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FUNCTIONALISED TETRATHIAFULVALENE (TTF) SYSTEMS DERIVED FROM 4,5-(PROPYLENEDITHIO)-1,3-DITHIOLE UNITS

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Abstract: A range of functionalised symmetrical and unsymmetrical tetrathiafulvalene (TTF) derivatives containing substituted 4,5-(propylenedithio)-1,3-dithiole units has been prepared. Key half-units are the t-butyldiphenylsilyl-protected 1,3-dithiole derivative **18** and the ketal-protected derivative **32**. Self-coupling and cross-coupling reactions of these half-units, with 1,3-dithiole-2-one and -2-thione derivatives **19-22** occurs in the presence of triethylphosphite. After deprotection, TTF derivatives **14, 24, 28, 34** and **40-43**, bearing hydroxy or ketone functionality are obtained. Functionalisation of the alcohol group(s) of **14, 24** and **28** has been achieved with acid chlorides and with isocyanates, to give compounds **16, 17, 25, 26** and **29**. Cyclic voltammetric studies establish that the new TTF derivatives are efficient π–electron donors; they undergo two reversible, single-electron redox waves. The X-ray crystal structures of 4,5-(2-hydroxypropylenedithio)-1,3-dithiole-2-thione **3** and the ketal-protected TTF derivative **37** are described.

Cation radical salts and charge-transfer complexes of the tetrathiafulvalene (TTF) series are well known as organic metals.[1] The attachment of chalcogen atoms to the TTF frame increases the dimensionality of these materials; this can both stabilise the metallic state, by suppressing Pierels distortions, and result in organic superconductivity.[2] For example, several salts of BEDT-TTF **1** superconduct at temperatures below *ca.* 12K.[3] The design and synthesis of new electron donors is central to the development of this field. However, until recently, TTF derivatives endowed with *functionalised* substituents have been largely neglected.[4] When suitable substituents are attached, such compounds can act as building blocks for the following classes of materials.

(i) salts and complexes with increased inter- and intra-stack interactions, *eg.* hydrogen bonding;
(ii) Langmuir-Blodgett films;
(iii) macrocyclic TTF derivatives;
(iv) polymeric TTF derivatives.

In this context, we now report our studies on the synthesis and reactions of new donor molecules which contain functionalised propylenedithio units fused to the TTF framework.[5] Reactions of the 4,5-(propylenedithio)-1,3-dithiole-2-thione half units, studied *en route* to the new TTF systems are also described.

RESULTS AND DISCUSSION

Synthesis and Reactions of 4,5-(2-hydroxypropylenedithio)-1,3-dithiole-2-thione **3**. Compound **3** was identified as an attractive building block for functionalised TTF derivatives for the following reasons:
(i) Compound **3** should be readily available in large quantities from zincate salt **2**,[6] or from caesium salt **6**;[7]

(ii) The alcohol group of compound **3** should serve as a reactive 'handle' enabling a variety of substituents to be attached to the system;
(iii) Coupling reactions of derivatives of **3**, to yield TTF derivatives, should proceed under standard conditions.[8]

Compound **3** has been prepared by three routes. Zincate salt **2**[6] reacted with 1,3-dibromo-propan-2-ol in refluxing acetonitrile to yield compound **3** (66% yield); a second highly insoluble product obtained from this reaction was tentatively identified (mass spectrometric evidence) as macrocycle **4** (5-10% yield). Alternatively, caesium salt **6** [which was prepared from di(thiobenzoyl) derivative **5**][7] reacted with 1,3-dichloropropan-2-ol to afford compound **3** (60% yield) without the formation of macrocycle **4**. While our work was in progress an alternative route to compound **3** (by reduction of compound **30**) was reported by Russian workers.[9] We have also used this two-step route, and found it to be appropriate for the preparation of large-scale batches (*ca.* 10 g) of alcohol **3**.

