



**Figure 1**

**Synthesis**

The acid chlorides below were used as a part of the study, which consisted of straight chain aliphatic acid chlorides **8a-g** and alkyl benzoyl acid chlorides **8h-i**, which should give many of the analogues of **3** and **4** and direct comparison between the esters and thioesters can be made (Figure 2).



Figure 2

Precursor to the cyanobiaryl **11** was achieved by a Suzuki cross coupling between boronic acid **9** with electron deficient aryl bromide **10** in good yield (Scheme 2). Compound **11** was treated with catalytic bismuth triflate with acid chlorides **8a-i**, following the same conditions, one hour stirring at ambient temperature in acetonitrile to give products **5a-i** in high yields.



Scheme 2

In addition, double thioether **12** was treated with 0.4 equivalents of bismuth triflate in the presence of the same acid chlorides to afford a second host of thioester products **6a-i** (Scheme 3). In the cases of the longer chain acid chlorides the desired product precipitated from the reaction solution; careful filtration allowed for the isolation of these products without the use of chromatography.



Scheme 3

Azulene **13**, which has a versatile aryl iodide functional handle, could be formed from its corresponding dihydroazulene following the literature procedure where DBU was used to eliminate hydrogen cyanide.8 Azulene **13** could then be reacted with boronic acid **9** in a palladium catalysed Suzuki reaction to furnish **14**, the precursor to the target system **5** (Scheme 4). For the final step, the reactions of only three acid chlorides were focused upon. Upon treatment with bismuth triflate and acid chlorides **8e-g**, these reactions lead to the formation of two sets of distinctive reaction products **15e-g** and **16e-g**, however, neither of which were desired products **7e-g**. For azulene 14 , the 3-position, despite having the electron withdrawing cyano substituent at the 1-position, also had the possibility of undergoing a Friedel-Crafts acylation, where the colour of this chromophore had changed from purple to pink. Indeed, there have been instances in literature of bismuth triflate working as a catalyst for Friedel-Crafts reaction on electron rich aromatics at elevated temperature.7 A Friedel-Crafts alkylation on trimethoxybenzene8 have also been achieved employing triflic acid, and exposure of bismuth triflate to residual moisture results in the formation of triflic acid11 These reactions were repeated instead using bismuth trichloride. In our earlier report, this reagent had also proven moderately successful in effecting the desired transformation, although a higher loading and extended reaction times had been necessary for the reaction to proceed. After four days and a high loading of bismuth trichloride (> 150 mol%), only **16e-g** were obtained. As intermediates **15e-g** were not present in these reaction mixtures, purification of **16e-g** by column chromatography was markedly easier. No further attempts were made to pursue **7e-g**.



Scheme 4

Table 1: Yields when using different bismuth reagents in the reaction of **14** with acid chlorides **8e-g**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Acid chloride | Catalyst BiX3a | Equiv. 1st added | Equiv. 2nd added | Time | Yields (%) |
| **8e** | Bi(OTf)3 | 0.35 | 0.44 | 2 h | 61 (**15e**), 30 (**16e**) |
| **8f** | Bi(OTf)3 | 0.30 | 0.30 | 2 h | 44 (**15f**), 26 (**16f**) |
| **8g** | Bi(OTf)3 | 0.31 | 0.35 | 2 h | 47 (**15g**), 8 (**16g**) |
| **8e** | BiCl3 | 1.67 | - | 4 days | 28 (**16e**) |
| **8f** | BiCl3 | 1.67 | - | 4 days | 29 (**16f**) |
| **8g** | BiCl3 | 1.56 | - | 4 days | 38 (**16g**) |

[a]Reaction performed in 1:1 CH3CN/toluene at ambient temperature.

## Physical properties

Upon examination of the 4-cyanobiphenyl derivatives **5a-i**, the transition temperatures from the DSC measurements were determined in conjunction with polarised optical microscopy (POM) (Table 2). Biphenyl derived compounds with shorter terminal chains (**5a-d**) were non-mesogenic; however, compounds with longer chains variously exhibited nematic and smectic A phases (**5e**-**g**). The analogous carboxylate materials incorporating carboxylate esters are all liquid crystalline, with clearing points generally higher than for the mesogenic thioester materials.

Derivatives **5h** and **5i**, each with an additional aromatic ring, had higher transition temperatures relative to the analogous two-ring materials (**5a-5g**). These two materials exhibited both a smectic A and a nematic phase. Microscopy images of the mesophases for **5h** are shown in Figure 3c-d. Though these mesophases could be observed under the microscope, there was decomposition associated with the high temperatures required to see mesophases. This was evident by the material turning from clear to brown. Perhaps surprisingly the thioester group appears to increase the thermal stability of the smectic A phase, as demonstrated by comparing **5e**, **5h** and **5i** with their analogous carboxylate materials **3e**, **3h** and **3i**. It is well known that the cyanobiphenyl group forms antiparallel pairs through dipole-dipole interactions,12 and this present observation of an enhanced smectic A phase stability possibly indicates that the thioester group is somehow moderating the degree of pairing.

Table 2: Experimental data from the DSC thermograms of the cyanobiphenyls **5a-i**, and transition temperatures of **3a-i**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| R = |  |  |  |  |
| -C4H9 | **5a** | Cr 52.2 Iso | **3a**13 | Cr 36.5 N 61.7 Iso |
| -C5H11 | **5b** | Cr 75.5 Iso | **3b**13 | Cr 56.1 N 70.7 Iso |
| -C6H13 | **5c** | Cr 58.5 Iso | **3c**13 | Cr 57.7 N 68.8 Iso |
| -C7H15 | **5d** | Cr 60.9 Iso | **3d**13 | Cr 77.5 (N74.1) Iso |
| -C8H17 | **5e** | Cr 45.3 SmA 53.5 N 60.2 Iso | **3e**13 | Cr 42.2 N 74 Iso |
| -C9H19 | **5f** | Cr 59.3 SmA 68.0 Iso | **3f**14 | Cr 51 SmA 76 N 76.5 Iso |
| -C10H21 | **5g** | Cr1 44.9 (Cr2 50.9) SmA 69.2 Iso |  |  |
| -C6H4C8H19 | **5h** | Cr 70.2 SmA 231.8 N 240 < decomp. | **3h**15 | Cr 88 SmA 183 N 215.3 Iso |
| - C6H4C10H21 | **5i** | Cr 68.8 SmA 220.3 N 225.7 Iso | **3i**16 | Cr 89 Sm 198 N 202 Iso |

|  |  |
| --- | --- |
| a) | b) |
| C:\Users\Anne\Desktop\microskope\NC_PhPh\NCPhPh_e_55C.bmp | C:\Users\Anne\Desktop\microskope\NC_PhPh\NCPhPh_e_47C.bmp |
| c) | d) |
| C:\Users\Anne\Desktop\microskope\NC_PhPh\NCPhPh_h_206C.bmp | C:\Users\Anne\Desktop\microskope\NC_PhPh\NCPhPh_h_150C.bmp |

Figure 3: a) Photomicrographs of a) **5e** in the nematic phase at 55 °C, b) **5e** in the smectic A phase at 47 °C, c) **5h** in the nematic phase at 206 °C, d) **5h** in the smectic A phase at 150 °C.

The enthalpies and entropies associated with each phase transition were determined by DSC at a heating/cooling rate of 10 °C min-1 and are summarised in Table 3. As expected, the associated enthalpy of the N-I phase transition is significantly smaller than that of the SmA-I phase transition as a consequence of the higher order within the smectic phase. Unfortunately, it was not possible to obtain reproducible results from the DSC measurements for **5h**, likely due to the instability of this compound at high temperature, and therefore enthalpy and entropy values are not given in Table 3. We place a lower estimate of 240 °C on the clearing point of **5h**, this being the onset temperature of the N-I transition on the first heating cycle. Despite the high temperatures used, the instability of **5h** may be due to the fact that the thioester linkage tends to be not as robust an ester and some degree cleavage products may have been present in the material, which may result in the lowering of transition temperatures.

