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Bismuth(III)-Promoted Acetylation of Thioethers into Thioacetates

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The thioacetate group is extensively employed as an anchoring group for attachment of molecules onto gold surfaces or between electrodes in molecular electronics. On account of its ready hydrolysis, it is often incorporated in the last step of a synthetic sequence from the corresponding *tert*-butyl thioether. Here we present a particularly convenient method for this conversion using AcCl in combination with $Bi(OTf)_3$, which is known as an environmentally friendly salt. A large variety of redox-active and photoactive substrates with *tert*-butyl thioether end-cap(s) was prepared, including molecules incorporating dithiafulvene, dicyanoethylene, dihydroazulene, fulleropyrrolidine, and triazole units, and successfully subjected to a Bi^{III} promoted conversion into products with thioacetate end-cap(s). The azide group could also withstand these conditions, which allowed us to prepare *S*-(4-azidophenyl) ethanethioate that presents a convenient building block for subsequent CuAAC reactions.

Introduction

Scientific advances in nanotechnology have allowed for the construction of elaborate and miniaturized devices incorporating small organic molecules and supramolecular assemblies to perform certain functions, such as electrical conductivity, photoactivity, catalysis, and redox activity (charge reservoirs), just to mention a few. Organic molecules integrated into molecular junctions in the field of molecular electronics[1] have required an additional design requirement for the secure and reliable anchoring of the molecule to electrodes or upon a 2-dimensional surface. Typically gold is used in such devices, due to its high stability and conductive properties. Several anchoring groups have been used; nonetheless, a thiol (thiolate) seems to be one of the most robust functional groups for the connection of an organic molecule to gold.[2] Unfortunately, the thiol moiety is susceptible to aerial oxidation and thus has to be typically liberated from the labile protected thioacetate in situ. To the dismay of synthetic chemists in this field, the thioacetate group is not tolerant to many reaction conditions. For this reason, the *tert*-butyl thioether has often been used to mask the thiol during harsh synthetic transformations until a terminal step, where the thioacetate can be generated from the *tert*-butyl thioether by treatment with either the Lewis acid boron tribromide[3] or from a lesser known procedure employing catalytic bromine,[4] in both cases in the presence of acetyl chloride. Alternatively, the thioacetate can be introduced by the treatment of an aryl halide with potassium thioacetate under cross-coupling conditions.[5] Nevertheless, not all functional groups present in the molecular wire/transistor may be compatible with these conditions, and as the demands for more specific and sometimes more complicated structures increase, so do the needs to develop alternative methods for the S*t*Bu to SAc conversion.

Bismuth(III) salts have been shown to be versatile catalysts in organic transformations, facilitating a wide variety of reactions and have been tagged as green reagents, due to non-toxic and environmentally safe properties.[6] This reactivity can be ascribed to the weak shielding of the outer f electrons, thus giving this non-toxic heavy metal salt Lewis acidic character, and thus it is capable of such transformations as carbon–carbon bond formation in Friedel–Crafts type chemistry, and both deprotection and formation of acetals, amongst others. More pertinent to our interests, reactions that have been reported are the deprotection of *tert*-butyl ethers connected to either furan or thiophene (**1**) by using either catalytic bismuth triflate [$Bi(OTf)_3$] or bismuth chloride, furnishing the lactone or thiolactone (**2**), respectively, in high yields (Scheme 1).[7] It has also been found that bismuth(III) salts provide a gentle non-toxic methodology to effect deprotection of thioacetals, where otherwise such reagents as boron trifluoride or mercury salts need be employed.[8] From these observations, it can be seen that Bi^{III} salts exhibit an affinity for both oxygen and sulfur lone pairs. The drive for the development of a new, versatile methodology to transform *tert*-butyl thioethers to their cor-

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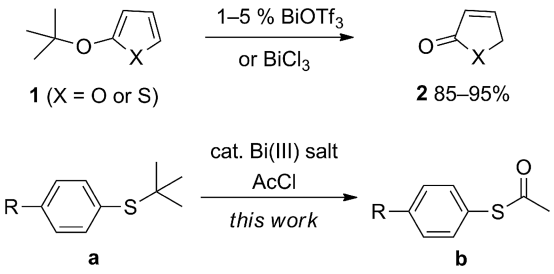
responding thioacetates encouraged us to investigate the possibility to employ a Bi^{III} salt together with acetyl chloride.[9]



Scheme 1. Lead reaction (top) and the focus of this work (bottom).

Treatment of a series of *tert*-butyl thioether derivatives (**3a**–**12a** and various functionalized fullerenes) with catalytic $Bi(OTf)_3$ was the focus of this study (Figure 1). This consisted of a combination of simple aryl derivatives with functionalization in the *para* position (I), a host of double thioethers (II) and additionally some fullerene/*tert*-butyl thioether hybrid compounds (III). Indeed, fullerene itself has also been shown to anchor to gold surfaces[10] and the hope was that this approach could lend itself to the synthesis of materials with two different anchoring groups. Additionally, structures **8a** and **11a** incorporate electron-donating, redox-active dithiafulvene (DTF) units, which have also found interest in molecular electronics; for example, a large selection of cruciform-like molecular wires with DTF groups has recently been studied in break-junctions and at self-assembled monolayers on gold.[11] Compound **12a** has a central dihydroazulene (DHA) unit which acts as a photoswitch, undergoing light-induced ring-opening to a vinylheptafulvene (VHF);[12] this conversion has been shown to be accompanied by electrical conductance switching.[13]

Results and Discussion

Synthesis of Thioether Substrates

Stemming from the bromide **13**, which could be routinely synthesized on a large scale from commercially available 4-bromothiophenol,[3a] a host of different compounds was made (Scheme 2), where some of this chemistry has been previously reported. Thus, preparation of compounds **3a**,[4] **4a**,[14] and **5a**[15] followed standard procedures. Aldehyde **14**[3a] was the precursor for addition of both electron poor and rich olefin derivatives. A Knoevenagel condensation

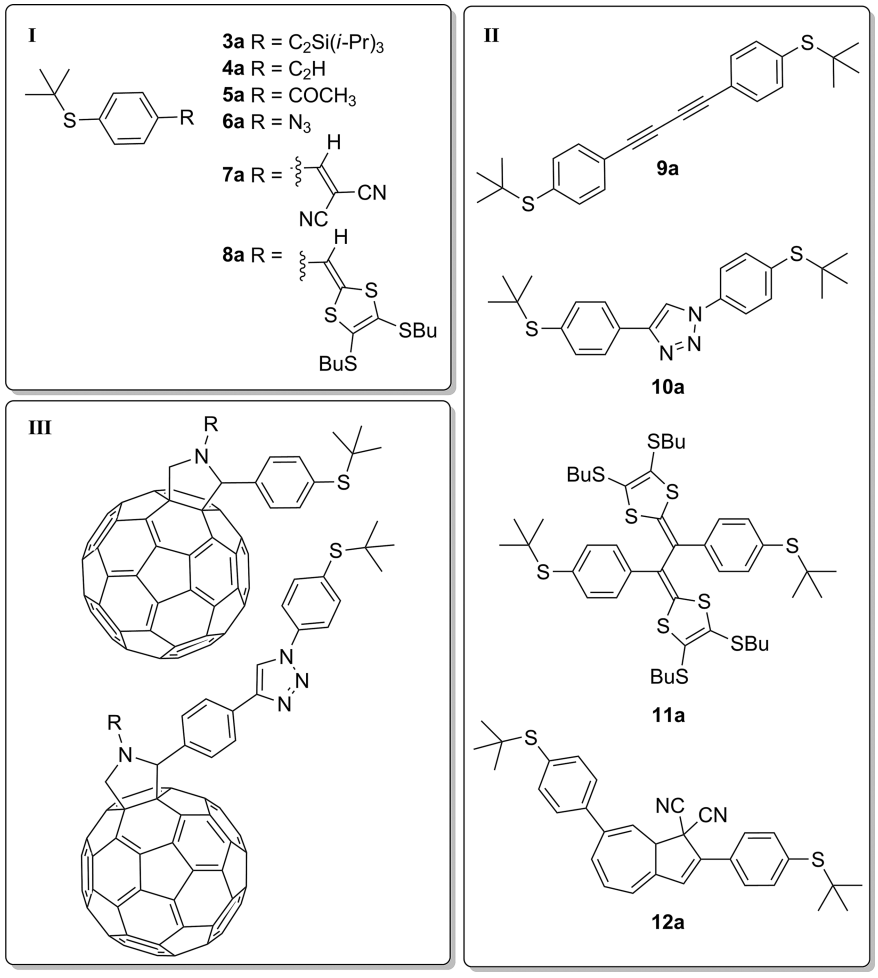
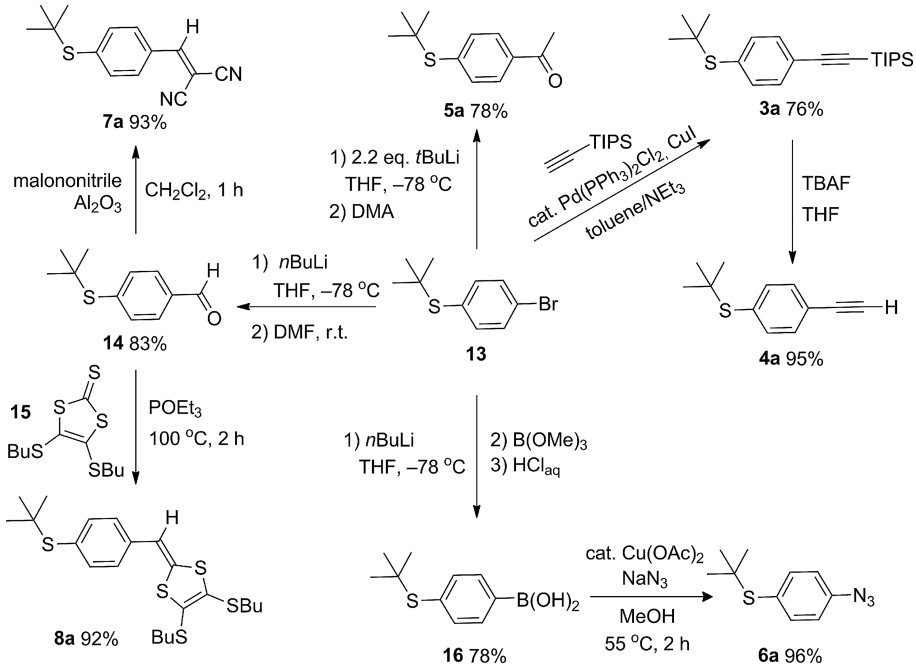


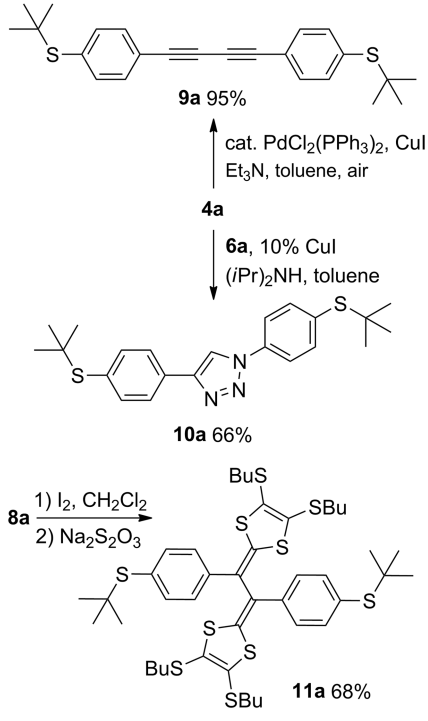
Figure 1. Substrates for probing the $Bi(OTf)_3$ catalyzed conversion of *tert*-butyl thioethers into thioacetates.