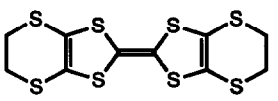
Functionalisation of the alcohol group of compound **3** has provided derivatives **7-13**. Acrylate and benzoyl ester derivatives **7** and **8**, respectively (*ca.* 75% yield) and long chain ester derivative **9** (40% yield) were obtained by reaction of alcohol **3** with the appropriate acid chloride at room temperature, in the presence of triethylamine. 2-Chloroethylisocyanate reacted with alcohol **3**, under similar conditions, to give urethane derivative **10** (56% yield). Tosylate derivative **11** was obtained (74% yield) by deprotonation of alcohol **3** using sodium hydride in THF at 0°C, followed by addition of tosyl chloride. Silyl derivative **12** was formed (98% yield) by reaction of alcohol **3** with t-butyldiphenylsilyl (tert-BDPSi) chloride in DMF in the presence of imidazole. Methyl ether derivative **13** was obtained in only 5% yield (sodium metal, followed by methyliodode in toluene).

Attempts to displace the tosylate group of **11** with nucleophiles have been unsuccessful. For example, both sodium bromide and sodium azide failed to react with **11**; starting material was recovered in both cases. Inspection of CPK molecular models of **11** suggests that this is because the tosylate group of **11** is sterically very hindered to displacement, due to the folded conformation of the seven-membered ring (*cf.* the X-ray crystal structures of compounds **3** and **37** below).

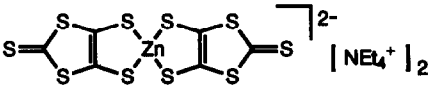
TTF Synthesis Using Silyl-Protected 1,3-Dithiole Half-Unit **12**. Attempted self-coupling of both acrylate and urethane derivatives **7** and **10**, respectively, in neat triethylphosphite at 130°C[8], was unsuccessful: no TTF derivative was detected. Likewise an amphiphilic TTF system could not be obtained by cross-coupling thiones **9** and **22** under the same conditions. Alcohol **3** self-coupled to give bis(2-hydroxy-1,3-propylenedithio)TTF **14**, but only in very low yield (<5%). A far more efficient synthesis of TTF derivative **14** was achieved in two steps (50% overall yield) by self-coupling the silyl derivative **12**, to yield **15**, followed by removal of the tert-BDPSi protecting group with fluoride ion. Diol **14** is only sparingly soluble in most common organic solvents. Nonetheless, both hydroxy groups of **14** could be functionalised to yield compounds **16** and **17** (*ca.* 70% yield) by reaction with acetyl chloride and 4-bromobutyryl chloride respectively, in refluxing toluene containing imidazole.

It should be noted that when thione **12** is self-coupled, compound **15** was formed as a mixture of diastereoisomers; consequently, the products **14-17** were also obtained as a mixture. The presence of both diastereoisomers was confirmed by the ^{1}H NMR data. The hydroxyl protons in compound **14** appear as two separate doublets in the 250 MHz spectrum, one from each of the two isomers. Furthermore, the 500 MHz spectrum of compound **15** shows two sets of complex multiplet systems, at very similar chemical shift values, from the methine protons. It was not necessary at this stage of our studies on these compounds to attempt to separate the diastereoisomers, which appear as one product on TLC.

Treatment of thione **12** with mercuric acetate quantitatively yielded ketone **18**, which was cross-coupled with half-unit **19**, in the presence of triethylphosphite, to yield the unsymmetrical TTF system **23** (30% yield) which could not be completely separated from self-coupled products, even after extensive



1 (BEDT-TTF)



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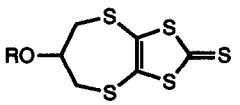


3; R = H

7; R = C(O)-CH=CH_2

8; R = C(O)Ph

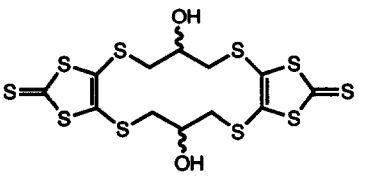
9; R = C(O)$(CH_2)_{14}$Me

10; R = C(O)NH-CH_2-CH_2-Cl

11; R = SO_2-C_6H_4-4-Me

12; R = $SiPh_2$-t-Bu

13; R = Me



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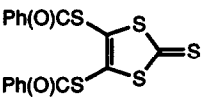

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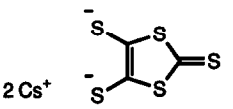