Table 3: The enthalpies (kJ mol-1) and dimensionless entropies associated with transition for compounds **5e-5i**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  | Cr-SmA | SmA-N | SmA-Iso | N-Iso |
| **5e** | ∆*H* | 29.1 | 0.122 | - | 0.664 |
|  | ∆*S*/*R* | 11.0 | 0.0449 | - | 0.240 |
| **5f** | ∆*H* | 24.0 | - | 2.04 | - |
|  | ∆*S*/*R* | 8.69 | - | 0.72 | - |
| **5g** | ∆*H* | 36.9a | - | 2.94 | - |
|  | ∆*S*/*R* | 13.9 | - | 1.03 | - |
| **5i** | ∆*H* | 24.1a | 0.539 | - | 0.844 |
|  | ∆*S*/*R* | 8.49 | 0.131 | - | 0.204 |

[a]Enthalpy was calculated from the first heating cycle, as there was not full crystallisation back to the same crystal, and therefore the enthalpy for the second and third melts were lower.

Small and wide angle X-ray scattering (SAXS/WAXS) was used to determine the spacing (*d*) between the layers which gives more information about the packing of the phases. The X-ray scattering data were obtained using a literature protocol, which comprised of a bored graphite rod furnace temperature control to an accuracy of +/- 0.1 °C in conjunction with a diffractometer using copper Kα radiation.17 The furnace sat in a magnetic field (0.6 T at sample) perpendicular to the incident radiation to align the liquid-crystalline materials during study. Compounds **5e**-**5i** were studied by SAXS/WAXS, typical two-dimensional patterns are presented in Figure 4. At wide angles the diffuse scattering confirms the lack of in-plane positional order in both nematic and smectic mesophases. At small angles there is only diffuse scattering in the nematic phase due to local short range lamellar fluctuations, whereas for the smectic A phase the lamellar structure leads to Bragg scattering. Both nematic and smectic A phases exhibit diffuse scattering at wide angles, this indicates the short positional correlation length parallel to the director in both phases. For materials exhibiting a direct Iso-SmA phase transition (**5f**, **5g**) the magnetic field strength at the sample position is insufficient to align the materials.

|  |  |  |
| --- | --- | --- |
| a) | b) | c) |
| C:\Users\Anne\Downloads\60.png | C:\Users\Anne\Downloads\30.png | D:\Phd\Chapter_4\x-ray-graf_e_flere temperature.emf |
| Compound **5e** at 60 °C in the nematic phase | Compound **5e** at 30 °C in the smectic A phase |

Figure 4: X-Ray diffraction of **5e** magnetically aligned at a) 60 °C and b) at 30 °C. Figure 5: c) Showing the intensities at 2*θ* at temperatures from **55** to 35 °C for **5e**. explanation for the x axis

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The peak at small *θ* can be used to calculate the *d*-spacing, using Bragg’s law and by plotting the intensity of the reflection to 2*θ* (Figure 5). This was done for the smectic phases for **5e-i** and values are shown in Table 4 together with calculated lengths (*l*) of the molecules.

Table 4: Values form XRD and from calculation of molecular length for **5e-i**.DFT calculations obtained at the B3LYP/6-31G(d) level of theory using Gaussian G09 rev e01.18

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Peak 2*θ* | *d*-spacing (Å) | Molecular length, *l* (Å) | *d*/*l* |
| **5e** | 2.7 | 32.75 | 21.66 | 1.51 |
| **5f** | 2.5 | 35.31 | 22.82 | 1.55 |
| **5g** | 2.4 | 36.88 | 23.74 | 1.55 |
| **5h** | 2.3 | 38.36 | 26.34 | 1.46 |
| **5i** | 2.5 | 35.33 | 28.53 | 1.24 |

For compounds **5e**, **5f** and **5g** the smectic layer spacing is ~ 1.5 times the molecular length, this demonstrates that the smectic A phase exhibited by these compounds is interdigitated and can therefore be identified as being of the subtype SmAd. For compound **5h** the layer spacing is marginally smaller, but still indicative of the subtype SmAd. The layer spacing of **5i** is significantly smaller both in *d*-spacing and *d*/*l* ratio; however, the values are still consistent with those of an interdigitated smectic A phase. These observations are consistent with behaviour reported for alkoxy cyanobiphenyls with linear terminal chains, and suggest that the thioester group does not impact on the degree of pairing.



Figure 6: Schematic drawing of the layers and spacing in the smectic phases. a) *d*-spacing equal to molecule length (SmA1), b) *d*-spacing equal to 1.5 of the molecule length (SmAd), c) *d*-spacing equal to twice the molecule length (SmA2).

Crystals of **5d** were grown from dichloromethane and heptane and were submitted to single crystal X-ray diffraction giving the structure shown in Figure 7. Here, the same type of antiparallel pairing of the biphenyl groups as proposed in Figure 6b can be seen, where two molecules pack having the cyano group facing the thioester group, showing that these interactions also affect the packing in the crystal structure. In this case, the distance from the methyl group upper molecule to the other was determined to be 27.7 Å, whilst the length was 20.7 Å for the lower projection, giving a *d*-spacing ratio of 1.33, slightly less than that found in the smectic phase.

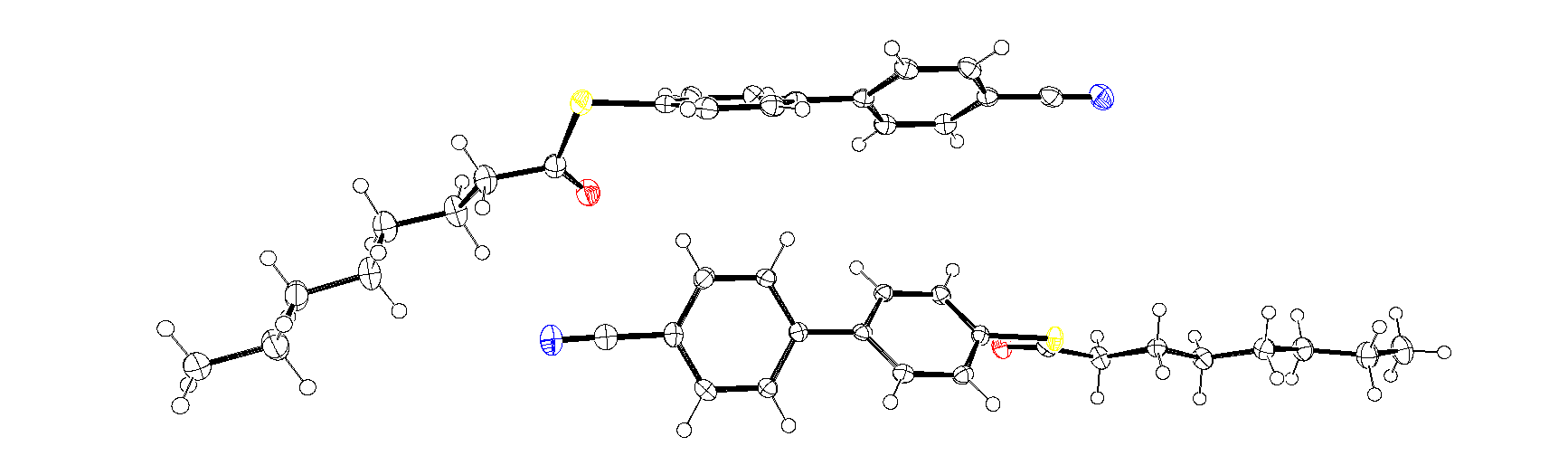


Figure 7: Crystal structure of **5d**, showing the asymmetric unit, with displacement ellipsoids at 50% probability for non-H atoms. CCDC-1578060.

Previously, comparison of the measured dielectric anisotropy and the ‘calculated’ dielectric anisotropy has been used as a probe for the degree of pairing within nematic liquid crystals.12b,19 Values of ∆*ε* (dielectric anisotropy) were calculated using the Maier-Meier relationship (eqn. 1), using molecular polarizabilities and dipole moments from DFT(B3LYP/6-31G(d)) calculations, an order parameter of 0.5 and a Kirkwood factor of 0.6, giving the values shown in Table 8.