Scheme 2. Synthetic outline for preparation of **3a**–**8a**; TIPS = triisopropylsilyl, TBAF = tetrabutylammonium fluoride.

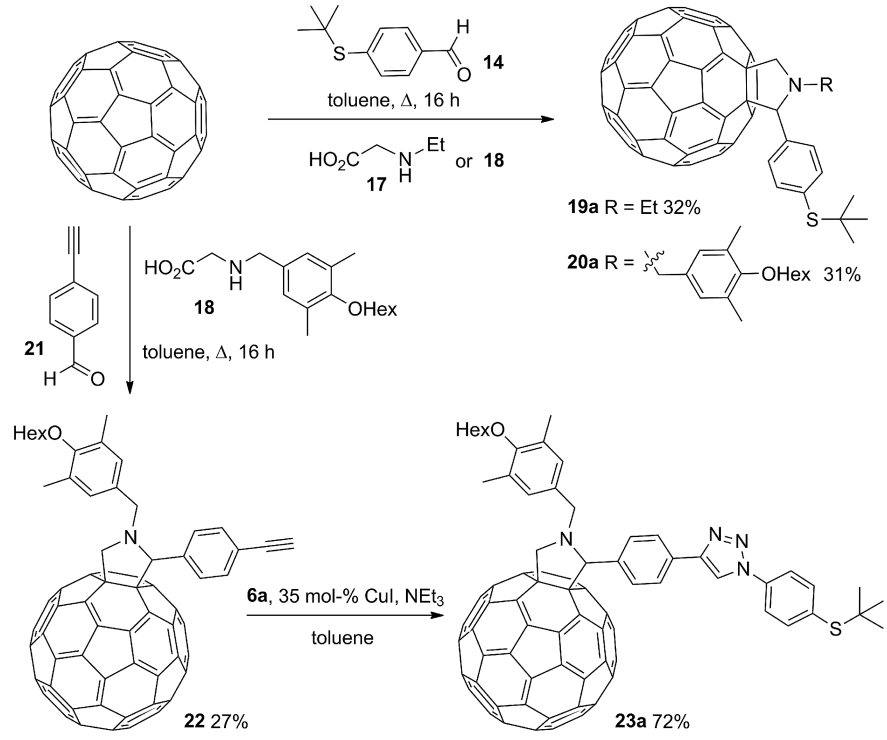
with malononitrile in the presence of basic alumina gave alkene **7a** in high yield. On the other hand, a phosphite-mediated coupling with the 1,3-dithiol-2-thione **15**[16] could be used to affix a DTF unit to the aryl by also creating a carbon–carbon double bond, thus furnishing **8a** in excellent yield, in analogy to a recent protocol.[17] Taking the previously reported boronic acid **16**[18] in methanol and subjecting it to treatment with sodium azide in the presence of copper acetate afforded azide **6a** in high yield, using a literature procedure for a related compound.[19]

Molecules with two sulfur end-caps were also targeted, allowing for anchoring to electrodes at both ends (Scheme 3). A homo-coupling reaction of **4a** under palladium catalysis and conducted in the presence of air gave butadiyne **9a**,[20] whilst a Cu^{I}-catalyzed alkyne-azide cycloaddition (CuAAC) reaction[21] using 0.1 equivalents of copper iodide formed triazole **10a** in moderate yield. DTF containing derivative **8a** could be treated with an excess of elemental iodine to afford **11a**, which contained both two DTF units and two *tert*-butyl thioether groups. All these compounds were fully characterized using NMR spectroscopy and elemental analyses agreed with their respective calculated values. Compound **12a** incorporating the DHA unit was made according to a previously published procedure.[15]



Scheme 3. Synthesis of dimeric thioethers **9a**–**11a**.

Aldehyde **14** could be carried over into other synthetic transformations. Thus, subjecting it to a standard 1,3-dipolar cycloaddition reaction with C_{60}, a Prato reaction,[22] using two different amino acids (**17** and **18**) produced fullerene derivatives **19a** and **20a**. Compound **19a** was derived from the commercially available amino acid *N*-ethylglycine **17**. In the case of derivative **20a**, the tailor-made amino acid **18**, which had been previously used by us,[23] was successfully employed. The advantage of using such an amino acid was to provide the fullerene derivatives with superior solubility in a broad range of solvents. It was also of interest to investigate a hybrid system, which had an increased distance between the two potential anchoring groups. For this purpose, a third fullerene derivative was synthesized in a two-step procedure. A Prato reaction with the known 4-ethynylbenzaldehyde **21**[24] yielded fulleropyrrolidine **22**, which, bearing a phenylacetylenic unit, was subsequently



Scheme 4. Synthesis of fullerene derivatives **19a**, **20a**, and **23a**.

reacted in a CuAAC reaction to form triazole **23a** in good yield (Scheme 4).

Bi^{III}-Catalyzed Acetylations

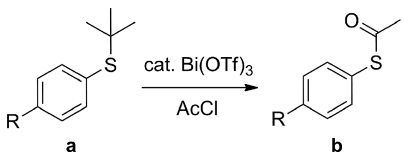
With a host of substrates in hand, the acetylation of these compounds was examined using $Bi(OTf)_3$ (Table 1, Scheme 5). A general set of conditions was employed where a solvent mixture of acetonitrile and toluene in 2:1 ratio was used in the presence of an excess of acetyl chloride in order to trap the air sensitive thiol. By using 0.2 molar equivalents (equiv.) of $Bi(OTf)_3$, product **3b** could be formed in 78% yield (Entry 1). However, lowering the catalyst loading to 0.1 equiv. resulted in an incomplete reaction, whether it was run for 30 minutes or 3 hours (Entries 2 and 3), suggesting that the catalyst was probably deactivated within half an hour. The starting material could be consumed with a loading of 0.1 equiv. (Entry 4) when the reaction was performed in CH_2Cl_2 and in the presence of a small amount of acetic acid, but with the desired product forming in very low yield. Under these conditions, the major product **24a** (Figure 2) corresponded to the loss of the silyl protecting group and addition of hydrogen chloride across the triple bond of the terminal acetylene. Conversion of **4a** and **5a** yielded **4b**[25] and **5b**[26] in medium to good yields, respectively (Entries 5 and 6). Conversion of **4a** to **4b** was complicated by a partial side reaction by addition of TfOH across the alkyne resulting in an inseparable mixture of **4b** and the vinyl triflate **24b**;[27] this mixture was also very unstable neat. Reaction of azide **6a** with 0.2 equiv. of catalyst (Entry 7) afforded thioacetate **6b** in high yield as was the case for converting **7a** into **7b** (Entry 8). Meanwhile, the reaction of the DTF derivative **8a**, despite leaving the contents of the vessel stirring for 3 hours in the presence of 0.25 equiv. of $Bi(OTf)_3$ (Entry 9), gave only small amounts of desired product **8b**. In this case, the DTF unit also was susceptible to a side reaction where some acetylation of the fulvene had occurred giving rise to products **25** and **26** (Figure 2). Formation of these side-products could be suppressed by increasing the catalyst loading; thus, using 0.5 equiv. of $Bi(OTf)_3$ in 30 min gave **8b** in fair yield (Entry 10). The reaction for the formation of the double thioacetate **9b**[28] worked efficiently well with similar loading (Entry 11), and this product conveniently precipitated from the reaction mixture. The yield could be somewhat improved when the reaction was conducted in neat acetonitrile (Entry 12). On the other hand, using a similar loading of $Bi(OTf)_3$ resulted in an incomplete reaction of **10a** into **10b** (Entry 13; products **27a**,**b** shown in Figure 2 where only one SAc had been formed were also identified), but with a stoichiometric amount of $Bi(OTf)_3$ the reaction was driven to completion (Entry 14). The triazole seemed to hinder the reactivity and this was also evidenced by reactions upon the fullerene derivatives (in CH_3CN/toluene/*o*-DCB, 2:1:2). With $Bi(OTf)_3$ loadings corresponding to 0.2–0.3 equiv., the reactions of fullerene derivatives **19a** and **20a** gave little to no reaction (Entries 18 and 20), but this hindrance could be overcome by raising the $Bi(OTf)_3$ loading to 1.5–1.6 equiv. Finally, the reaction of triazole-fullerene thioether **23a** in the presence of 2 equiv. of $Bi(OTf)_3$ afforded **23b** in low yield (Entry 22), where unfortunately significant amounts of starting material were isolated and in this case ac-

companied by significant decomposition. The structures of **10a** and **7b** were confirmed by X-ray crystallographic analysis (Figure 3). The larger $Bi(OTf)_3$ loadings needed for the triazole substrates may be the result of undesired coordination between Bi^{III} and the triazole unit. Several examples of triazoles acting as ligands towards metal ions are known[29] as are complexes between Bi^{III} and ligands with nitrogen donor atoms.[30] Yet, maybe more important, the triazole should become protonated by any triflic acid present [generated from $Bi(OTf)_3$], and as we shall see below this acid also promotes the acetylation reaction. For C_{60} Prato adduct substrates, protonation of the pyrrolidine unit may also play an inhibiting role.

Table 1. $Bi(OTf)_3$ catalyzed acetylation reactions; see Scheme 5.

Entry[a]	Substrate	Equiv. $Bi(OTf)_3$	Time [h]	Product(s) [%][b]
1	**3a**	0.2	0.5	**3b** (78)
2	**3a**	0.1	0.5	**3a** (35) **3b** (55)
3	**3a**	0.1	3	**3a** (21) **3b** (58)
4[c]	**3a**	0.1	24	**3b** (10) **24a** (30)
5	**4a**	0.2	0.5	**4b** (40) **24b** (9)[d]
6	**5a**	0.2	1	**5b** (47)
7	**6a**	0.2	0.5	**6b** (82)
8	**7a**	0.2	0.5	**7b** (86)
9	**8a**	0.25	3	**8b** (7) **25** (19) **26** (4)
10	**8a**	0.5	0.5	**8b** (55)
11	**9a**	0.5	0.5	**9b** (63)[e]
12[f]	**9a**	0.5	1	**9b** (95)[e]
13	**10a**	0.5	2	**10a** (61) **27a/27b** (27) **10b** (12)
14	**10a**	1.0	0.5	**10b** (97)
15	**11a**	1.0	0.5	**11b** (78) **28** (9)
16	**12a**	0.9	0.5	**12b** (84)
17[f]	**12a**	0.9	0.5	**12b** (88)
18[g]	**19a**	0.3	2	**19a** (80) **19b** (10)
19[g]	**19a**	1.5	0.5	**19a** (13) **19b** (77)
20[g]	**20a**	0.2	2	**20a** (95) **20b** (0)
21[g]	**20a**	1.6	0.5	**20b** (89)
22[g]	**23a**	2.0	0.5	**23a** (23) **23b** (24)

[a] All reactions were performed in a mixture of CH_3CN/toluene (2:1) (if not otherwise stated) in an excess of acetyl chloride, with the exception of Entry 4. [b] Unless otherwise stated, yields (in brackets) are isolated yields from column chromatography. [c] The reaction was performed in CH_2Cl_2/toluene (2:1), with added acetic acid. [d] Products isolated as a mixture; yields are based on ratios determined by ^1H NMR spectroscopy. [e] The reaction products were isolated by filtration. [f] No toluene was used as a co-solvent (i.e., neat MeCN was used); the reaction was conducted under ultra-sonication in Entry 12 (but not in 17). [g] Solvent system: CH_3CN/toluene/*o*-DCB (2:1:2). *o*-DCB = *ortho*-dichlorobenzene.