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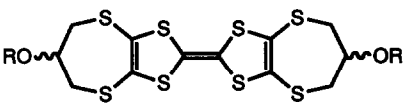
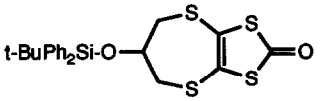


14; R = H

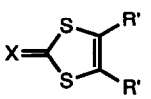
15; R = $SiPh_2$-t-Bu

16; R = C(O)Me

17; R = C(O)-$(CH_2)_3$-Br



18

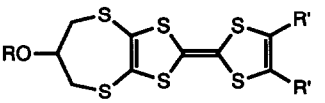


19; R' = SMe; X = O

20; R'-R' = S-$(CH_2)_2$-S; X = O

21; R' = H; X = S

22; R' = Me, X = S



23; R' = SMe; R = $SiPh_2$-t-Bu

24; R' = SMe; R = H

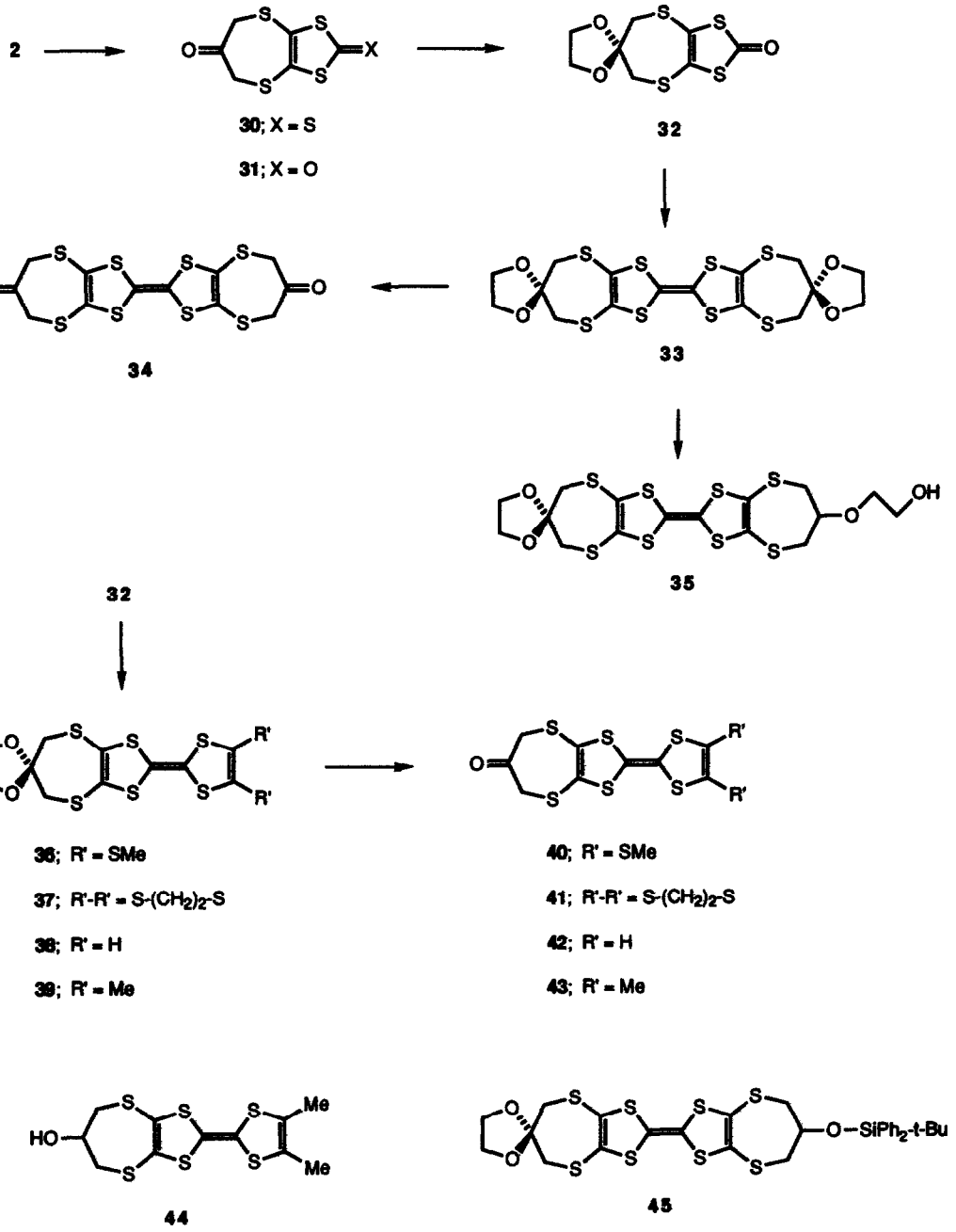
25, R' = SMe; R = C(O)-CH=CH_2

26; R' = SMe; R= C(O)NH-$(CH_2)_2$-Cl

27; R' = H; R = $SiPh_2$-t-Bu

28; R' = R = H

29; R' = H; R = C(O)NH-$C_{18}H_{37}$


2
30; X = S
31; X = O
32
33
34
35
32
36; R' = SMe
37; R'-R' = S-(CH2)2-S
38; R' = H
39; R' = Me
40; R' = SMe
41; R'-R' = S-(CH2)2-S
42; R' = H
43; R' = Me
44
45
O—SiPh2-t-Bu

chromatography. Deprotection of derivative **23** afforded the TTF-alcohol **24** (*ca.* 67% yield) which was obtained analytically pure. Functionalisation of the alcohol group of TTF derivative **24** to yield compounds **25** (31%) and **26** (80%) was achieved under the same conditions used to prepare **7** and **10**. Analogous cross-coupling of units **18** and **21** yielded **27** (32% yield) and, hence, compound **28** (65% yield). Reaction of alcohol **28** with octadecylisocyanate yielded the hydrophobic derivative **29** (10% yield) which may be suitable for Langmuir-Blodgett film formation.

TTF Synthesis Using the Ketal-Protected 1,3-dithiole-2-one Half-Unit **32**. We have also explored the reactions of 1,3-dithiole derivative **30** with the aim of obtaining propylenedithio-TTF derivatives with exocyclic ketone functionality. Zincate salt **2** reacted with 1,3-dichloropropan-2-one to yield keto-thione **30** (76% yield) which was converted into diketone **31**, in quantitative yield, by mercuric acetate oxidation. Attempts to self-couple