(1)

S is the order parameter, h is the cavitation factor, F is the reaction field vector, α is the polarizability,

μ is the dipole moment and T the temperature

Table 8: B3LYP/6-31G(d) calculations of **5c-g** to find ∆*ε* with an order parameter set to 0.5 and a Kirkwood factor of 0.6.

|  |  |  |
| --- | --- | --- |
|  |  | ∆*ε* |
| -C6H13 | **5c** | 15.87 |
| -C7H15 | **5d** | 14.92 |
| -C8H17 | **5e** | 13.92 |
| -C9H19 | **5f** | 12.99 |
| -C10H21 | **5g** | 12.09 |

To measure the dielectric anisotropy experimentally, the material has to be in the nematic phase, and the cells used for the measurement also has an operating temperature limit of 155 °C. As only compound **5e** showed a nematic phase within this temperature range, this measurement was only performed on **5e**; however, the terminal chain length should have minimal impact on the measured value of Δ*ε* which is a consequence of the polarizability/dipole moment associated with the biphenyl unit. Though high values for the dielectric anisotropy were found (Δε = 25-30), these measurements were not found to be reproducible, as **5e** was prone to decomposition under the conditions of this experiment although it is not clear if this was a consequence of the applied field (up to ~ 6 v μm-1) or the elevated temperature (50 °C). In comparison, the dielectric anisotropy measured for other cyanobiphenyls with direct attachment of an alkyl chain such as 4-pentyl-4’-cyanobiphenyl (5CB) was found to be significantly lower, where Δε = 13,20 whilst where an electron donating ether linker was used to connect the aliphatic chain 4-octyloxy-4’-cyanobiphenyl (8OCB) gave Δε = 10.9.12b No such values could be found for the dielectric anisotropy for cyanobiphenyls with an ester linkage to the aliphatic component. This in essence indicates that the strength of the pairing in the nematic phase is somewhat diminished with the use of a thioester linkage, be it due to the slightly electron withdrawing character of this moiety, resulting in a mismatch for effective  stacking or poor ability of orbital of sulphur to overlap with  system allowing for free rotation of the thioester and hence movement of the carbonyl oxygen atom from the plane.

The physical properties of the butadiyne derivatives **6a-g** were examined by POM and DSC. These materials did not show evidence of liquid crystalline properties as expected upon the basis on the properties shown by ester analogues **4a-g**. However it was found that several of these compounds showed signs of polymorphism, by having multiple crystallisation events. Furthermore, thioesters **6a-g** were non-mesogenic.

Table 5: Experimental values taken from the DSC thermograms at a heat/cool rate of 10 °Cmin-1 of compounds **6a-i**, and transition temperatures for previously reported **4a-g**5,6

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| R = |  |  | | |
| -C4H9 | **6a** | Cr 137.6 Iso | **4a**5 | Cr1 106.4 Cr2 132.5 N 160.2 Iso |
| -C5H11 | **6b** | Cr1 -22.0 Cr2 139.3 Iso | **4b**6 | Cr1 70 Cr2 123 Cr3 134 N 157 Iso |
| -C6H13 | **6c** | Cr 133.0 Iso | **4c**6 | Cr1 32 Cr2 45 Cr3 129 N 138 Iso |
| -C7H15 | **6d** | Cr1 13.4 Cr2 134.2 Iso | **4d**5 | Cr1 82.3 Cr2 129.3 N 136.5 Iso |
| -C8H17 | **6e** | Cr1 35.8 Cr2 130.9 Iso | **4e**5 | Cr 127.4 (N 129.6) Iso |
| -C9H19 | **6f** | Cr1 40.1 Cr2 132.7 Iso | **4f**6 | Cr1 95 Cr2 130 Iso |
| -C10H21 | **6g** | Cr1 53.5 Cr2 130.3 Iso | **4g**5 | Cr1 68.4 Cr2 88.4 N 125.1 Iso |
| -C6H4C8H17 | **6h** | Cr1 -28.3 Cr2 176.8 N <250 decomp. |  |  |
| -C6H4C10H21 | **6i** | Cr1 1.1 Cr2 168.8 SmA 187.7 N <250 decomp. |  |  |

As for compounds **6h-i**, which both had two additional rings in the structure, liquid crystalline properties were observed, though the transition temperatures were high and the material decomposed before the transition into an isotropic liquid. The enthalpies and entropies for the transition temperatures that occurred beneath the decomposition temperature are given in Table 6. Compound **6h** has a nematic appearing at 176.8 °C, but heating to above 250 °C resulted in decomposition. For compound **6i**, the transition into a smectic phase was found to be at a slightly lower temperature with the transition occurring at 168.8 °C. Compound **6i** also exhibited a nematic phase at 187.7 °C, but as found with **6h**, it started to decompose when heated above 250 °C. The smectic phase was determined as being SmA by the texture shown in Figure 8 for **6i** at 178 °C. Due to the decomposition of the sample, SAXS/WAXS studies on **6**i were not performed.

Table 6: The enthalpies (kJ mol-1) and dimensionless entropies associated with transition for compounds **6h** and **6i**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  | Cr1-Cr2 | Cr2-SmA | SmA-N | Cr2-N |
| **6h** | ∆*H* | 5.66 | - | - | 32.2 |
|  | ∆*S*/*R* | 2.78 | - | - | 8.60 |
| **6i** | ∆*H* | 14.1 | 30.0 | 2.72 | - |
|  | ∆*S*/*R* | 6.20 | 8.16 | 0.71 | - |

1Enthalpy for transition above 250 °C was not calculated due to decomposition.

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Figure 8: Photomicrographs of the smectic phase of **6i** at 178 °C, enlarged 100 times.

## Conclusions

A variety of simple derivatives containing long chain thioesters was conveniently prepared from the corresponding *tert*-butylthioether using bismuth triflate and long chain acid chlorides and studied for their liquid crystalline properties. Some cyanobiphenyl thioesters studied showed liquid crystalline properties, the nononyl thioester showed a nematic phase and a smectic A phase, while extending the aliphatic chain by one and two gave materials which only exhibited a smectic A phase. By SAXS/WAXS, the assignment of the phases was confirmed for the cyanobiphenyl thioester **5e** and spacing between the layers was determined to be around 1.5 times the molecular length. The packing of these layers seemed to be influenced by the interaction of the biphenyl rings between neighbouring molecules. By attaching a bulky group at the end of the alkyl chain, the layers could be potentially be pushed apart, reducing the interaction between the biphenyls.21 If this were the case, the layer spacing would change to one or two times the molecule length. It was found that **5e**, which exhibited the lowest temperature for the nematic phase, was not stable under the conditions used for measurement of dielectric anisotropy. It was found that even though diphenyl butadiynes furnished with peripheral long chain esters have liquid crystalline properties, the thioester analogues did not. Extension of the synthetic methodology for synthesis of thioesters was attempted upon a 1-cyanoazulene derivative. The presence of the azulene did not allow for the formation of the desired product, but instead a Friedel-Crafts reaction on the 3-position predominated. Though this was not the desired reaction, this opens the possibility for further functionalization of azulenes. However, this synthetic strategy may be a possibility if prior to the transformation using bismuth triflate, the 3-position was substituted.

## Experimental

### General Experimental

Chemicals were used as purchased from commercial sources. Purification of products was carried out by flash chromatography on silica gel (40−63 μm, 60 Å). Thin-layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel. 1H NMR (500 MHz) and 13C NMR (125 MHz) spectra were recorded on an instrument with a non-inverse cryoprobe using the residual solvent as the internal standard (CDCl3, 1H 7.26 ppm and 13C 77.16 ppm). All chemical shifts are quoted on the δ scale (ppm), and all coupling constants (*J*) are expressed in Hz. In APT spectra, CH and CH3 correspond to negative signals and C and CH2 correspond to positive signals. High resolution mass spectra (HRMS) were acquired using MALDI. Dielectric measurements were done on an INSTEC ALCT Property Tester. Melting points are uncorrected. UV-Vis absorption spectra were obtained by scanning the wavelength from 800 to 200 nm, using a Carey Bio-50 spectrophotometer and performed in a 1-cm path length cuvette. Polarized optical microscopy was performed on a Olympus BX41 microscope, with a Olympus SC100 camera mounted on top, using a Linkam HFS91 hotstages controlled by a Linkam TP 93, or on a Zeiss Axioskop 40Pol microscope fitted with a an InfinityX-21 MP digital camera mounted atop, using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Differential scanning calorimetry was performed on a Perkin Elmer DSC 8000 using Pyris Series-DCS 8000 software or using a Mettler DSC822e operating with Mettler Stare software and calibrated before use against an indium standard (onset = 156.55 ± 0.2 °C, ΔH = 28.45 ± 0.40 Jg-1) under an atmosphere of dry nitrogen. Small and wide angle X-ray diffraction (SAXS/WAXS) was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was copper Kα (λ = 0.154056 nm) from a 1 μS microfocus source. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample, allowing simultaneous collection of small angle and wide angle scattering data. Samples were filled into 1mm capillary tubes and aligned with a pair of 1T magnets (0.6 T at sample position). Diffraction patterns were collected as a function of temperature in 1.1 °C intervals. Compounds **9**22, **12**2 and **13**8 were made by their respective literature procedures.