Scheme 5. For substrates and conditions, see Table 1.

A previous report featured the treatment of the photoswitch DHA **12a** with boron tribromide in order to facilitate the functional group transformation of the *tert*-butyl thioethers to the corresponding thioacetates.[15] Prior to this work, it had been found that the treatment of DHA with

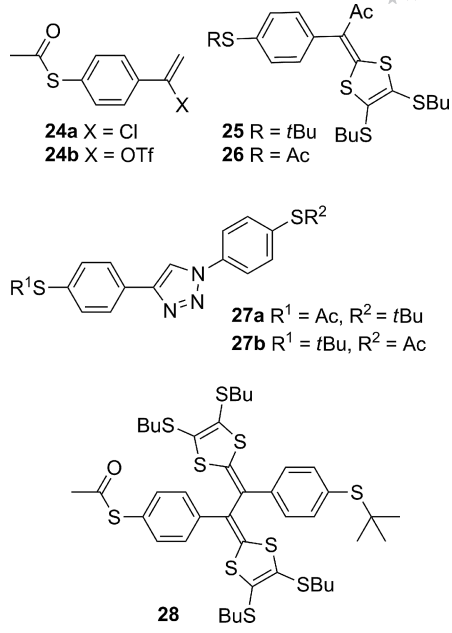


Figure 2. Side-products.

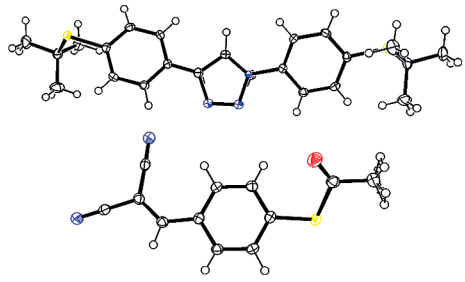
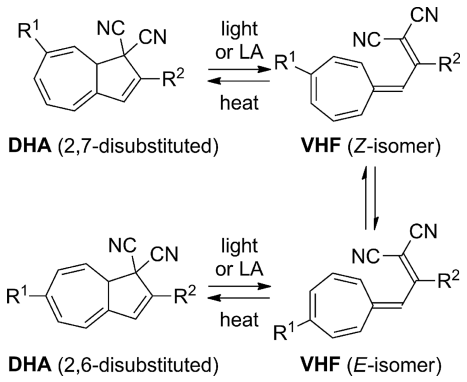


Figure 3. Top: Molecular structure of **10a** (crystals grown from CH_2Cl_2/heptane). Space group: *C2*. There is some disorder in the triazole unit; the C and N atoms connected to the benzene rings are superimposed, thus contributing 50% each in both positions. Bottom: Molecular structure of **7b** (crystals grown from acetone/heptane). Space group: $P2_1/c$. There is some disorder in the methyl group, where the hydrogen atoms can be placed in two positions. For both structures, the thermal ellipsoids are shown at the 50% probability level. CCDC-1055456 (for **10a**) and -1055455 (for **7b**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

strong Lewis acids resulted in ring-opening reaction to the corresponding vinylheptafulvalene (VHF), which otherwise is a light-driven process (Scheme 6).[31] This can lead to isomerization for DHA molecules with substituents in the seven-membered ring as the VHF can isomerize between *Z* and *E* configurations, before returning to a DHA, as illustrated in Scheme 6. Indeed, with the substituent residing upon the DHA 7-position, as is the case for **12a**, the BBr_3/AcCl protocol resulted in an inseparable mixture of 7- and 6-substituted DHA isomers. Gratifyingly, this regioisomeric phenomenon was not observed when $Bi(OTf)_3$ was employed, and the desired transformation to the product **12b** could be effected rapidly with a catalyst loading of 91% (Table 1, Entry 16), while in the case of the former protocol,

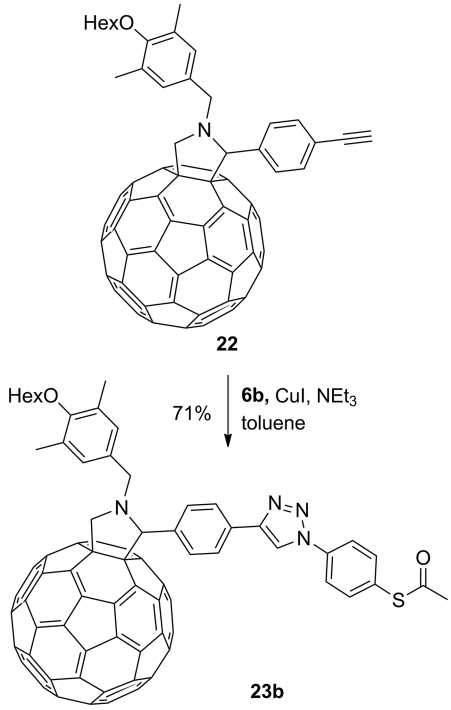
a large excess of BBr_3 was necessary in order to drive the reaction to completion. The 2,7-disubstitution of **12b** was confirmed by X-ray crystallographic analysis of single crystals, but there was significant disorder in the structure (see SI).



Scheme 6. Isomerization of substituted DHAs after one ring-opening/ring-closure cycle, which can be induced by a strong Lewis acid (LA).

Alternative Synthesis via the CuAAC Reaction

In an attempt to get around the large amount of the bismuth(III) salt needed for the preparation of **23b** and its low yield of formation, it was decided to investigate the CuAAC reaction for formation of this fullerene derivative. Indeed, it was found that treatment of **22** with the azide **6b** with catalytic copper iodide did form **23b** in good yield (Scheme 7) and the product could be conveniently purified



Scheme 7. CuAAC reaction between **6b** and the acetylenic fullerene derivative **22**.

by column chromatography. This method shows that **6b**, conveniently prepared from **6a** by using the $Bi(OTf)_3$/AcCl protocol as described above, is a useful building block for CuAAC reactions.

Determination of the Role of Bi^{III}

In order to shed further light on the role of Bi^{III} for the acetylation, we performed a series of acetylation reactions on the substrate **3a**. The results are summarized in Table 2, where the first entry corresponds to Entry 1 from Table 1. First of all, we note that no conversion into **3b** is obtained if **3a** is treated with AcCl solely (Entry 2). Thus, any HCl present in the AcCl reagent is not strong enough to facilitate the reaction, even after 24 h. It is likely that TfOH will be present during the reaction when using $Bi(OTf)_3$ as a reaction between $Bi(OTf)_3$ and any water would give TfOH and Bi_2O_3.[32] Indeed, we found that some of substrate **4a** was converted into **24b** by addition of TfOH. The extent of hydrolysis is difficult to determine (and no precautions to preclude water were taken during the course of the total study), but typically our reactions are done with 20 mol-% $Bi(OTf)_3$ and full hydrolysis would correspond to 60 mol-% TfOH. TfOH could possibly also be generated using the *t*Bu carbocation released from **3a** as a proton source. We therefore performed reactions with AcCl and various equivalents of TfOH (Entries 3–5). These experiments clearly show that TfOH is capable of effecting the reaction. With 0.6 equiv. of TfOH (Entry 4), corresponding to the maximum amount possible when using 0.2 equiv. of $Bi(OTf)_3$, the product **3b** was isolated in a significant yield of 46%, but lower still than the one obtained with $Bi(OTf)_3$ (78%; Entry 1). Entries 6 and 7 show that $BiCl_3$ also has some activity, albeit not as high as $Bi(OTf)_3$. Thus, it took 24 h to reach a yield of 68% of **3b**. These experiments signal that Bi^{III} is not the only species responsible for the high yield obtained in Entry 1. Substituting AcCl for AcOAc resulted in no product formation when using $BiCl_3$ (Entry 8), but around 30% with $Bi(OTf)_3$ no matter the reaction time (0.5 or 24 h; Entries 9 and 10). Entries 11 and 12 show that Bi_2O_3 has some activity for the conversion, but it took 24 h to reach a yield of 49%. Using AcOAc/Bi_2O_3 resulted in no reaction (Entry 13); here the Bi_2O_3 remained suspended during the course of the reaction. Next, we conducted an experiment with $Er(OTf)_3$, which does not hydrolyze readily to TfOH[33] (Entry 14). The reaction was quite slow, and after 24 h only 22% of **3b** was obtained. Using instead $Sm(OTf)_3$ only gave 11% of **3b** after 24 h. Taken together, the experiments show that both Bi^{III} and TfOH have an influence on the acetylation reaction and the high yield obtained after 0.5 h using $Bi(OTf)_3$ is probably a result of the individual action of both these two species.

Acetylation of the triazole-containing substrate **10a** was also studied in further detail (Table 2, Entries 16–19). Again, we found that treatment with AcCl only, with no additive, did not give any of the desired product, **10b** (Entry 16). In this case, when using TfOH (Entry 17) instead of

Table 2. Acetylation of **3a** and **10a** under different conditions in CH_3CN/toluene (2:1).

Entry	Substrate	Reagents	Time [h]	Product(s) [%]
1	**3a**	AcCl/$Bi(OTf)_3$ (0.2 equiv.)	0.5	**3b** (78)
2	**3a**	AcCl	24	no reaction
3	**3a**	AcCl/TfOH (0.2 equiv.)	0.5	**3a** (64) **3b** (25)
4	**3a**	AcCl/TfOH (0.6 equiv.)	0.5	**3a** (37) **3b** (46)
5	**3a**	AcCl/TfOH (1.0 equiv.)	0.5	**3a** (18) **3b** (58)
6	**3a**	AcCl/$BiCl_3$ (0.25 equiv.)	0.5	**3a** (79) **3b** (15)
7	**3a**	AcCl/$BiCl_3$ (0.23 equiv.)	24	**3a** (26) **3b** (68)
8	**3a**	AcOAc/$BiCl_3$ (0.25 equiv.)	24	no reaction
9	**3a**	AcOAc/$Bi(OTf)_3$ (0.2 equiv.)	0.5	**3a** (72) **3b** (28)
10	**3a**	AcOAc/$Bi(OTf)_3$ (0.2 equiv.)	24	**3a** (65) **3b** (34)
11	**3a**	AcCl/Bi_2O_3 (0.15 equiv.)	0.5	**3a** (94) **3b** (3)
12	**3a**	AcCl/Bi_2O_3 (0.1 equiv.)	24	**3a** (44) **3b** (49)
13	**3a**	AcOAc/Bi_2O_3 (0.1 equiv.)	24	no reaction
14	**3a**	AcCl/$Er(OTf)_3$ (0.2 equiv.)	24	**3a** (64) **3b** (22)
15	**3a**	AcCl/$Sm(OTf)_3$ (0.2 equiv.)	24	**3a** (68) **3b** (11)
16	**10a**	AcCl	24	no reaction
17	**10a**	AcCl/TfOH (0.4 equiv.)	0.5	**10b** (trace) **27a/27b** (trace)
18	**10a**	AcCl/$BiCl_3$ (0.3 equiv.)	24	**10a** (41) **10b** (18) **27a/27b** (36)
19	**10a**	AcCl/$BiCl_3$ (0.5 equiv.)	24	**10a** (3) **10b** (62) **27a/27b** (26)

$Bi(OTf)_3$, the product **10b** was only formed in trace amount, signaling, as proposed above, that the triazole acts as a base towards TfOH. Using AcCl in combination with $BiCl_3$ and a reaction time of 24 h turned out more successful. With 0.3 equiv. of $BiCl_3$, **10b** was obtained in 18% (Entry 18), while using 0.5 equiv. of $BiCl_3$, the yield increased to 62% (Entry 19). The intermediates **27a/27b** were also isolated.