either thione **30** or ketone **31**, using triethylphosphite, gave complex product mixtures from which no TTF derivative could be isolated. However, when the ketone group of compound **31** was protected as the ketal **32**, self-coupling proceeded smoothly to afford the symmetrical TTF derivative **33** (66% yield). Removal of the ketal protecting group of compound **33** required remarkably harsh conditions. Compound **33** was recovered unchanged from refluxing in a 10% solution of hydrochloric acid in THF; however, upon refluxing in a 15% solution of sulfuric acid in THF, diketone **34** was obtained in 87% yield (an overall yield of 37% from zincate salt **2**). We attempted to open the ketal rings of compound **33**, to form hydroxyethoxy side-chains, which should be suitable for further functionalisation, by reaction of **33** with lithium aluminium hydride in the presence of aluminium chloride;[10] a small amount of compound **35** was formed (mass spectroscopic evidence) but the product could not be purified.

The ketal-protected half-unit **32** has been cross-coupled with the 1,3-dithiole-2-one (or 2-thione) derivatives **19-22** to give compounds **36-39** (18-37% yields). For these reactions, the yield of the desired cross-coupled product was optimised by using the ketone derivatives **19** and **20** of the 4,5-alkylthio-substituted half-units (1 mol. equiv.), and the thione derivatives **21** and **22** of the unsubstituted and 4,5-dimethyl-substituted half units (3 mol. equiv.). After deprotection, the unsymmetrical ketone-substituted TTF donors **40-43**, respectively, were obtained in high yield. The ketone group of compounds **42** and **43** was cleanly reduced with lithium aluminium hydride to yield alcohols **28** and **44**, respectively (80-95% yield) thereby providing an alternative route to mono-alcohol substituted TTF systems.