### Synthetic procedures

**4'-(*tert*-Butylthio)-[1,1'-biphenyl]-4-carbonitrile (11)**

A degassed biphasic mixture of 4-*tert*-butylthiophenylboronic acid **9** (1.02 g, 4.85 mmol), K3PO4 (2.40 g, 11.3 mmol), 4-bromobenzonitrile **10** (1.04 g, 5.75 mmol), Pd(OAc)2 (67 mg, 0.30 mmol) and RuPhos (262 mg, 0.561 mmol) in toluene (100 mL) and water (25 mL) was stirred at ambient temperature for 36 h. The contents of the cooled vessel were diluted with water (50 mL) and Et2O (100 mL). The phases were separated and the aqueous phase extracted with Et2O (50 mL). The combined organics were dried over MgSO4, filtered and the solvent removed under reduced pressure. Purification of the crude residue by flash column chromatography (80% toluene/heptane) afforded **11** (1.12 g, 86%) as a white solid. M.p. = 109.5-112 °C. R*f* = 0.33(80% toluene/heptane). 1H NMR (500 MHz, CDCl3) *δ* = 7.74 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 1.33 (s, 9H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 145.0, 139.5, 138.1, 133.9, 132.8, 127.8, 127.3, 119.0, 111.4, 46.5, 31.2 ppm.HRMS (ESMS +ve):*m/z* calcd for C17H18NS ([M+H]+) = 268.1155; exp 268.1156.Analysis calcd (%) for C17H17NS (267.39): C 76.36, H 6.41, N 5.24; found C 76.66, H 6.29, N 5.16.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) pentanethioate (5a)**

To a suspension of **11** (40 mg, 0.150 mmol) and valeroyl chloride **8a** (0.30 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (35 mg, 0.053 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution 66% CH2Cl2/heptane to CH2Cl2) to give **5a** (41 mg,93%) as a white solid.M.p. = Cr 52.2 Iso °C.R*f* = 0.30(66% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.74 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.72 (p, *J* = 7.5 Hz, 2H), 1.42 (h, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* **=** 197.4, 144.8, 140.2, 135.2, 132.8, 128.9, 128.0, 127.9, 118.9, 111.6, 43.8, 27.8, 22.3, 13.9 ppm.MS (ESMS +ve):*m/z* = 318 ([M+Na]+), 296 ([M+H]+).Analysis calcd (%) for C18H17NOS (295.40): C 73.19, H 5.80, N 4.74; found C 73.21, H 5.71, N 4.66.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) hexanethioate (5b)**

To a suspension of **11** (42 mg, 0.157 mmol) and hexanoyl chloride **8b** (0.30 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (35 mg, 0.053 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution 66% CH2Cl2/heptane to CH2Cl2) to give **5b** (47 mg,97%) as a white solid.M.p. = Cr 75.5 Iso °C.R*f* = 0.31(66% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.74 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.74 (p, *J* = 7.5 Hz, 2H), 1.39–1.33 (m, 4H), 0.92 (d, *J* = 7.0 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* **=** 197.4, 144.8, 140.2, 135.2, 132.8, 128.9, 128.0, 127.9, 118.9, 111.6, 44.0, 31.2, 25.4, 22.5, 14.0 ppm.MS (ESMS +ve):*m/z* = 332 ([M+Na]+), 310 ([M+H]+).Analysis calcd (%) for C19H19NOS (309.43): C 73.75, H 6.19, N 4.53; found C 73.60, H 6.08, N 4.46.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) heptanethioate (5c)**

To a suspension of **11** (42 mg, 0.157 mmol) and heptanoyl chloride **8c** (0.30 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (34 mg, 0.052 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution 66% CH2Cl2/heptane to CH2Cl2) to give **5c** (47 mg,93%) as a white solid.M.p. = Cr 58.5 Iso °C.R*f* = 0.33(66% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.74 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.42–1.29 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* **=** 197.3, 144.8, 140.2, 135.2, 132.8, 128.9, 128.0, 127.9, 118.9, 111.6, 44.0, 31.6, 28.8, 25.7, 22.6, 14.2 ppm.MS (ESMS +ve):*m/z* = 346 ([M+Na]+), 324 ([M+H]+).Analysis calcd (%) for C20H21NOS (323.45): C 74.27, H 6.54, N 4.33; found C 74.36, H 6.58, N 4.25.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) octanethioate (5d)**

To a suspension of **11** (39 mg, 0.146 mmol) and octanoyl chloride **8d** (0.30 mL) in CH3CN (1.0 mL) was added Bi(OTf)3 (33 mg, 0.050 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution 66% CH2Cl2/heptane to CH2Cl2) to give **5d** (48 mg,97%) as a white solid.M.p. = Cr 60.9 Iso °C. R*f* = 0.34(66% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.74 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.41–1.26 (m, 8H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* **=** 197.4, 144.8, 140.2, 135.2, 132.8, 128.9, 128.0, 127.9, 118.9, 111.6, 44.1, 31.8, 29.1, 29.1, 25.8, 22.7, 14.2 ppm.MS (ESMS +ve):*m/z* = 338 ([M+H]+).Analysis calcd (%) for C21H23NOS (337.48): C 74.74, H 6.87, N 4.15; found C 74.81, H 6.72, N 4.31.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) nonanethioate (5e)**

To a suspension of **11** (40 mg, 0.150 mmol) and nonanoyl chloride **8e** (0.30 mL) in CH3CN (1.0 mL) was added Bi(OTf)3 (31 mg, 0.047 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution 66% CH2Cl2/heptane to CH2Cl2) to give **5e** (46 mg,87%) as a white solid.M.p. = Cr 45.3 SmA 53.5 N 60.2 Iso °C.R*f* = 0.35(66% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.74 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.41–1.24 (m, 10H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* **=** 197.4, 144.8, 140.2, 135.2, 132.8, 128.9, 128.0, 128.0, 118.9, 111.6, 44.1, 31.9, 29.4, 29.2, 29.1, 25.8, 22.8, 14.2 ppm.MS (ESMS +ve):*m/z* = 352([M+H]+).Analysis calcd (%) for C22H25NOS (351.51): C 75.17, H 7.17, N 3.98; found C 75.14, H 7.02, N 3.87.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) decanethioate (5f)**

To a suspension of **11** (42 mg, 0.157 mmol) and decoyl chloride **8f** (0.30 mL) in CH3CN (1.0 mL) was added Bi(OTf)3 (33 mg, 0.050 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent pressure. The residue was purified by flash column chromatography (gradient elution 66% CH2Cl2/heptane to CH2Cl2) to give **5f** (55 mg, 96%) as a white solid.M.p. = Cr 59.3 SmA 68.0 Iso °C.R*f* = 0.38(66% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* =7.74 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.41–1.24 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* =197.4, 144.8, 140.2, 135.2, 132.8, 128.9, 128.0, 128.0, 118.9, 111.6, 44.1, 32.0, 29.5, 29.4, 29.1, 25.8, 22.8, 14.3 ppm.MS (ESMS +ve):*m/z* = 366 ([M+H]+).Analysis calcd (%) for C23H27NOS (365.54): C 75.57, H 7.45, N 3.83; found C 75.92, H 7.33, N 3.75.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) undecanethioate (5g)**

To a solution of **11** (40 mg, 0.150 mmol) and undecoyl chloride **8g** (0.30 mL) in CH3CN (1.0 mL) was added Bi(OTf)3 (30 mg, 0.46 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution from 80% toluene/heptane to toluene) to give **5g** (54 mg,95%) as a white solid.M.p. = Cr1 44.9 (Cr2 50.9) SmA 69.2 Iso °C.R*f* = 0.40(66% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.74 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.41–1.24 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 197.4, 144.8, 140.2, 135.2, 132.8, 128.9, 128.0, 127.9, 118.9, 111.6, 44.1, 32.0, 29.7, 29.6, 29.4, 29.4, 29.1, 25.8, 22.8, 14.3 ppm.MS (ESMS +ve):*m/z* = 380 ([M+H]+).Analysis calcd (%) for C24H29NOS (379.56): C 75.95, H 7.70, N 3.69; found C 76.10, H 7.73, N 3.49.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) 4-octylbenzothioate (5h)**

To a suspension of **11** (38 mg, 0.142 mmol) and 4-octylbenzoyl chloride **8h** (0.30 mL) in CH3CN (1.0 mL) was added Bi(OTf)3 (33 mg, 0.050 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution 66% CH2Cl2/heptane to CH2Cl2) to give **5h** (58 mg,95%) as a white solid.M.p. = Cr 70.2 SmA 231.8 N 240 < decomposes °C.R*f* = 0.33(66% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* =7.96 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.32–1.24 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 189.5, 150.0, 144.9, 140.3, 135.9, 134.2, 132.8, 129.0, 128.6, 128.1, 128.0, 127.8, 118.9, 111.6, 36.2, 32.0, 31.2, 29.6, 29.4, 29.4, 22.8, 14.2 ppm.MS (ESMS +ve):*m/z* = 450 ([M+Na]+), 428 ([M+H]+).Analysis calcd (%) for C28H29NOS (427.61): C 78.65, H 6.84, N 3.28; found C 78.57, H 6.84, N 3.26.