Conclusions

A new methodology using the weak Lewis acid $Bi(OTf)_3$ in combination with acetyl chloride has been shown to be capable of converting a large selection of aryl *tert*-butyl thioethers to corresponding aryl thioacetates. In some instances, undesired side reactions did occur due to some functional group sensitivity under the conditions employed, but it was possible to prepare derivatives containing both redox-active DTF groups, electron-withdrawing dicyanoethylene units, and light-sensitive dihydroazulene photoswitches. In the latter case, the mild conditions prevented isomerization reactions to occur in the seven-membered ring of DHA. Mechanistically, it seems that both Bi^{III} and TfOH are effecting the conversions, and both species are likely present under the reaction conditions. In addition, it was found that Bi^{III} was superior as a promoter in comparison to Er^{III} and Sm^{III}. Using high loadings of the bismuth salt, C_{60}-containing substrates could also be employed in this protocol. The methodology had, however, some limitations for molecules incorporating the triazole unit, which in some cases could be simply overcome by using more $Bi(OTf)_3$. Gratifyingly, the reaction tolerated the azide functionality, and 4-azidophenyl(*tert*-butyl)sulfane was readily converted to its thioacetate that could subsequently be employed in the CuAAC reaction with a terminal alkyne substrate to form a triazole. In all, the protocol provides access to a wide variety of molecular wires with suitable electrode anchoring groups, of importance for molecular electronics, and an important azide building block.

Experimental Section

General Methods: 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 ^{13}C NMR (125 MHz) spectra were recorded on an instrument with a noninverse cryoprobe using the residual solvent as the internal standard ($CDCl_3$, ^1H 7.26 ppm and ^{13}C 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 CH_3 correspond to negative signals and C and CH_2 correspond to positive signals. ^{19}F NMR (282 MHz) spectra were recorded on an instrument using locktube containing trifluoroacetic acid which was referenced to –71.55 ppm. High resolution mass spectra (HRMS) were acquired either using an electrospray method of ionization or using MALDI. IR spectra were recorded of neat samples using the attenuated total reflectance (ATR) sampling technique. Melting points are uncorrected. Compounds **4a**,[14] **5a**,[15] **12a**,[15] **13**,[3a] **14**,[3a] **15**,[16] **16**,[18] **18**,[23] and **21**[24] were made by their respective literature methods. For experiments pertaining to Table 2, see SI.

{[4-(*tert*-Butylthio)phenyl]ethynyl}triisopropylsilane (3a):[4] To a degassed solution of **13** (4.00 g, 16.3 mmol) and triisopropylsilylacetylene (5.0 mL, 22.3 mmol) in diisopropylamine (50 mL) and THF (50 mL) was added CuI (124 mg, 0.65 mmol) and $Pd(PPh_3)_2Cl_2$ (533 mg, 0.759 mmol) and the resulting mixture heated to reflux point for 1 h. The solvent was removed in vacuo and the crude residue purified by flash column chromatography (5% CH_2Cl_2/petroleum spirit) to afford **3a** (4.27 g, 76%) as a colorless oil. R_f = 0.27 (petroleum spirit). IR: $\tilde{\nu}$ = 2157 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.2 Hz, 2 H), 7.43 (d, J = 8.2 Hz, 2 H), 1.28 (s, 9 H), 1.13 (s, 21 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.3, 133.4, 132.1, 124.0, 106.6, 92.5, 46.6, 31.1, 18.8, 11.5 ppm. GC–MS: m/z = 346 [$M^{\cdot+}$], 303, 247, 57.

***tert*-Butyl(4-ethynylphenyl)sulfane (4a):** To a solution of **3a** (1.92 g, 5.54 mmol) in THF (50 mL) was added a solution of TBAF (6.0 mL, 1 M in THF, 6.0 mmol) and the resulting solution stirred for 1 h at rT. The reaction mixture was partitioned between ether and water and the phases separated. The organic phase was dried with Na_2SO_4, filtered and the solvent removed under reduced pres-

sure. The crude oil was purified by flash column chromatography (5% CH_2Cl_2/petroleum spirit) to give **4a** as a colorless oil (1.00 g, 95%). R_f = 0.17 (petroleum spirit). IR: $\tilde{\nu}$ = 3292, 2110, 1591 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 3.14 (s, 1 H), 1.29 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.3, 134.1, 132.2, 122.6, 83.3, 78.7, 46.6, 31.3 ppm. GC–MS: m/z = 190 [$M^{\cdot+}$], 134, 57.

(4-Azidophenyl)(*tert*-butyl)sulfane (6a): This compound was made using a previously reported procedure.[19] A solution of **16** (934 mg, 4.45 mmol), NaN_3 (488 mg, 7.51 mmol) and $Cu(OAc)_2$ (57 mg, 0.46 mmol) in methanol (25 mL) was heated to 60 °C for 3 h. The solvent was carefully removed using rotary evaporation at room temperature and the residue was extracted with diethyl ether (3× 50 mL) and filtered. Volatiles were removed under reduced pressure and the residue purified by flash column chromatography (20% CH_2Cl_2/petroleum spirit) to give **6a** (882 mg, 96%) as a pale yellow oil. R_f = 0.41 (20% CH_2Cl_2/petroleum spirit). IR: $\tilde{\nu}$ = 2126, 2092, 1589 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.5 Hz, 2 H), 6.99 (d, J = 8.5 Hz, 2 H), 1.27 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.9, 139.0, 129.1, 119.2, 46.2, 31.0 ppm. GC–MS: m/z = 207 [$M^{\cdot+}$], 57. HRMS (MALDI +ve) calcd. for $C_{10}H_{14}N_3S$ [[M + H]$^+$]: m/z = 208.0903, found 208.0905.

2-[4-(*tert*-Butylthio)benzylidene]malononitrile (7a): To a solution of **14** (217 mg, 1.12 mmol) and malononitrile (89 mg, 1.35 mmol) in CH_2Cl_2 (10 mL) was added basic Al_2O_3 Brockmann I (381 mg) and the resulting suspension stirred for 30 min. The alumina was removed by filtration and the solvent removed in vacuo. The crude residue was purified by flash column chromatography (80% CH_2Cl_2/pentane) to afford **7a** (253 mg, 93%) as a yellow solid, m.p. 103–104.5 °C. R_f = 0.49 (toluene). IR: $\tilde{\nu}$ = 2229, 1593, 1581, 1544 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.3 Hz, 2 H), 7.75 (s, 1 H), 7.65 (d, J = 8.3 Hz, 2 H), 1.37 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.0, 143.0, 136.6, 130.5, 130.3, 113.8, 112.7, 83.0, 48.0, 31.3 ppm. GC–MS: m/z = 242 [$M^{\cdot+}$], 186, 57. HRMS (MALDI +ve) calcd. for $C_{14}H_{15}N_2S$ [[M + H]$^+$]: m/z = 243.0951, found 243.0950. $C_{14}H_{14}N_2S$ (242.34): calcd. C 69.39, H 5.82, N 11.56; found C 69.48, H 5.90, N 11.51.

4,5-Bis(butylthio)-2-[4-(*tert*-butylthio)benzylidene]-1,3-dithiole (8a): A thoroughly degassed solution of **14** (491 mg, 2.53 mmol) and thione **15** (1.21 g, 3.90 mmol) in dry triethyl phosphite (5 mL) was heated to 100 °C for 2 h. The phosphite was removed under high vacuum and the residue subjected to flash column chromatography (30% CH_2Cl_2/petroleum spirit) to afford **8a** (1.06 g, 92%) as an orange paste, m.p. 32–33 °C. R_f = 0.49 (30% CH_2Cl_2/petroleum spirit). IR: $\tilde{\nu}$ = 1587, 1570, 1541 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.9 Hz, 2 H), 7.16 (d, J = 7.9 Hz, 2 H), 6.46 (s, 1 H), 2.84 (t, J = 6.7 Hz, 2 H), 2.83 (t, J = 6.7 Hz, 2 H), 1.67–1.60 (m, 4 H), 1.49–1.41 (m, 4 H), 1.28 (s, 9 H), 0.93 (t, J = 7.1 Hz, 3 H), 0.92 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.7, 136.7, 134.0, 129.9, 127.9, 126.7, 125.0, 113.5, 46.4, 36.0, 35.9, 32.0, 31.9, 31.1, 21.8, 21.8, 13.8, 13.8 ppm. HRMS (MALDI +ve) calcd. for $C_{22}H_{32}S_5$ [$M^{\cdot+}$]: m/z = 456.1102, found 456.1119. $C_{22}H_{32}S_5$ (457.80): calcd. C 57.85, H 7.06; found C 57.94, H 7.09.

1,4-Bis[4-(*tert*-butylthio)phenyl]buta-1,3-diyne (9a): To a solution of **4a** (319 mg, 1.68 mmol) in toluene (10 mL) and triethylamine (0.20 mL) under an aerial atmosphere was added CuI (32 mg, 0.168 mmol) and $Pd(PPh_3)_2Cl_2$ (33 mg, 0.047 mmol) and the resulting solution stirred, whilst open to air for 4 h. The solvent was removed under reduced pressure and the residue purified by column chromatography (20% CH_2Cl_2/heptane) to give **9a** (300 mg, 95%) as a white solid, m.p. 161–164 °C. R_f = 0.35 (20% CH_2Cl_2/heptane). IR: $\tilde{\nu}$ = 2151, 1585 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.5 Hz, 4 H), 7.47 (d, J = 8.5 Hz, 4 H), 1.30 (s, 18 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.3, 135.0, 132.5, 122.1, 81.8, 75.3, 46.9, 31.2 ppm. HRMS (MALDI +ve) calcd. for $C_{24}H_{26}S_2$ [$M^{\cdot+}$]: m/z = 378.1470, found 378.1469. $C_{24}H_{26}S_2$ (378.59): calcd. C 76.14, H 6.92; found C 76.11, H 6.95.