Cross-coupling of half-units **18** and **32** yielded TTF derivative **45** (37% yield). This is a particularly attractive system, as selective removal of the two different hydroxy protecting groups should provide an efficient method for unsymmetrical functionalisation of diol **14**.

Electrochemical Redox Properties of the New TTF Derivatives. The solution redox chemistry of the new TTF derivatives **14**, **23-26**, **28**, **34**, and **40-43** has been studied by cyclic voltammetry. Each donor shows two, single-electron, reversible redox waves at the expected potentials for TTF derivatives with a C_6S_6 or C_6S_8 core.[11] These data are a reliable confirmation that the TTF system has remained in tact during all the synthetic transformations accomplished at the periphery of the molecule. The oxidation potential of a TTF derivative is known to be raised by the attachment of alkylthio substituents and lowered by attachment of alkyl groups. Thus, of the new donors, compound **43**, which carries two methyl substituents, is the most easily oxidised. The oxidation potentials are not affected by the presence of the substituents on the propylenedithio bridge(s), which are electronically isolated from the TTF core in all the new derivatives. Data are collated in Table 1.

Table 1. Cyclic Voltammetric Data for Tetrathiafulvalene Derivatives.[a]

Compound	$E_1^{1/2}$/V	$E_2^{1/2}$/V
14[b]	0.66	1.03
24[b]	0.56	0.92
25[b]	0.57	0.93
26[b]	0.56	0.92
28[b]	0.50	0.89
34[c]	0.68	1.04
40[c]	0.64	0.98
41[c]	0.64	1.02
42[c]	0.60	0.91
43[c]	0.51	0.96

[a] Data were obtained *versus* Ag/AgCl, under argon using a platinum button electrode and a platinum wire counter electrode, *ca.* 5 x 10^{-4} M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 $mVsec^{-1}$, using a BAS 100 Electrochemical Analyser.

[b] Solvent dichloromethane.

[c] Solvent 1,1,2-trichloroethane.

X-Ray Crystal Structures of Compounds **3** and **37**. The structures of compounds **3** and **37** have been examined by single crystal X-ray analysis. Compound **3** was studied to establish the solid state conformation of the molecule and the preferred configuration of the hydroxyl group. The molecular structure of compound **3** is shown in Figure 1. Atoms S(3), S(4) and S(7) are in the same plane as the 1,3-dithiole ring. Bond angles at S(3) and S(4) are 100.6° and 101.9°, respectively. The fragment O(2)-C(4)-C(5)-S(4) is exclusively in the *s-trans* configuration. The only intermolecular contact that is significantly shorter than the sum of the van der Waals radii is the S(1)---S(1) distance of 3.334Å. The shortest intermolecular sulfur-oxygen distances are S(7)---O(2) 3.363Å and S(2)---O(2) 3.411Å, which are indicative of very weak hydrogen bonded interactions. In the latter stages of refinement of the structure, a peak of 1.80 $eÅ^3$ was observed in the difference Fourier map, at a distance of 1.23(1)Å from C(4). This peak which is 2-3 times the height of a normal hydrogen atom, was modelled as a partially occupied (20%) carbonyl oxygen. However, the mass spectrum of the sample did not suggest any contamination from the carbonyl compound **30**.

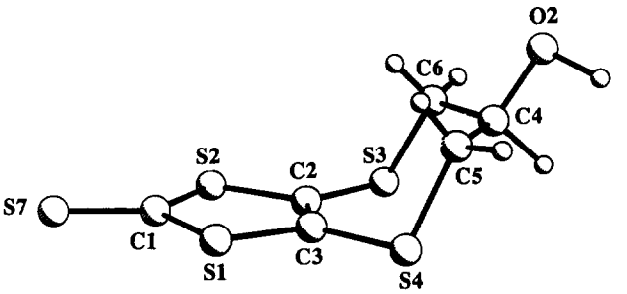


Figure 1. **X-Ray molecular structure of compound 3 and crystallographic numbering scheme.**

The structure of compound **37** was determined for the following reasons: (i) relatively few structural studies have been reported on neutral, *unsymmetrical* TTF derivatives, although their potential in the construction of organic conductors is well recognised;[12] (ii) compound **37** provided a unique opportunity to study the effect of *spiro* substitution on the crystal packing of the molecules, and (iii) we considered the possibility that the oxygen atoms of the ketal group might engage in close intermolecular O---S contacts. Such interactions have been observed recently in the structure of bis(ethylenedioxo)-TTF, (BEDO-TTF)[13] and it would, therefore, be of interest to find other TTF systems possessing similar O---S contacts.