***S*-(4'-Cyano-[1,1'-biphenyl]-4-yl) 4-decylbenzothioate (5i)**

To a suspension of **11** (41 mg, 0.153 mmol) and 4-decylbenzoyl chloride **8i** (0.30 mL) in CH3CN (1.0 mL) was added Bi(OTf)3 (31 mg, 0.047 mmol) and the resulting solution stirred at rT for 1 h. During the course of the reaction, a white precipitate had formed, which was collected and the cake washed with CH3CN to give **5i** (37 mg,57%) as a white solid.M.p. = Cr 68.8 SmA 220.3 N 225.7 Iso °C.R*f* = 0.34(66% CH2Cl2/heptane). 1H NMR (500 MHz, CDCl3) *δ* = 7.95 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H), 1.64 (p, *J* = 7.3 Hz, 2H), 1.35–1.24 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 189.5, 150.0, 144.9, 140.3, 135.9, 134.2, 132.9, 129.0, 128.6, 128.1, 128.0, 127.8, 118.9, 111.6, 36.2, 32.0, 31.2, 29.7, 29.7, 29.6, 29.5, 29.4, 22.8, 14.2 ppm.MS (ESMS +ve):*m/z* = 456 ([M+H]+). Analysis calcd (%) for C28H29NOS (427.61): C 78.65, H 6.84, N 3.28; found C 79.16, H 7.35, N 3.00.

***S,S'*-(Buta-1,3-diyne-1,4-diylbis(4,1-phenylene)) dipentanethioate (6a)**

To a suspension of **12** (31 mg, 0.0819 mmol) and valeroyl chloride **8a** (0.30 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (30 mg, 0.046 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold aqueous saturated NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (50% CH2Cl2/heptane) to give **6a** (30 mg,84%) as a white solid.M.p. = Cr 137.6 Iso °C.R*f* = 0.33(50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.54 (d, *J* = 8.5 Hz, 4H), 7.39 (d, *J* = 8.5 Hz, 4H), 2.67 (t, *J* = 7.5 Hz, 4H), 1.70 (p, *J* = 7.5 Hz, 4H), 1.40 (sextet, *J* = 7.5 Hz, 4H), 0.94 (t, *J* = 7.5 Hz, 6H) ppm.13C NMR (125 MHz, CDCl3) *δ* **=** 196.7, 134.3, 133.1, 129.8, 122.7, 81.6, 75.3, 43.8, 27.7, 22.2, 13.8 ppm.MS (ESMS +ve):*m/z* = 457 ([M+Na]+), 435 ([M+H]+).Analysis calcd (%) for C26H26O2S2 (434.61): C 71.85, H 6.03; found C 71.65, H 5.89.

***S,S'*-(Buta-1,3-diyne-1,4 (4,1-phenylene)) dihexanethioate (6b)**

To a suspension of **12** (35 mg, 0.0924 mmol) and hexanoyl chloride **8b** (0.30 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (30 mg, 0.046 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (50% CH2Cl2/heptane) to give **6b** (38 mg,89%) as a white solid.M.p. = Cr1 -22.0 Cr2 139.3 Iso °C.R*f* = 0.38(50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3)*δ* = 7.54 (d, *J* = 8.4 Hz, 4H), 7.39 (d, *J* = 8.4 Hz, 4H), 2.66 (t, *J* = 7.5 Hz, 4H), 1.72 (p, *J* = 7.4 Hz, 4H), 1.37–1.32 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 6H) ppm.13C NMR (125 MHz, CDCl3) *δ* **=** 196.7, 134.3, 133.1, 129.8, 122.7, 81.6, 75.4, 44.0, 31.2, 25.4, 22.4, 14.0 ppm.MS (ESMS +ve):*m/z* = 485 ([M+Na]+), 463 ([M+H]+).Analysis calcd (%) for C28H30O2S2 (462.67): C 72.69, H 6.54; found C 72.83, H 6.46.

***S,S'*-(Buta-1,3-diyne-1,4-diylbis(4,1-phenylene)) diheptanethioate (6c)**

To a suspension of **12** (35 mg, 0.0924 mmol) and heptanoyl chloride **8c** (0.30 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (34 mg, 0.052 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (45% CH2Cl2/heptane) to give **6c** (34 mg,75%) as a white solid.M.p. = Cr 133.0 Iso °C.R*f* = 0.39 (50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3)*δ* = 7.54 (d, *J* = 8.4 Hz, 4H), 7.39 (d, *J* = 8.4 Hz, 4H), 2.66 (t, *J* = 7.5 Hz, 4H), 1.71 (p, *J* = 7.5 Hz, 4H), 1.40–1.28 (m, 12H), 0.90 (t, *J* = 6.9 Hz, 6H) ppm. 13C NMR (125 MHz, CDCl3) *δ* **=** 196.7, 134.3, 133.1, 129.8, 122.7, 81.6, 75.4, 44.1, 31.2, 28.7, 25.7, 22.6, 14.2 ppm**.** MS (ESMS +ve):*m/z* = 513 ([M+Na]+), 491 ([M+H]+).Analysis calcd (%) for C30H34O2S2 (490.72): C 73.43, H 6.98; found C 73.59, H 6.92.

***S,S'*-(Buta-1,3-diyne-1,4-diylbis(4,1-phenylene)) dioctanethioate (6d)**

To a suspension of **12** (31 mg, 0.0819 mmol) and octanoyl chloride **8d** (0.35 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (33 mg, 0.050 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (40% CH2Cl2/heptane) to give **6d** (40 mg,94%) as a white solid.M.p. = Cr1 13.4 Cr2 134.2 Iso °C. R*f* = 0.42(50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.54 (d, *J* = 8.5 Hz, 4H), 7.39 (d, *J* = 8.5 Hz, 4H), 2.66 (t, *J* = 7.5 Hz, 4H), 1.71 (p, *J* = 7.5 Hz, 4H), 1.39–1.25 (m, 16H), 0.89 (t, *J* = 7.0 Hz, 6H) ppm.13C NMR (125 MHz, CDCl3) *δ* **=** 196.7, 134.3, 133.1, 129.8, 122.7, 81.6, 75.4, 44.1, 31.7, 29.0, 25.7, 22.7, 14.2 ppm, 1C masked**.** MS (ESMS +ve):*m/z* = 541 ([M+Na]+), 519 ([M+H]+).Analysis calcd (%) for C32H38O2S2 (518.77): C 74.09, H 7.38; found C 74.04, H 7.26.

***S,S'*-(Buta-1,3-diyne-1,4-diylbis(4,1-phenylene)) dinonanethioate (6e)**

To a suspension of **12** (29 mg, 0.0766 mmol) and nonoyl chloride **8e** (0.30 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (31 mg, 0.047 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (40% CH2Cl2/heptane) to give **6e** (40 mg,95%) as a white solid.M.p. = Cr1 35.8 Cr2 130.9 Iso °C. R*f* = 0.44(50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.54 (d, *J* = 8.5 Hz, 4H), 7.39 (d, *J* = 8.5 Hz, 4H), 2.66 (t, *J* = 7.5 Hz, 4H), 1.71 (p, *J* = 7.5 Hz, 4H), 1.38–1.25 (m, 20H), 0.89 (t, *J* = 7.0 Hz, 6H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 196.7, 134.4, 133.1, 129.8, 122.7, 81.6, 75.4, 44.1, 31.9, 29.3, 29.2, 29.1, 25.7, 22.8, 14.2 ppm.MS (ESMS +ve):*m/z* = 569 ([M+Na]+), 547 ([M+H]+).Analysis calcd (%) for C34H42O2S2 (546.83): C 74.68, H 7.74; found C 74.81, H 7.65.