1,4-Bis[4-(*tert*-butylthio)phenyl]-1*H*-1,2,3-triazole (10a): To a solution of **4a** (201 mg, 1.06 mmol) and **6a** (201 mg, 0.970 mmol) in degassed diisopropylamine (0.20 mL) and tetrahydrofuran (15 mL) was added CuI (24 mg, 0.126 mmol) and the resulting solution stirred for 16 h at ambient temperature. The solution was dry loaded onto celite and purified by silica gel column chromatography (gradient elution of CH_2Cl_2 to 5% ethyl acetate/CH_2Cl_2) and the solvent removed in vacuo. The material was then triturated from CH_2Cl_2/toluene (50:10 mL) giving **10a** (253 mg, 66%) as a white fluffy solid, m.p. > 230 °C. R_f = 0.43 (1% ethyl acetate/$CHCl_3$). IR: $\tilde{\nu}$ = 1594, 1550, 1501 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 7.88 (d, J = 8.1 Hz, 2 H), 7.78 (d, J = 8.5 Hz, 2 H), 7.71 (d, J = 8.5 Hz, 2 H), 7.63 (d, J = 8.1 Hz, 2 H), 1.33 (s, 9 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.1, 138.9, 138.1, 137.2, 134.1, 133.3, 130.5, 125.9, 120.4, 117.8, 46.8, 46.4, 31.1, 31.1 ppm. HRMS (MALDI +ve) calcd. for $C_{22}H_{28}N_3S_2$ [[M + H]$^+$]: m/z = 398.1719, found 398.1730. $C_{22}H_{27}N_3S_2$ (397.60): calcd. C 66.46, H 6.85, N 10.57; found C 66.52, H 6.80, N 10.56.

1,2-Bis[4,5-bis(butylthio)-1,3-dithiol-2-ylidene]-1,2-bis[4-(*tert*-butylthio)phenyl]ethane (11a): To a degassed solution of **8a** (487 mg, 1.07 mmol) in CH_2Cl_2 (100 mL) was added I_2 (785 mg, 3.09 mmol) and the resulting solution stirred 12 h at room temp. A saturated aqueous solution of $Na_2S_2O_3$ (25 mL) was added and the contents stirred a further 3 h. The phases were separated and the organic phase was dried with Na_2SO_4. Filtration and removal of the solvent under reduced pressure gave a crude oil, which was purified by flash column chromatography (25% CH_2Cl_2/heptane) gave pure **11a** (330 mg, 68%) as an orange oil. R_f = 0.49 (30% CH_2Cl_2/petroleum spirit). IR: $\tilde{\nu}$ = 1681, 1586, 1549, 1523 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.2 Hz, 4 H), 7.35 (d, J = 8.2 Hz, 4 H), 2.83 (t, J = 7.3 Hz, 4 H), 2.77 (t, J = 7.3 Hz, 4 H), 1.28 (s, 18 H), 1.66–1.55 (m, 8 H), 1.49–1.36 (m, 8 H), 0.93 (t, J = 7.3 Hz, 6 H), 0.88 (t, J = 7.3 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.0, 137.7, 137.4, 131.0, 129.2, 126.6, 125.4, 123.7, 46.4, 36.0, 35.7, 319, 31.2, 21.8, 21.8, 13.8, 13.8 ppm, 1C masked. HRMS (MALDI +ve) calcd. for $C_{44}H_{62}S_{10}$ [$M^{\cdot+}$]: m/z = 910.2053, found 910.2066. $C_{44}H_{62}S_{10}$ (911.58): calcd. C 57.97, H 6.86; found C 58.40, H 6.92.

Compound 19a: A mixture consisting of C_{60} (148 mg, 0.205 mmol), **14** (47 mg, 0.242 mmol) and amino acid **17** (116 mg, 1.12 mmol) in toluene (75 mL) was heated to reflux point for 16 h. The solvent was removed in vacuo and the residue purified by flash column chromatography (gradient elution of CS_2 to 20% toluene/CS_2) to afford **19a** (63 mg, 32%) as a dark brown solid. R_f = 0.63 (10% toluene/CS_2). IR: $\tilde{\nu}$ = 1596 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.79 (br. s, 2 H), 7.56 (d, J = 8.0 Hz, 2 H), 5.13 (d, J = 9.3 Hz, 1 H), 5.11 (s, 1 H), 4.18 (d, J = 9.3 Hz, 1 H), 3.38 (dq, J = 14.3, 7.2 Hz, 1 H), 2.67 (dq, J = 14.3, 7.2 Hz, 1 H), 1.52 (t, J = 7.2 Hz, 3 H), 1.20 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.6, 154.4, 153.4, 147.5, 146.8, 146.6, 146.5, 146.4, 146.4, 146.3, 146.3, 146.3, 146.2, 146.1, 145.9, 145.7, 145.7, 145.6, 145.5, 145.5, 145.4, 145.4, 145.3, 145.3, 144.9, 144.8, 144.6, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.4, 142.4, 142.3, 142.2, 142.2, 142.2, 142.1, 142.1, 141.9, 141.8, 141.7, 140.3, 140.3, 140.0, 139.4, 138.4, 137.7, 136.9, 136.7, 136.0, 135.9, 133.1, 129.5, 81.9, 69.0, 66.6, 47.3, 46.2, 31.1,

13.6 ppm, 1 sp^3 C masked. HRMS (MALDI -ve) calcd. for $C_{74}H_{21}NS$ [$M^{\cdot-}$]: *m*/*z* = 955.1400, found 955.1406. $C_{74}H_{21}NS$ (956.05): calcd. C 92.97, H 2.21, N 1.47; found C 92.99, H 2.37, N 1.51.

Compound 20a: A mixture consisting of C_{60} (142 mg, 0.197 mmol), **14** (50 mg, 0.26 mmol) and amino acid **18** (190 mg, 0.648 mmol) in toluene (75 mL) was heated to reflux point for 16 h. The solvent was removed in vacuo and the residue purified by flash column chromatography (gradient elution of CS_2 to 20% toluene/CS_2) to afford **20a** (69 mg, 31%) as a dark brown solid. R_f = 0.33 (20% toluene/CS_2). IR: $\tilde{\nu}$ = 1596 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.90 (br. s, 2 H), 7.61 (d, *J* = 7.8 Hz, 2 H), 7.26 (s, 2 H), 5.17 (s, 1 H), 4.87 (d, *J* = 9.5 Hz, 1 H), 4.48 (d, *J* = 13.1 Hz, 1 H), 4.16 (d, *J* = 9.5 Hz, 1 H), 3.84 (t, *J* = 6.6 Hz, 2 H), 3.60 (d, *J* = 13.1 Hz, 1 H), 2.39 (s, 6 H), 1.87–1.82 (m, 2 H), 1.57–1.51 (m, 2 H), 1.40–1.36 (m, 4 H), 1.21 (s, 9 H), 0.93 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.5, 155.8, 154.3, 153.4, 153.3, 147.5, 147.4, 146.8, 146.6, 146.4, 146.4, 146.4, 146.3, 146.3, 146.2, 146.1, 146.1, 145.9, 145.7, 145.7, 145.5, 145.4, 145.4, 145.3, 145.3, 144.8, 144.8, 144.5, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.2, 142.2, 142.2, 142.2, 142.1, 142.1, 141.9, 141.8, 141.7, 140.3, 140.2, 140.0, 139.4, 138.1, 137.8, 137.0, 136.6, 136.1, 135.8, 133.2, 132.5, 131.3, 129.5, 81.0, 76.8, 72.6, 68.8, 66.8, 56.6, 46.2, 31.9, 31.1, 30.6, 26.0, 22.8, 16.7, 14.3 ppm. HRMS (MALDI -ve) calcd. for $C_{87}H_{39}NOS$ [$M^{\cdot-}$]: *m*/*z* = 1145.2758, found 1145.2839. $C_{87}H_{39}NOS$ (1146.34): calcd. C 91.16, H 3.43, N 1.22; found C 91.04, H 3.52, N 1.27.

Compound 22: A mixture consisting of C_{60} (365 mg, 0.506 mmol), **21** (76 mg, 0.58 mmol) and amino acid **18** (718 mg, 2.45 mmol) in toluene (170 mL) was heated to reflux point for 16 h. The solvent was removed in vacuo and the residue purified by column chromatography (gradient elution of CS_2 to 20% toluene/CS_2) to afford **22** (150 mg, 27%) as a dark brown solid. R_f = 0.48 (20% toluene/CS_2). IR: $\tilde{\nu}$ = 3295 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.88 (br. s, 2 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.22 (s, 2 H), 5.14 (s, 1 H), 4.86 (d, *J* = 9.6 Hz, 1 H), 4.39 (d, *J* = 13.1 Hz, 1 H), 4.15 (d, *J* = 9.6 Hz, 1 H), 3.83 (t, *J* = 6.7 Hz, 2 H), 3.57 (d, *J* = 13.1 Hz, 1 H), 3.10 (s, 1 H), 2.38 (s, 6 H), 1.87–1.81 (m, 2 H), 1.40–1.37 (m, 6 H), 0.93 (t, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.5, 155.8, 154.2, 153.3, 153.2, 147.5, 146.8, 146.5, 146.4, 146.4, 146.3, 146.3, 146.3, 146.2, 146.1, 146.1, 146.1, 145.9, 145.7, 145.7, 145.6, 145.5, 145.5, 145.4, 145.4, 145.4, 145.3, 144.8, 144.8, 144.5, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.2, 142.2, 142.2, 142.1, 142.0, 142.0, 141.8, 141.7, 140.3, 140.2, 140.0, 139.7, 138.3, 137.1, 136.6, 136.1, 135.8, 132.7, 132.2, 131.2, 129.6, 122.3, 83.6, 81.1, 78.0, 76.7, 72.6, 68.8, 66.8, 56.6, 31.9, 30.6, 26.0, 22.8, 16.7, 14.3 ppm. HRMS (MALDI -ve) calcd. for $C_{85}H_{31}NO$ [$M^{\cdot-}$]: *m*/*z* = 1081.2411, found 1081.2381. $C_{85}H_{31}NO$ (1081.19): calcd. C 94.34, H 2.89, N 1.29; found C 94.17, H 3.02, N 1.25.