The molecular structure of compound **37**, and the atom numbering scheme are shown in Figure 2; the crystal packing is shown in Figure 3. The TTF framework of compound **37** adopts a non-planar, boat-like conformation, which is typical of many neutral (symmetrical) TTF derivatives, *eg.* BEDT-TTF **1**:[14] the central tetrathioethane fragment of compound **37** is essentially planar with both 1,3-dithiole rings folded in the same direction, by 15° along the S(1)---S(2) axis, and by 20° along the S(5)---S(6) axis. The conformation of the seven-membered ring of compound **37** is essentially identical to that of compound **3**, and the six-membered ring of compound **37** is a similar shape to that of BEDT-TTF **1**,[14] with bond angles C(9)-S(7)-C(11) and C(8)-S(8)-C(10) of 102.3 and 97.5°, respectively. The bond angles at the *spiro* centre C(4) are in the range 107-115°, the angle C(5)-C(4)-C(6), within the seven-membered ring, showing the largest deviation from tetrahedral geometry.

The packing of the molecules of compound **37** within the crystal is shown in Figure 3. Centrosymmetrically related pairs of molecules are arranged in columns along the *c* axis of the crystal, with the axes of the TTF framework at 45° and 135°, respectively, in adjacent colums. This results in the arrangement

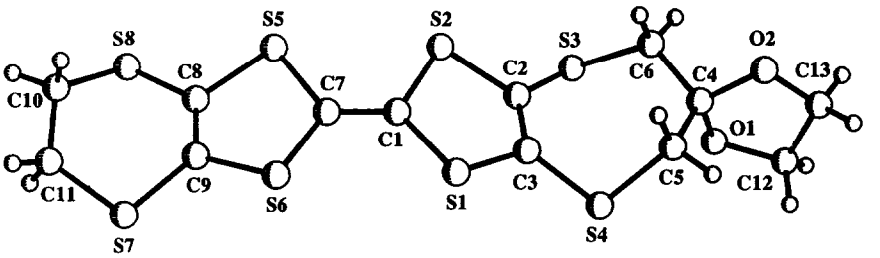


Figure 2. X-Ray molecular structure of compound **37** and crystallographic numbering scheme.

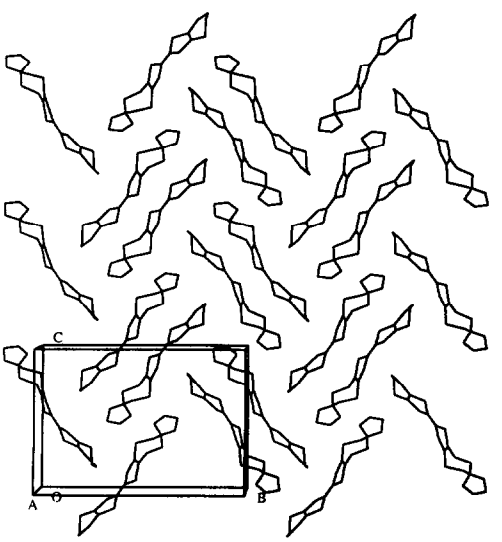


Figure 3. X-Ray crystal structure of compound **37** projected along the *a* axis.

of molecules along the *b* direction forming a 'herring-bone'-like packing. The closest intermolecular contacts involving sulfur and oxygen are as follows: S(1)---S(1) 3.498(7), S(2)---S(4) 3.475(7), S(3)---O(1) 3.390(9) and O(1)---O(1) = 3.31(2) Å, none of which is significantly shorter than the sum of the van der Waals radii for the two atoms (1.80 Å for sulfur and 1.40 Å for oxygen.)