***S,S'*-(Buta-1,3-diyne-1,4-diylbis(4,1-phenylene)) bis(decanethioate) (6f)**

To a suspension of **12** (35 mg, 0.0924 mmol) and decanoyl chloride **8f** (0.40 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (35 mg, 0.053 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (40% CH2Cl2/heptane) to give **6f** (51 mg,96%) as a white solid.M.p. = Cr1 40.1 Cr2 132.7 Iso °C.R*f* = 0.47(50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.54 (d, *J* = 8.5 Hz, 4H), 7.39 (d, *J* = 8.5 Hz, 4H), 2.66 (t, *J* = 7.5 Hz, 4H), 1.71 (p, *J* = 7.5 Hz, 4H), 1.37–1.25 (m, 24H), 0.88 (t, *J* = 7.0 Hz, 6H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 196.7, 134.4, 133.1, 129.8, 122.7, 81.6, 75.4, 44.1, 32.0, 29.5, 29.4, 29.1, 25.7, 22.8, 14.3 ppm, 1C masked. MS (ESMS +ve):*m/z* = 597 ([M+Na]+), 575 ([M+H]+).Analysis calcd (%) for C36H46S2O2 (574.88): C 75.21, H 8.07; found C 75.21, H 7.83.

***S,S'*-(Buta-1,3-diyne-1,4-diylbis(4,1-phenylene)) diundecanethioate (6g)**

To a suspension of **12** (49 mg, 0.129 mmol) and undecanoyl chloride **8g** (0.50 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (50 mg, 0.076 mmol) and the resulting solution stirred at rT for 1 h. The reaction mixture was added to cold saturated aqueous NaHCO3 (20 mL) and extracted with small portions of CH2Cl2 (20 mL in total). The combined organics were passed through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (40% CH2Cl2/heptane) to give **6g** (72 mg,93%) as a white solid.M.p. = Cr1 53.5 Cr2 130.3 Iso °C.R*f* = 0.54(50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.54 (d, *J* = 8.4 Hz, 4H), 7.39 (d, *J* = 8.4 Hz, 4H), 2.66 (t, *J* = 7.5 Hz, 4H), 1.71 (p, *J* = 7.5 Hz, 4H), 1.39–1.24 (m, 28H), 0.89 (t, *J* = 7.0 Hz, 6H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 196.70, 134.34, 133.07, 129.80, 122.71, 81.60, 75.36, 44.06, 32.03, 29.67, 29.54, 29.43, 29.37, 29.08, 25.70, 22.82, 14.25 ppm. MS (ESMS +ve):*m/z* = 603 ([M+H]+).Analysis calcd (%) for C38H50S2O2 (602.94): C 75.70, H 8.36; found C 75.87, H 8.58.

***S,S'*-(Buta-1,3-diyne-1,4-diylbis(4,1-phenylene)) bis(4-octylbenzothioate) (6h)**

To a suspension of **12** (60 mg, 0.158 mmol) and 4-octylbenzoyl chloride **8h** (0.50 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (63 mg, 0.096 mmol) and the resulting solution stirred at rT for 1 h. During the course of the reaction, a white precipitate had formed, which was collected and the cake washed with CH3CN to give **6h** (98 mg,89%) as a white solid.M.p. = Cr1 -28.3 Cr2 176.8 N <250 decomposes °C.R*f* = 0.41(50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.93 (d, *J* = 8.2 Hz, 4H), 7.60 (d, *J* = 8.5 Hz, 4H), 7.50 (d, *J* = 8.5 Hz, 4H), 7.29 (d, *J* = 8.2 Hz, 4H), 2.68 (t, *J* = 7.6 Hz, 4H), 1.64 (p, *J* = 7.6 Hz, 4H), 1.35–1.24 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 12H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 189.0, 150.0, 135.1, 134.1, 133.1, 129.5, 129.0, 127.8, 122.9, 81.7, 75.5, 36.2, 32.0, 31.2, 29.6, 29.4, 29.4, 22.8, 14.3 ppm.Analysis calcd (%) for C46H50S2O2 (699.02): C 79.04, H 7.21; found C 79.03, H 7.14.

***S,S'*-(Buta-1,3-diyne-1,4-diylbis(4,1-phenylene)) bis(4-decylbenzothioate) (6i)**

To a suspension of **12** (60 mg, 0.158 mmol) and 4-decylbenzoyl chloride **8i** (0.50 mL) in CH3CN (1.0 mL) and toluene (0.50 mL) was added Bi(OTf)3 (65 mg, 0.099 mmol) and the resulting solution stirred at rT for 1 h. During the course of the reaction, a white precipitate had formed, which was collected and the cake washed with CH3CN to give **6i** (104 mg,87%) as a white solid.M.p. = Cr1 1.1 Cr2 168.8 SmA 187.7 N <250 decomposes °C.R*f* = 0.49(50% CH2Cl2/heptane).1H NMR (500 MHz, CDCl3) *δ* = 7.93 (d, *J* = 8.3 Hz, 4H), 7.60 (d, *J* = 8.5 Hz, 4H), 7.50 (d, *J* = 8.5 Hz, 4H), 7.29 (d, *J* = 8.3 Hz, 4H), 2.68 (t, *J* = 7.8 Hz, 4H), 1.64 (p, *J* = 7.4 Hz, 4H), 1.34–1.25 (m, 28H), 0.88 (t, *J* = 7.0 Hz, 6H) ppm.13C NMR (125 MHz, CDCl3) *δ* = 189.0, 150.0, 135.1, 134.1, 133.1, 129.5, 129.0, 127.8, 122.9, 81.7, 75.5, 36.2, 32.0, 31.2, 29.7, 29.7, 29.6, 29.5, 29.4, 22.8, 14.3 ppm. Analysis calcd (%) for C50H58S2O2 (755.13): C 79.53, H 7.74; found C 79.31, H 7.61.

**2-(4'-(*tert*-Butylthio)-[1,1'-biphenyl]-4-yl)azulene-1-carbonitrile (14)**

To a stirring degassed biphasic mixture of **13** (597 mg, 1.68 mmol), (4-(*tert*-butylthio)phenyl)boronic acid **9** (568 mg, 2.70 mmol) and K3PO4 (1.33 g, 6.27 mmol) in toluene (60 mL) and water (10 mL) were added RuPhos (82 mg, 0.18 mmol) and Pd(OAc)2 (22 mg, 0.098 mmol) and the resulting mixture was heated to 80 °C for 16 h under an argon atmosphere. The mixture was allowed to cool to rt and water (50 mL) was added to the vessel. The mixture was extracted with toluene (3 x 50 mL). The combined organics were dried over MgSO4, filtered and the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (gradient elution of 90% toluene/heptane to toluene) followed by recrystallisation from CH2Cl2/heptane to give **14** (593 mg, 90%). *R*f=0.38 (toluene). M.p. = 183-184 °C. 1H NMR (500 MHz, CDCl3): *δ* = 8.64 (d, *J* = 9.8 Hz, 1H), 8.41 (d, *J* = 9.8 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 2H), 7.80–7.76 (m, 3H), 7.63 (s, 4H), 7.58 (s, 1H), 7.54 (dd, *J* = 9.8, 9.8 Hz, 1H), 7.48 (dd, *J* = 9.8, 9.8 Hz, 1H), 1.35 (s, 9H) ppm. 13C NMR (125 MHz, CDCl3): *δ* = 151.5, 145.9, 142.7, 141.4, 140.6, 139.0, 138.0, 138.0, 135.9, 133.7, 132.5, 129.2, 128.2, 128.0, 127.9, 127.2, 118.3, 116.5, 94.2, 46.4, 31.2 ppm. HRMS (MALDI +ve) calcd for C27H24NS [(M+H)+]: *m/z* = 394.1624, exp 394.1634, Analysis calcd (%) for C27H23NS (393.55): C 82.40, H 5.89, N 3.56; found: C 82.52, H 5.50, N 3.60. UV-Vis (CH2ClCH2Cl): Absorbance maxima *λ* = 332 nm (*ԑ* = 63 · 103 M-1cm-1), *λ* = 396 nm (*ԑ* = 21 · 103 M-1cm-1).