Compound 23a: To a stirring degassed solution of **22** (49 mg, 0.0453 mmol) and **6a** (26 mg, 0.125 mmol) in triethylamine (0.10 mL) and toluene (10 mL) was added CuI (3 mg, 0.016 mmol) and the resulting solution stirred 24 h at ambient temperature. The solvent was removed in vacuo and the residue purified by column chromatography (0.25% ethyl acetate/toluene) to give **23a** (42 mg, 72%) as a dark brown solid. R_f = 0.20 (0.25% ethyl acetate/toluene). IR: $\tilde{\nu}$ = 1593, 1503 (shoulder) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (s, 1 H), 8.01 (br. d, includes br. s, *J* = 7.4 Hz, 4 H), 7.76 (d, *J* = 8.7 Hz, 2 H), 7.70 (d, *J* = 8.7 Hz, 2 H), 7.26 (s, 2 H), 5.20 (s, 1 H), 4.88 (d, *J* = 9.5 Hz, 1 H), 4.47 (d, *J* = 13.2 Hz, 1 H), 4.18 (d, *J* = 9.5 Hz, 1 H), 3.84 (t, *J* = 6.6 Hz, 2 H), 3.62 (d, *J* = 13.2 Hz, 1 H), 2.39 (s, 6 H), 1.87–1.82 (m, 2 H), 1.40–1.37 (m, 6 H), 0.93 (t, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.6, 155.8, 154.3, 153.5, 153.5, 148.4, 147.4, 146.9, 146.6, 146.4, 146.4, 146.4, 146.3, 146.3, 146.2, 146.1, 146.1, 145.9, 145.7, 145.7, 145.7, 145.7, 145.5, 145.4, 145.4, 145.4, 145.3, 144.8, 144.7, 144.5, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.2, 142.2, 142.2, 142.2, 142.1, 142.0, 141.8, 141.7, 140.3, 140.2, 140.1, 139.7, 138.8, 137.8, 137.3, 137.1, 136.6, 136.1, 135.8, 134.1, 132.3, 131.2, 130.4, 129.7, 126.4, 120.4, 117.8, 81.2, 76.8, 72.6, 68.9, 66.8, 56.6, 46.8, 31.9, 31.1, 30.6, 26.0, 22.8, 16.7, 14.2 ppm. HRMS (MALDI -ve) calcd. for $C_{95}H_{44}N_4OS$ [$M^{\cdot-}$]: *m*/*z* = 1288.3241, found 1288.3238. $C_{95}H_{44}N_4OS$ (1288.48): calcd. C 88.49, H 3.44, N 4.34; found C 88.35, H 3.36, N 4.46.

Acetylation Reactions (see Table 1)

Entry 1: To a solution of **3a** (55 mg, 0.159 mmol) and acetyl chloride (0.25 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (23 mg, 0.035 mmol) and the contents of the vessel stirred for 30 min at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 (30% CH_2Cl_2/petroleum spirit) to afford **3b** (41 mg, 78%) as a colorless oil.

Entry 2: To a solution of **3a** (57 mg, 0.164 mmol) and acetyl chloride (0.25 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (11 mg, 0.017 mmol) and the contents of the vessel stirred for 30 min at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (20 mL in total). The combined organics were filtered through a pad of cotton and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (30% CH_2Cl_2/petroleum spirit) to afford **3b** (30 mg, 55%) as a colorless oil in addition to **3a** (20 mg, 35%).

Entry 3: To a solution of **3a** (58 mg, 0.167 mmol) and acetyl chloride (0.25 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (12 mg, 0.018 mmol) and the contents of the vessel stirred for 3 h at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 (30% CH_2Cl_2/petroleum spirit) to afford **3b** (32 mg, 58%) as a colorless oil in addition to recovered **3a** (12 mg, 21%).

Entry 4: To a solution of **3a** (98 mg, 0.283 mmol) in CH_2Cl_2 (3 mL), toluene (1.5 mL), acetyl chloride (0.5 mL) and acetic acid (2 drops) was added $Bi(OTf)_3$ (21 mg, 0.032 mmol) and the contents of the vessel stirred for 24 h. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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% CH_2Cl_2/petroleum spirit) to afford **3b** (10 mg, 10%) as a colorless oil and **24a** (20 mg, 30%), a pungent smelling colorless oil.

***S*-{4-[(Triisopropylsilyl)ethynyl]phenyl} Ethanethioate (3b):** R_f = 0.33 (30% CH_2Cl_2/petroleum spirit). IR: $\tilde{\nu}$ = 2156, 1715 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 2.42 (s, 3 H), 1.13 (s, 21 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.6, 134.3, 132.8, 128.2, 124.9, 106.3, 92.9, 30.4, 18.8, 11.4 ppm. GC–MS: *m*/*z* = 332 [$M^{\cdot+}$], 289, 247, 207.

***S*-[4-(1-Chlorovinyl)phenyl] Ethanethioate (24a):** R_f = 0.26 (40% CH_2Cl_2/petroleum spirit). IR: $\tilde{\nu}$ = 1709, 1608 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.4 Hz, 2 H), 7.41 (d, J = 8.4 Hz, 2 H), 5.82 (d, J = 2.0 Hz, 1 H), 5.58 (d, J = 2.0 Hz, 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.7, 139.2, 138.0, 134.4, 129.1, 127.2, 114.0, 30.5 ppm. HRMS (MALDI +ve) calcd. for $C_{10}H_{10}ClOS$ [[M + H]$^+$]: m/z = 213.0135, found 213.0137.

Entry 5: To a solution of **4a** (62 mg, 0.326 mmol) and acetyl chloride (0.50 mL) in toluene (1.0 mL) and CH_3CN (2.0 mL) was added $Bi(OTf)_3$ (39 mg, 0.594 mmol) and the contents of the vessel stirred for 30 min at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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% CH_2Cl_2/petroleum spirit) to afford a mixture of **4b/24b** (33 mg, 40:9%) as a colorless oil, which was unstable neat.

Mixture of *S*-(4-Ethynylphenyl) Ethanethioate (4b) and *S*-(4-{1-[(Trifluoromethanesulfonyl)oxy]vinyl}phenyl) Ethanethioate (24b): R_f = 0.46 (50% CH_2Cl_2/petroleum spirit). IR: $\tilde{\nu}$ = 3283, 1704, 1651, 1589 cm^{-1}. **4b**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, J = 8.4 Hz, 2 H), 7.37 (d, J = 8.4 Hz, 2 H), 3.15 (s, 1 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.4, 134.3, 132.9, 128.9, 123.5, 83.0, 79.0, 30.4 ppm. HRMS (MALDI +ve) calcd. for $C_{10}H_9OS$ [[M + H]$^+$]: m/z = 177.0369, found 177.0373. **24b**: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.6 Hz, 2 H), 7.47 (d, J = 8.6 Hz, 2 H), 5.67 (d, J = 4.1 Hz, 1 H), 5.45 (d, J = 4.1 Hz, 1 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.1, 152.7, 134.8, 133.0, 130.8, 126.0, 118.6 (q, ^{CF}J = 320 Hz), 105.5, 30.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –67.5 ppm. HRMS (MALDI +ve) calcd. for $C_{11}H_{10}F_3O_4S_2$ [[M + H]$^+$]: m/z = 326.9971, found 326.9974.

Entry 6: To a solution of **5a** (34 mg, 0.163 mmol) and acetyl chloride (0.25 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (24 mg, 0.035 mmol) and the contents of the vessel stirred for 1 h. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 (1% ethyl acetate/CH_2Cl_2) to afford **5b** (15 mg, 47%) as a white solid.

***S*-(4-Acetylphenyl) Ethanethioate (5b):** M.p. 62–63 °C (ref.[26b] 62.5–63.5 °C). R_f = 0.30 (CH_2Cl_2). IR: $\tilde{\nu}$ = 1708, 1685, 1592 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.5 Hz, 2 H), 7.52 (d, J = 8.5 Hz, 2 H), 2.62 (s, 3 H), 2.46 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.5, 192.8, 137.5, 134.3, 133.9, 129.0, 30.6, 26.8 ppm. HRMS (MALDI +ve) calcd. for $C_{10}H_{11}OS_2$ [[M + H]$^+$]: m/z = 195.0474, found 195.0476.

Entry 7: To a solution of **6a** (69 mg, 0.333 mmol) and acetyl chloride (0.50 mL) in toluene (1.0 mL) and CH_3CN (2.0 mL) was added $Bi(OTf)_3$ (46 mg, 0.070 mmol) and the contents of the vessel stirred for 1 h. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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% CH_2Cl_2/pentane) to afford **6b** (53 mg, 82%) as a white glassy solid.

***S*-(4-Azidophenyl) Ethanethioate (6b):** M.p. 25–27 °C. R_f = 0.45 (50% CH_2Cl_2/pentane). IR: $\tilde{\nu}$ = 2130, 2094, 1710, 1590, 1571 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.6 Hz, 2 H), 7.07 (d, J = 8.6 Hz, 2 H), 2.42 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.1, 141.6, 136.1, 124.0, 120.0, 30.2 ppm. HRMS (MALDI +ve) calcd. for $C_8H_8N_3OS$ [[M + H]$^+$]: m/z = 194.0383, found 194.0386.

Entry 8: To a solution of **7a** (72 mg, 0.297 mmol) and acetyl chloride (0.50 mL) in toluene (1.0 mL) and CH_3CN (2.0 mL) was added $Bi(OTf)_3$ (43 mg, 0.066 mmol) and the contents of the vessel stirred for 3 h. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 (CH_2Cl_2) to afford **7b** (58 mg, 86%) as an off-yellow crystalline solid.

***S*-[4-(2,2-Dicyanovinyl)phenyl] Ethanethioate (7b):** M.p. 108–109 °C. R_f = 0.56 (CH_2Cl_2). IR: $\tilde{\nu}$ = 2229, 1706, 1586, 1550 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.3 Hz, 2 H), 7.77 (s, 1 H), 7.59 (d, J = 8.3 Hz, 2 H), 2.48 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.9, 158.8, 136.2, 134.8, 131.3, 131.0, 113.6, 112.4, 84.1, 30.8 ppm. HRMS (MALDI +ve) calcd. for $C_{12}H_9N_2OS$ [[M + H]$^+$]: m/z = 229.0430, found 229.0431. $C_{12}H_8N_2OS$ (228.27): calcd. C 63.14, H 3.53, N 12.27; found C 63.11, H 3.49, N 12.20.

Entry 9: To a solution of **8a** (69 mg, 0.151 mmol) and acetyl chloride (0.25 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (24 mg, 0.037 mmol) and the contents of the vessel stirred for 3 h. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 30% CH_2Cl_2/heptane to 2% ethyl acetate/CH_2Cl_2) to afford **8b** (5 mg, 7%) as an orange oil, **25** (14 mg, 19%) and **26** (3 mg, 4%), both yellow oils. In addition, starting material **8a** (25 mg) was isolated.

Entry 10: To a solution of **8a** (68 mg, 0.149 mmol) and acetyl chloride (0.25 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (50 mg, 0.076 mmol) and the contents of the vessel stirred for 30 min. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 30% CH_2Cl_2/heptane to CH_2Cl_2) to afford **8b** (36 mg, 55%) as an orange oil. In addition, **8a** (12 mg) was recovered.

***S*-(4-{[4,5-Bis(butylthio)-1,3-dithiol-2-ylidene]methyl}phenyl) Ethanethioate (8b):** R_f = 0.59 (70% CH_2Cl_2/heptane). IR: $\tilde{\nu}$ = 1709, 1570, 1545 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.3 Hz, 2 H), 7.24 (d, J = 8.3 Hz, 2 H), 6.45 (s, 1 H), 2.83 (t, J = 7.4 Hz, 2 H), 2.83 (t, J = 7.4 Hz, 2 H), 2.41 (s, 3 H), 1.67–1.60 (m, 4 H), 1.49–1.41 (m, 4 H), 0.94 (t, J = 7.3 Hz, 3 H), 0.93 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.5, 137.6, 134.9, 134.7, 127.9, 127.4, 125.1, 124.6, 113.2, 36.0, 35.9, 32.0, 31.9, 30.3, 21.8, 21.8, 13.8, 13.7 ppm. HRMS (MALDI +ve) calcd. for $C_{20}H_{26}OS_5$ [M$^{+\cdot}$]: m/z = 442.0582, found 442.0584. $C_{20}H_{26}OS_5$ (442.73): calcd. C 54.26, H 5.92; found C 54.31, H 5.96.

1-[4,5-Bis(butylthio)-1,3-dithiol-2-ylidene]-1-[4-(*tert*-butylthio)phenyl]propan-2-one (25): R_f = 0.62 (CH_2Cl_2). IR: $\tilde{\nu}$ = 1620, 1503 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.1 Hz, 2 H), 7.23 (d, J = 8.1 Hz, 2 H), 2.95 (t, J = 7.4 Hz, 2 H), 2.74 (t, J = 7.4 Hz, 2 H), 2.02 (s, 3 H), 1.65 (p, J = 7.4 Hz, 2 H), 1.57–1.36 (m, 6 H), 1.33 (s, 9 H), 0.93 (t, J = 7.4 Hz, 3 H), 0.87 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.0, 160.9, 139.1, 138.7, 134.3, 133.4, 130.0, 126.5, 122.4, 46.4, 36.3, 35.8, 32.0, 31.7, 31.2, 27.2, 21.9, 21.7, 13.8, 13.7 ppm. HRMS (MALDI +ve) calcd. for

$C_{24}H_{34}OS_5$ [[M + H]$^+$]: m/z = 499.1286, found 499.1289. $C_{24}H_{34}OS_5$ (498.84): calcd. C 57.79, H 6.87; found C 57.86, H 6.76.

***S*-(4-{1-[4,5-Bis(butylthio)-1,3-dithiol-2-ylidene]-2-oxopropyl}-phenyl) Ethanethioate (26):** R_f = 0.22 (CH_2Cl_2). IR: $\tilde{\nu}$ = 1713, 1685, 1592 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 2.95 (t, J = 7.3 Hz, 2 H), 2.75 (t, J = 7.3 Hz, 2 H), 2.46 (s, 3 H), 2.03 (s, 3 H), 1.66 (p, J = 7.3 Hz, 2 H), 1.54 (p, J = 7.3 Hz, 2 H), 1.46 (sextet, J = 7.3 Hz, 2 H), 1.39 (sextet, J = 7.3 Hz, 2 H), 0.93 (t, J = 7.3 Hz, 3 H), 0.88 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.6, 190.9, 161.3, 139.7, 135.6, 134.4, 130.7, 128.5, 126.6, 122.0, 36.3, 35.8, 32.0, 31.6, 30.5, 27.3, 21.9, 21.7, 13.8, 13.7 ppm. HRMS (MALDI +ve) calcd. for $C_{22}H_{28}O_2S_5$ [[M + H]$^+$]: m/z = 485.0766, found 485.0766.

Entry 11: To a suspension of **9a** (60 mg, 0.158 mmol) and acetyl chloride (0.30 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (49 mg, 0.075 mmol) and the contents of the vessel stirred for 30 min. The precipitate was filtered and washed successively with CH_3CN, diethyl ether and pentane to give pure **9b** (35 mg, 63%) as a white solid.

Entry 12: To a suspension of **9a** (59 mg, 0.156 mmol) and acetyl chloride (0.30 mL) in CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (48 mg, 0.073 mmol) and the contents of the vessel subjected to ultra-sonication for 1 h. The precipitate was filtered and washed with CH_3CN to give pure **9b** (52 mg, 95%) as a white solid.

***S*-(3-{[4-(Acetylthio)phenyl]buta-1,3-diyn-1-yl}phenyl) Ethanethioate (9b):** M.p. 195.5–197.5 °C (ref.[28] 279–280 °C). R_f = 0.70 (CH_2Cl_2). IR: $\tilde{\nu}$ = 2155, 1701, 1586 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, J = 8.4 Hz, 4 H), 7.39 (d, J = 8.4 Hz, 4 H), 2.44 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.2, 134.3, 133.2, 129.7, 122.9, 81.6, 75.4, 30.5 ppm. HRMS (MALDI +ve) calcd. for $C_{20}H_{14}O_2S_2$ [M$^{\cdot+}$]: m/z = 350.0430, found 350.0430.

Entry 13: To a suspension of **10a** (62 mg, 0.156 mmol) and acetyl chloride (0.30 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (49 mg, 0.0747 mmol) and the contents of the vessel stirred for 3 h. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 (5% ethyl acetate/toluene) to afford **10b** (7 mg, 12%) as a white crystalline solid, **27** (16 mg, 27%), a white solid, and recovered **10a** (38 mg, 61%).

Entry 14: To a suspension of **10a** (59 mg, 0.148 mmol) and acetyl chloride (0.30 mL) in toluene (0.50 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (96 mg, 0.146 mmol) and the contents of the vessel stirred for 30 min. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 (10% ethyl acetate/toluene) to afford **10b** (53 mg, 97%) as a white crystalline solid.

Mixture of *S*-(4-{1-[4-(*tert*-Butylthio)phenyl]-1*H*-1,2,3-triazol-4-yl}phenyl) Ethanethioate (27a) and *S*-(4-{4-[4-(*tert*-Butylthio)-phenyl]-1*H*-1,2,3-triazol-1-yl}phenyl) Ethanethioate (27b): M.p. 188–190 °C. R_f = 0.48 (5% ethyl acetate/toluene). IR: $\tilde{\nu}$ = 1699, 1596, 1503 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24 (s, 1 H), 8.24 (s, 1 H), 7.96 (d, J = 8.3 Hz, 2 H), 7.88–7.85 (m, 4 H), 7.77 (d, J = 8.6 Hz, 2 H), 7.71 (d, J = 8.6 Hz, 2 H), 7.63 (d, J = 8.2 Hz, 2 H), 7.60 (d, J = 8.6 Hz, 2 H), 7.51 (d, J = 8.3 Hz, 2 H), 2.48 (s, 3 H), 2.45 (s, 3 H), 1.33 (s, 9 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.0, 193.2, 148.2, 147.8, 138.8, 138.1, 137.6, 137.2, 136.0, 135.1, 134.2, 133.4, 131.3, 130.5, 128.9, 128.2, 126.6, 126.0, 121.0, 120.4, 118.0, 117.7, 46.8, 46.4, 31.1, 31.1, 30.5, 30.4 ppm. HRMS (MALDI +ve) calcd. for $C_{20}H_{22}N_3OS_2$ [[M + H]$^+$]: m/z = 384.1197, found 384.1199. $C_{20}H_{21}N_3OS_2$ (383.53): calcd. C 62.63, H 5.52, N 10.96; found C 62.51, H 5.50, N 10.84.

***S*,*S*′-[(1*H*-1,2,3-Triazole-1,4-diyl)bis(4,1-phenylene)] Diethanethioate (10b):** M.p. 221–225 °C. R_f = 0.40 (10% ethyl acetate/toluene). IR: $\tilde{\nu}$ = 1712 (shoulder), 1703, 1595, 1504 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24 (s, 1 H), 7.96 (d, J = 8.2 Hz, 2 H), 7.86 (d, J = 8.6 Hz, 2 H), 7.60 (d, J = 8.6 Hz, 2 H), 7.51 (d, J = 8.2 Hz, 2 H), 2.48 (s, 3 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.0, 193.2, 147.9, 137.6, 136.0, 135.1, 131.3, 129.0, 128.3, 126.7, 121.0, 117.9, 30.5, 30.4 ppm. HRMS (MALDI +ve) calcd. for $C_{18}H_{16}N_3O_2S_2$ [[M + H]$^+$]: m/z = 370.0678, found 370.0676. $C_{18}H_{15}N_3O_2S_2$ (369.46): calcd. C 58.52, H 4.09, N 11.37; found C 58.60, H 3.91, N 11.23.

Entry 15: To a suspension of **11a** (88 mg, 0.0965 mmol) and acetyl chloride (0.30 mL) in toluene (0.5 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (65 mg, 0.099 mmol) and the contents of the vessel stirred for 30 min. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 50 to 70% CH_2Cl_2/heptane) to afford **11b** (63 mg, 78%) as a pasty yellow solid and **28** (8 mg, 9%) as a bright yellow oil.

***S*-(4-{1,2-Bis[4,5-bis(butylthio)-1,3-dithiol-2-ylidene]-2-[4-(*tert*-butylthio)phenyl]ethyl}phenyl) Ethanethioate (28):** R_f = 0.43 (50% CH_2Cl_2/heptane). IR: $\tilde{\nu}$ = 1710, 1587, 1550, 1522 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.5 Hz, 2 H), 7.44 (d, J = 8.6 Hz, 2 H), 7.35 (d, J = 8.5 Hz, 2 H), 7.34 (d, J = 8.6 Hz, 2 H), 2.83 (t, J = 7.3 Hz, 4 H), 2.77 (t, J = 7.3 Hz, 2 H), 2.76 (t, J = 7.3 Hz, 2 H), 2.41 (s, 3 H), 1.66–1.54 (m, 8 H), 1.49–1.36 (m, 8 H), 1.29 (s, 9 H), 0.93 (t, J = 7.3 Hz, 3 H), 0.93 (t, J = 7.3 Hz, 3 H), 0.88 (t, J = 7.3 Hz, 3 H), 0.88 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.3, 139.0, 138.3, 138.2, 137.7, 137.2, 134.6, 131.0, 129.4, 129.0, 127.3, 126.5, 125.7, 125.6, 125.1, 123.5, 123.4, 46.4, 36.0, 36.0, 35.8, 35.7, 31.9, 31.2, 21.8, 21.8, 13.8, 13.8, 13.8, 13.8 ppm, 6 C masked. HRMS (MALDI +ve) calcd. for $C_{42}H_{56}OS_{10}$ [M$^{\cdot-}$]: m/z = 896.1483, found 896.1514. $C_{42}H_{56}OS_{10}$ (897.51): calcd. C 56.21, H 6.29; found C 56.28, H 6.29.

***S*,*S*′-({1,2-Bis[4,5-bis(butylthio)-1,3-dithiol-2-ylidene]ethane-1,2-diyl}bis(4,1-phenylene)) Diethanethioate (11b):** M.p. 76.5–79 °C. R_f = 0.18 (50% CH_2Cl_2/heptane). IR: $\tilde{\nu}$ = 1709, 1587, 1554, 1523 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.6 Hz, 4 H), 7.34 (d, J = 8.6 Hz, 4 H), 2.83 (t, J = 7.3 Hz, 4 H), 2.77 (t, J = 7.3 Hz, 4 H), 2.41 (s, 6 H), 1.66–1.54 (m, 4 H), 1.49–1.35 (m, 4 H), 0.93 (t, J = 7.4 Hz, 6 H), 0.88 (t, J = 7.4 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.2, 139.2, 138.1, 134.6, 129.2, 127.2, 125.8, 125.4, 123.1, 36.0, 35.8, 31.9, 30.4, 21.8, 21.8, 13.8, 13.8 ppm; 1 C masked. HRMS (MALDI +ve) calcd. for $C_{40}H_{50}O_2S_{10}$ [M$^{\cdot-}$]: m/z = 882.0963, found 882.1000. $C_{40}H_{50}O_2S_{10}$ (883.44): calcd. C 54.38, H 5.70; found C 54.37, H 5.72.

Entry 16: To a solution of **12a** (39 mg, 0.0767 mmol) and acetyl chloride (0.30 mL) in toluene (0.5 mL) and CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (46 mg, 0.070 mmol) and the contents of the vessel stirred for 30 min. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 (2% ethyl acetate/tolu-

ene) to give an orange oil which was crystallized (CH_2Cl_2/heptane) to afford **12b** (31 mg, 84%) as a yellow solid.