**Reaction of 14 with nonanoyl chloride catalyzed by bismuth triflate**

To a solution of **14** (57 mg 0.14 mmol) and nonanoyl chloride **8e** (0.30 mL, 1.7 mmol) in CH3CN (1 mL) and toluene (1 mL) was added Bi(OTf)3 (32 mg, 0.049 mmol) and the contents of the vessel stirred for 1 h at rt. TLC analysis indicated that the reaction was not complete and another portion of Bi(OTf)3 (40 mg, 0.061 mmol) was added. After 1 h more of stirring, the reaction was quenched with cooled saturated aqueous NaHCO3 (20 mL) and the mixture was extracted with CH2Cl2 (3 x 20 mL), and filtered through cotton. The solvent was removed by rotary evaporation and the residue was subjected to flash column chromatography (gradient elution of toluene to 10% CH2Cl2/toluene), followed by a second flash column chromatography (75% CH2Cl2/toluene) giving some of the product **15e** pure, and fraction with a mixture of both **15e** and **16e**, which was separated by flash column chromatography (gradient elution toluene to 2% EtOAc/toluene) to finally give **15e** (47 mg, 61%) and **16e** (27 mg, 30%) both as pink glassy solids.

**2-(4'-(*tert*-Butylthio)-[1,1'-biphenyl]-4-yl)-3-nonanoylazulene-1-carbonitrile (15e)**

*R*f=0.10 (toluene), *R*f=0.30 (50% CH2Cl2/toluene). M.p. = 130.5-133 °C. 1H NMR (500 MHz, CDCl3): *δ* = 9.20 (dd, *J* = 10.2, 0.7 Hz, 1H), 8.79 (dd, *J* = 9.9, 0.8 Hz, 1H), 8.00 (t, *J* = 9.8 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.79–7.74 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.65 (s, 4H), 2.44 (t, *J* = 7.4 Hz, 2H), 1.52 (q, *J* = 7.2 Hz, 2H), 1.35 (s, 9H), 1.20–1.04 (m, 10H), 0.79 (t, *J* = 7.2 Hz, 3H) ppm. 13C NMR (125 MHz, CDCl3): *δ* = 202.9, 153.3, 145.0, 141.6, 141.2, 141.2, 140.4, 139.7, 138.1, 137.6, 133.7, 132.8, 131.7, 130.6, 130.2, 127.7, 127.4, 127.3, 116.8, 97.8, 46.4, 44.0, 31.9, 31.2, 29.3, 29.2, 29.2, 25.3, 22.7, 14.2 ppm. HRMS (MALDI +ve) calcd for C36H40NOS [(M+H)+]: *m/z* = 534.2825; exp 538.2837. Analysis calcd (%) for C36H39NOS (533.77): C 81.01, H 7.36, N 2.62; found: C 80.88, H 7.14, N 2.63. UV-Vis (CH2ClCH2Cl): Absorbance maxima *λ* = 336 nm (*ԑ* = 43 · 103 M-1cm-1), *λ* = 292 nm (*ԑ* = 39 · 103 M-1cm-1).

***S*-(4'-(1-Cyano-3-nonanoylazulen-2-yl)-[1,1'-biphenyl]-4-yl) nonanethioate (16e)**

*R*f = 0.10 (toluene), *R*f = 0.24 (50% CH2Cl2/toluene). M.p. = 52-54 °C. 1H NMR (500 MHz, CDCl3): *δ* = 9.21 (dd, *J* = 10.1, 0.7 Hz, 1H), 8.80 (dd, *J* = 9.8, 0.8 Hz, 1H), 8.00 (dd, *J* = 9.9, 9.9 Hz, 1H), 7.81–7.74 (m, 4H), 7.72 (d, *J* = 6.5 Hz, 2H), 7.70 (d, *J* = 6.5 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.44 (t, *J* = 7.5 Hz, 2H), 1.74 (p, *J* = 7.5 Hz, 2H), 1.52 (q, *J* = 7.3 Hz, 2H), 1.42–1.36 (m, 2H), 1.33–1.28 (m, 8H), 1.21–1.16 (m, 2H), 1.15–1.05 (m, 8H), 0.89 (t, *J* = 7.2, 3H), 0.81 (t, *J* = 7.2 Hz, 3H) ppm. 13C NMR (125 MHz, CDCl3): *δ* = 202.9, 197.6, 153.2, 145.0, 141.4, 141.2, 141.2, 141.2, 139.7, 137.6, 135.1, 133.9, 131.7, 130.6, 130.2, 128.0, 127.8, 127.8, 127.5, 116.8, 97.8, 44.0, 44.0, 32.0, 31.9, 29.4, 29.3, 29.2, 29.2, 29.2, 29.1, 25.8, 25.3, 22.8, 22.7, 14.3, 14.2 ppm. HRMS (MALDI +ve) calcd for C41H48NO2S [(M+H)+]: *m/z* = 618.3400; exp 618.3414. UV-Vis (CH2ClCH2Cl): Absorbance maxima *λ* = 334 nm (*ԑ* = 43 · 103 M-1cm-1), *λ* = 290 nm (*ԑ* = 37 · 103 M-1cm-1).

**Reaction of 14 with decanoyl chloride catalyzed by bismuth triflate**

To a solution of **14** (61 mg 0.16 mmol) and decanoyl chloride **8f** (0.30 mL, 1.5 mmol) in CH3CN (1 mL) and toluene (1 mL) was added Bi(OTf)3 (33 mg, 0.050 mmol) and the contents of the vessel stirred for 1 h at rt. TLC analysis indicated that the reaction was not complete and another portion of Bi(OTf)3 (40 mg, 0.048 mmol) was added. After 1 h more of stirring, the reaction was quenched with cooled saturated aqueous NaHCO3 (20 mL) and the mixture was extracted with CH2Cl2 (3 x 20 mL), and filtered through cotton. The solvent was removed in vacuo and the residue was subjected to flash column chromatography (gradient elution of toluene to 50% CH2Cl2/toluene), followed by a second flash column chromatography (toluene) giving some of the product **15f** pure, and fraction with a mixture of both **15f** and **16f**, which was subjected to further flash column chromatography (gradient elution of toluene to 2% EtOAc/toluene) to finally give **15f** (37 mg, 44%) and **16f** (26 mg, 26%) both as pink glassy solids.

**2-(4'-(*tert*-Butylthio)-[1,1'-biphenyl]-4-yl)-3-decanoylazulene-1-carbonitrile (15f)**

*R*f=0.10 (toluene), *R*f=0.24 (50% CH2Cl2/toluene). M.p. = 128.5-130 °C. 1H NMR (500 MHz, CDCl3): *δ* = 9.20 (dd, *J* = 10.0, 0.7 Hz, 1H), 8.78 (dd, *J* = 10.0, 0.8 Hz, 1H), 7.99 (dd, *J* = 9.9, 9.9 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.79–7.73 (m, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.65 (s, 4H), 2.44 (t, *J* = 7.5 Hz, 2H), 1.56–1.50 (m, 2H), 1.34 (s, 9H), 1.21–1.07 (m, 12H), 0.82 (t, *J* = 7.1 Hz, 3H) ppm. 13C NMR (125 MHz, CDCl3): *δ* = 202.8, 153.2, 145.0, 141.5, 141.2, 141.2, 140.4, 139.6, 138.1, 137.5, 133.7, 132.7, 131.7, 130.6, 130.2, 127.7, 127.4, 127.2, 116.8, 97.8, 46.4, 44.0, 31.9, 31.2, 29.4, 29.3, 29.2, 25.2, 22.7, 14.2 ppm. HRMS (MALDI +ve) calcd for C37H42NOS [(M+H)+]: *m/z* = 548.2981; exp 548.2993. Analysis calcd (%) for C37H41NOS (368.52): C 81.13, H 7.54, N 2.56; found: C 80.79, H 7.61, N 2.57. UV-Vis (CH2ClCH2Cl): Absorbance maxima *λ* = 336 nm (*ԑ* = 44 · 103 M-1cm-1), *λ* = 292 nm (*ԑ* = 40 · 103 M-1cm-1).