Entry 17: To a thick suspension of **12a** (88 mg, 0.173 mmol) and acetyl chloride (0.30 mL) in CH_3CN (1.0 mL) was added $Bi(OTf)_3$ (101 mg, 0.154 mmol), resulting in immediate dissolution and the resulting solution stirred at rT for 30 min. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (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 (2% ethyl acetate/toluene) to give an orange oil, which was crystallized (CH_2Cl_2/heptane) to afford **12b** (73 mg, 88%) as a yellow solid.

***S*,*S*′-[(3,3-Dicyano-3,3a-dihydroazulene-2,5-diyl)bis(4,1-phenylene)] Diethanethioate (12b):** M.p. 148–151 °C. R_f = 0.40 (2% ethyl acetate/toluene). IR: $\tilde{\nu}$ = 2254, 1705 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.4 Hz, 2 H), 7.53 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.4 Hz, 2 H), 7.41 (d, J = 8.4 Hz, 2 H), 6.95 (s, 1 H), 6.84 (dd, J = 11.5, 5.5 Hz, 1 H), 6.77 (d, J = 11.5 Hz, 1 H), 6.41 (br. d, J = 5.5 Hz, 1 H), 6.01 (d, J = 4.6 Hz, 1 H), 3.85 (dd, J = 4.6, 1.5 Hz, 1 H), 2.46 (s, 3 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.0, 193.1, 141.1, 140.4, 140.4, 139.2, 135.1, 134.7, 132.9, 132.8, 132.0, 131.3, 130.6, 128.6, 128.0, 126.9, 121.1, 117.1, 115.0, 112.9, 51.0, 45.0, 30.6, 30.4 ppm. HRMS (ESI +ve) calcd. for $C_{28}H_{20}N_2O_2S_2Na$ [[M + Na]$^+$]: m/z = 503.0858, found 503.0871. $C_{28}H_{20}N_2O_2S_2$ (480.60): calcd. C 69.97, H 4.19, N 5.83; found C 69.85, H 4.23, N 5.83.

Entry 18: To a solution of **19a** (20 mg, 0.021 mmol) and acetyl chloride (0.10 mL) in toluene (0.50 mL), CH_3CN (1.0 mL) and 1,2-dichlorobenzene (1.0 mL) was added $Bi(OTf)_3$ (4 mg, 0.0061 mmol) and the contents of the vessel stirred for 30 min at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CS_2 (20 mL in total). The combined organics were dried with Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (toluene) to afford **19b** (2 mg, 10%) as a dark brown solid in addition to recovered **19a** (16 mg).

Entry 19: To a solution of **19a** (45 mg, 0.0471 mmol) and acetyl chloride (0.10 mL) in toluene (0.50 mL), CH_3CN (1.0 mL) and 1,2-dichlorobenzene (1.0 mL) was added $Bi(OTf)_3$ (46 mg, 0.0701 mmol) and the contents of the vessel stirred for 30 min at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CS_2 (20 mL in total). The combined organics were dried with Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution of 75% toluene/CS_2 to toluene) to afford **19b** (34 mg, 77%) as a dark brown solid, in addition to recovered **19a** (6 mg, 13%).

Compound 19b: R_f = 0.58 (toluene). IR: $\tilde{\nu}$ = 1727 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$/CS_2, 2:1): δ = 7.86 (br. s, 1 H), 7.46 (br. d, J = 7.7 Hz, 1 H), 5.13 (d, J = 9.3 Hz, 1 H), 5.12 (s, 1 H), 4.18 (d, J = 9.3 Hz, 1 H), 3.38 (dq, J = 14.3, 7.2 Hz, 1 H), 2.65 (dq, J = 14.3, 7.2 Hz, 1 H), 2.41 (s, 3 H), 1.54 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$/CS_2, 2:1): δ = 193.1, 156.3, 154.1, 153.2, 152.9, 147.3, 146.6, 146.4, 146.3, 146.3, 146.2, 146.2, 146.2, 146.1, 146.0, 146.0, 145.9, 145.8, 145.6, 145.6, 145.5, 145.4, 145.4, 145.3, 145.3, 145.3, 145.2, 145.2, 144.7, 144.6, 144.4, 144.4, 143.2, 143.0, 142.7, 142.6, 142.6, 142.6, 142.3, 142.3, 142.2, 142.2, 142.1, 142.1, 142.1, 142.0, 141.9, 141.9, 141.7, 141.6, 140.3, 140.2, 140.0, 139.5, 138.8, 137.0, 136.6, 135.9, 135.7, 134.6, 130.0, 128.3, 81.8, 76.6, 68.8, 66.5, 47.4, 30.2, 13.6 ppm. HRMS (MALDI +ve) calcd. for $C_{72}H_{15}NOS$ [M$^{\cdot-}$]: m/z = 941.0907, found 941.0886. $C_{72}H_{15}NOS$ (941.98): calcd. C 91.81, H 1.61, N 1.49; found C 91.70, H 1.72, N 1.54.

Entry 20: To a solution of **20a** (40 mg, 0.0349 mmol) and acetyl chloride (0.10 mL) in toluene (0.50 mL), CH_3CN (1.0 mL) and 1,2-dichlorobenzene (1.0 mL) was added $Bi(OTf)_3$ (5 mg, 0.0076 mmol) and the contents of the vessel stirred for 2 h at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (20 mL in total). The combined organics were dried with Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (toluene) giving back **20a** (39 mg) as a dark brown solid.

Entry 21: To a solution of **20a** (40 mg, 0.0349 mmol) and acetyl chloride (0.10 mL) in toluene (0.50 mL), CH_3CN (1.0 mL) and 1,2-dichlorobenzene (1.0 mL) was added $Bi(OTf)_3$ (37 mg, 0.0564 mmol) and the contents of the vessel stirred for 2 h at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (20 mL in total). The combined organics were dried with Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (toluene) to afford **20b** (35 mg, 89%) as a dark brown solid.

Compound 20b: R_f = 0.59 (toluene). IR: $\tilde{\nu}$ = 1712 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.97 (br. s, 2 H), 7.52 (br. d, J = 8.3 Hz, 1 H), 7.25 (s, 2 H), 5.18 (s, 1 H), 4.87 (d, J = 9.5 Hz, 1 H), 4.45 (d, J = 13.1 Hz, 1 H), 4.15 (d, J = 9.5 Hz, 1 H), 3.83 (t, J = 6.6 Hz, 2 H), 3.55 (d, J = 13.1 Hz, 1 H), 2.41 (s, 3 H), 2.38 (s, 6 H), 1.87–1.82 (m, 2 H), 1.55–1.51 (m, 2 H), 1.40–1.36 (m, 4 H), 0.93 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.9, 156.5, 155.8, 154.2, 153.3, 153.2, 147.5, 147.5, 146.8, 146.5, 146.4, 146.4, 146.4, 146.3, 146.3, 146.1, 146.1, 146.1, 146.1, 145.7, 145.7, 145.7, 145.5, 145.5, 145.4, 145.4, 145.3, 144.8, 144.8, 144.6, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.2, 142.2, 142.1, 142.0, 141.8, 141.7, 140.3, 140.2, 140.1, 139.6, 138.9, 137.1, 136.6, 136.1, 135.8, 134.8, 132.4, 131.2, 130.3, 129.5, 128.4, 81.1, 76.7, 72.6, 68.9, 66.9, 56.8, 31.9, 30.6, 30.4, 26.0, 22.8, 16.7, 14.3 ppm. HRMS (MALDI +ve) calcd. for $C_{85}H_{33}NO_2S$ [M$^{\cdot-}$]: m/z = 1131.2238, found 1131.2320. $C_{85}H_{33}NO_2S$ (1132.26): calcd. C 90.17, H 2.94, N 1.24; found C 90.11, H 3.03, N 1.28.

Entry 22: To a solution of **23a** (30 mg, 0.0233 mmol) and acetyl chloride (0.10 mL) in toluene (0.50 mL), CH_3CN (1.0 mL) and 1,2-dichlorobenzene (1.0 mL) was added $Bi(OTf)_3$ (30 mg, 0.046 mmol) and the contents of the vessel stirred for 30 min at ambient temperature. The reaction mixture was added to ice water (20 mL) and extracted with small portions of CH_2Cl_2 (20 mL in total). The combined organics were dried with Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution 0.25%–0.5% ethyl acetate/toluene) to afford **23b** (7 mg, 24%) as a dark brown solid in addition to recovered **23a** (7 mg, 23%).

Compound 23b: R_f = 0.40 (2% ethyl acetate/toluene). IR: $\tilde{\nu}$ = 1726, 1596 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 8.01 (br. d on top of br. s, J = 7.7 Hz, 4 H), 7.85 (d, J = 8.7 Hz, 2 H), 7.59 (d, J = 8.7 Hz, 2 H), 7.26 (s, 2 H), 5.20 (s, 1 H), 4.88 (d, J = 9.6 Hz, 1 H), 4.47 (d, J = 13.1 Hz, 1 H), 4.18 (d, J = 9.6 Hz, 1 H), 3.84 (t, J = 6.6 Hz, 2 H), 3.62 (d, J = 13.1 Hz, 1 H), 2.47 (s, 3 H), 2.39 (s, 6 H), 1.87–1.82 (m, 2 H), 1.57–1.51 (m, 2 H), 1.40–1.36 (m, 4 H), 0.93 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.2, 156.6, 155.8, 154.3, 153.5, 153.5, 148.5, 147.5, 146.9, 146.6, 146.4, 146.4, 146.4, 146.3, 146.3, 146.2, 146.1, 146.1, 145.9, 145.7, 145.7, 145.7, 145.7, 145.5, 145.4, 145.4, 145.4, 145.3, 144.9, 144.8, 144.6, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5,

142.4, 142.3, 142.3, 142.2, 142.2, 142.2, 142.1, 142.1, 142.0, 141.8, 141.7, 140.3, 140.2, 140.1, 139.7, 137.9, 137.7, 137.1, 136.7, 136.1, 136.0, 135.8, 132.3, 131.2, 130.3, 129.7, 128.9, 126.4, 121.0, 117.7, 81.2, 76.8, 72.6, 68.9, 66.8, 56.6, 31.9, 30.6, 30.5, 26.0, 22.8, 16.7, 14.3 ppm. HRMS (MALDI -ve) calcd. for $C_{93}H_{38}N_4O_2S$ [M^-]: *m/z* = 1274.2721, found 1274.2729. $C_{93}H_{38}N_4O_2S$ (1273.49): calcd. C 87.58, H 3.00, N 4.39; found C 87.49, H 3.23, N 4.46.

CuAAC Reaction Between 22 and 6b: A solution of **22** (49 mg, 0.453 mmol), **6b** (22 mg, 0.114 mmol) and copper(I) iodide (6 mg, 0.032 mmol) in toluene (10 mL) and triethylamine (0.10 mL) was stirred at ambient temperature under an argon atmosphere 16 h. The solvent was removed in vacuo and the resulting residue purified by column chromatography (2% ethyl acetate/toluene) to afford pure **23b** (41 mg, 71%) as a dark brown solid.

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