***S*-(4'-(1-Cyano-3-decanoylazulen-2-yl)-[1,1'-biphenyl]-4-yl) decanethioate** **(16f)**

*R*f=0.10 (toluene), *R*f=0.12 (50% CH2Cl2/toluene). M.p. = 58-59.5 °C. 1H NMR (500 MHz, CDCl3): *δ* = 9.20 (dd, *J* = 10.1, 0.7 Hz, 1H), 8.79 (dd, *J* = 9.8, 0.8 Hz, 1H), 7.99 (dd, *J* = 9.8, 9.8 Hz, 1H), 7.82–7.74 (m, 4H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.74 (p, *J* = 7.4 Hz, 2H), 1.53 (p, *J* = 7.4 Hz, 2H), 1.45–1.02 (m, 24H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 3H) ppm. 13C NMR (125 MHz, CDCl3): *δ* = 202.9, 197.6, 153.2, 145.0, 141.4, 141.2, 141.2, 141.2, 139.7, 137.6, 135.1, 133.9, 131.7, 130.6, 130.2, 128.0, 127.8, 127.8, 127.4, 116.8, 97.8, 44.0, 44.0, 32.0, 31.9, 29.5, 29.5, 29.4, 29.4, 29.4, 29.3, 29.2, 29.1, 25.8, 25.3, 22.8, 22.8, 14.3, 14.2 ppm. HRMS (MALDI +ve) calcd for C43H52NO2S [(M+H)+]: *m/z* = 646.3713; exp 646.3727. UV-Vis (CH2ClCH2Cl): Absorbance maxima *λ* = 335 nm (*ԑ* = 48 · 103 M-1cm-1), *λ* = 290 nm (*ԑ* = 41 · 103 M-1cm-1).

**Reaction of 14 with undecanoyl chloride catalysed by bismuth triflate**

To a solution of **14** (60 mg 0.15 mmol) and undecanoyl chloride **8g** (0.30 mL, 1.4 mmol) in CH3CN (1 mL) and toluene (1 mL) was added Bi(OTf)3 (30 mg, 0.046 mmol) and the contents of the vessel stirred for 1 h at rt. TLC analysis indicated that the reaction was not complete and another portion of Bi(OTf)3 (35 mg, 0.053 mmol) was added. After 1 h more of stirring, the reaction was quenched with cooled saturated aqueous NaHCO3 (20 mL) and the mixture was extracted with CH2Cl2 (3 x 20 mL), and filtered through cotton. The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (gradient elution of toluene to 10% CH2Cl2/toluene), followed by a second flash column chromatography (toluene) giving some of the **15g** (40 mg, 47%), as a glassy pink solid, and a fraction with **16g** containing traces of **15g**, which were separated by flash column chromatography (gradient elution of toluene to 2% EtOAc/toluene) to give **16g** (8 mg, 8%) as pink-red paste.

**2-(4'-(*tert*-Butylthio)-[1,1'-biphenyl]-4-yl)-3-undecanoylazulene-1-carbonitrile (15g)**

*R*f = 0.10 (toluene), *R*f=0.28 (50% CH2Cl2/toluene). M.p. = 95-96.5 °C. 1H NMR (500 MHz, CDCl3): *δ* = 9.2 (dd, *J* = 10.0, 0.7 Hz, 1H), 8.79 (dd, *J* = 9.9, 0.8 Hz, 1H), 7.99 (t, *J* = 9.8, 9.8 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.79–7.73 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.65 (s, 4H), 2.44 (t, *J* = 7.5 Hz, 2H), 1.56–1.49 (m, 2H), 1.25–1.21 (m, 2H), 1.19–1.07 (m, 12H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm. 13C NMR (125 MHz, CDCl3): *δ* = 202.9, 153.2, 145.0, 141.6, 141.2, 141.2, 140.4, 139.6, 138.1, 137.6, 133.7, 132.7, 131.7, 130.6, 130.2, 127.7, 127.4, 127.2, 116.8, 97.8, 46.4, 44.0, 32.0, 31.2, 29.6, 29.5, 29.4, 29.3, 29.2, 25.3, 22.8, 14.2 ppm. HRMS (MALDI +ve) calcd for C38H44NOS [(M+H)+]: *m/z* = 562.3138; exp 562.3150. UV-Vis (CH2ClCH2Cl): Absorbance maxima *λ* = 336 nm (*ԑ* = 43 · 103 M-1cm-1), *λ* = 292 nm (*ԑ* = 39 · 103 M-1cm-1).

***S*-(4'-(1-Cyano-3-undecanoylazulen-2-yl)-[1,1'-biphenyl]-4-yl) undecanethioate (16g)**

*R*f = 0.10 (toluene), *R*f=0.26 (50% CH2Cl2/toluene). M.p. = 44-47 °C. 1H NMR (500 MHz, CDCl3): *δ* = 9.21 (dd, *J* = 10.1, 0.7 Hz, 1H), 8.80 (dd, *J* = 9.9, 0.9 Hz, 1H), 8.00 (dd, *J* = 10.0, 10.0 Hz, 1H), 7.80–7.74 (m, 4H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 1H), 2.41 (t, *J* = 7.5 Hz, 1H), 1.74 (p, *J* = 7.5 Hz, 2H), 1.55–1.50 (m, 2H), 1.41–1.36 (m, 2H), 1.35–1.19 (m, 14H), 1.19–1.03 (m, 12H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm. 13C NMR (125 MHz, CDCl3): *δ* = 202.9, 197.6, 153.2, 145.0, 141.5, 141.2, 141.2, 141.2, 139.7, 137.6, 135.1, 133.9, 131.7, 130.6, 130.2, 128.0, 127.8, 127.8, 127.5, 116.8, 97.8, 44.0, 44.0, 32.1, 32.0, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 29.4, 29.2, 29.1, 25.8, 25.3, 22.8, 22.8, 14.3, 14.3 ppm. HRMS (MALDI +ve) calcd for C45H56NO2S [(M+H)+]: *m/z* = 674.4026, exp 674.4039. Analysis calcd (%) for C45H55NO2S (674.00): C 80.19, H 8.23, N 2.08; found: C 80.60, H 7.99, N 2.18. UV-Vis (CH2ClCH2Cl): Absorbance maxima *λ* = 335 nm (*ԑ* = 47 · 103 M-1cm-1), *λ* = 291 nm (*ԑ* = 40 · 103 M-1cm-1).

**Reaction of 14 with nonanoyl chloride catalyzed by bismuth chloride**

To a solution of **14** (59 mg 0.15 mmol) and nonanoyl chloride **8e** (1.0 mL, 5.6 mmol) in CH3CN (1 mL) and toluene (1 mL) was added BiCl3 (79 mg, 0.25 mmol) and the contents of the vessel stirred for 4 days at rt. TLC analysis indicated that there was no change upon going from 3 to 4 days and the reaction was quenched with cooled saturated aqueous NaHCO3 (20 mL). The mixture was extracted with CH2Cl2 (3 x 20 mL) and filtered through cotton. The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (gradient elution of toluene to 1% EtOAc/toluene), followed by a second flash column chromatography (toluene) and finally a gravity column chromatography (CH2Cl2) to afford **16e** (26 mg, 28%).

**Reaction of 14 with decanoyl chloride catalyzed by bismuth chloride**

To a solution of **14** (59 mg 0.15 mmol) and decanoyl chloride **8f** (1.0 mL, 4.8 mmol) in CH3CN (1 mL) and toluene (1 mL) was added BiCl3 (78 mg, 0.25 mmol) and the contents of the vessel stirred for 4 days at rt. TLC analysis indicated that there was no change between 3 and 4 days and the reaction was quenched with cooled saturated aqueous NaHCO3 (20 mL). The mixture was extracted with CH2Cl2 (3 x 20 mL) and filtered through cotton. The solvent was removed in vacuo and the residue was subjected to flash column chromatography (gradient elution of toluene to 5% EtOAc/toluene), followed by a second flash column chromatography (toluene) and lastly a gravity column chromatography (CH2Cl2) to give **16f** (28 mg, 29%).

**Reaction of 14 with undecanoyl chloride catalyzed by bismuth chloride**

To a solution of **14** (61 mg 0.16 mmol) and undecanoyl chloride **8g** (1.0 mL, 4.9 mmol) in CH3CN (1 mL) and toluene (1 mL) was added BiCl3 (72 mg, 0.23 mmol) and the contents of the vessel stirred for 4 days at rt. TLC analysis indicated that there was no change upon going from 3 to 4 days and the reaction was quenched with cooled saturated aqueous NaHCO3 (20 mL). The mixture was extracted with CH2Cl2 (3 x 20 mL) and filtered through cotton. The solvent was removed and the residue was subjected to flash column chromatography (gradient elution toluene to 1% EtOAc/toluene), followed by a second flash column chromatography (toluene) and finally a gravity column chromatography (CH2Cl2) gave **16f** (40 mg, 38%).

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**Conflict of interest**

The authors declare no conflicts of interest.

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