EXPERIMENTAL

General Details. These have been reported previously.[15] Additional instrumentation used in the present work is a Varian UNITY 500 NMR spectrometer.

Compound **3**. Method(a): from caesium salt **6**. Caesium salt **6**[7] (9.20 g, 0.02 mol) was dissolved in dry dimethylformamide (100 mL); 1,3-dichloropropan-2-ol (5.0 g, excess) was added and the mixture was stirred for 16 h at 20°C under nitrogen. Precipitated caesium chloride was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The brown product was washed sequentially with water and with ether, then recrystallised from ethanol, using decolourising charcoal, to afford compound **3** (3.0 g, 59%) as a yellow solid, m.p. 188-189°C. (Found: C, 28.4; H, 2.4; S, 63.2; $C_6H_6S_5O$ requires C, 28.4; H, 2.4; S, 63.0); m/z(EI) 254 (M^+); δ_H [$(CD_3)_2SO$] 5.62 (1H, broad s), 4.04 (1H, m), 3.05 (2H, m) and 2.64 (2H, m); ν_{max}(KBr)/cm^{-1} 3436 (OH) and 1056 (C=S).

Method (b): from zincate salt **2**. To a solution of zincate salt **2** (8.20 g, 11.4 mmol) in dry acetonitrile (150 mL), 1,3-dibromopropan-2-ol (5.0 g, 22.9 mmol) was added and the mixture was refluxed with stirring under nitrogen for 4 h. A highly-insoluble yellow precipitate was removed by filtration and tentatively identified as *macrocycle* **4** (0.58 g, 10%), m.p. >350°C; m/z (EI) 508 (M^+). Evaporation of the filtrate *in vacuo*, followed by purification of the residue on a silica column, eluent dichloromethane, gave compound **3** (3.83 g, 66%) identical with the sample described above.

Compounds **7-10**. General Procedure. To a solution of alcohol **3** (500 mg, 1.97 mmol) in dry dichloromethane (80 mL) was added either acryloyl chloride (0.19 mL, 2.34 mmol), benzoyl chloride (0.28 mL, 2.40 mmol), hexadecanoyl chloride (0.6 mL, 1.97 mmol) or 2-chloro-ethylisocyanate (0.20 mL, 2.35 mmol) followed by dry triethylamine (0.55 mL, 3.95 mmol). The mixture was stirred at 20°C for 16 h under nitrogen. Water (50 mL) was added and the mixture extracted into dichloromethane (2 x 50 mL). The combined organic extracts were water washed, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed [silica column, eluent cyclohexane/ dichloromethane (2:1 v/v) to afford products **7**, **8** and **10**; neutral alumina column, eluent toluene to obtain product **9**. There was obtained:

Compound **7**, a yellow solid (450 mg, 74%), m.p. 122-123°C (from dichloromethane / hexane). (Found: C, 34.9; H, 2.6. $C_9H_8O_2S_5$ requires C, 35.0; H, 2.6%); m/z (DCI) 309 (M^++1); δ_H($CDCl_3$) 6.46, 6.12 and 5.92 (3H, ABX, J_{AX} 17.18, J_{BX} 10.30 and J_{AB} ca. 1.0 Hz), 5.37 (1H, m), 3.09 (2H, m) and 2.80 (2H, m); ν_{max} (nujol)/cm^{-1} 1715 (C=O) and 1070 (C=S).

Compound **8**, a yellow solid (520 mg, 74%) m.p. 155-157°C (from dichloromethane/hexane). (Found: C, 43.4; H, 2.7. $C_{13}H_{10}O_2S_5$ requires C, 43.5; H, 2.8%); m/z (DCI) 359 (M^++1); δ_H($CDCl_3$) 8.04 (2H, m), 7.61 (1H, m), 7.49 (2H, m), 5.58 (1H, m), 3.19 (2H, m) and 2.94 (2H, m); ν_{max}(nujol)/cm^{-1} 1720 (C=O) and 1065 (C=S).

Compound **9**, a yellow solid (400 mg, 41%), m.p. 95-97°C. (Found: C, 54.0; H, 7.1. $C_{22}H_{36}O_2S_5$ requires C, 53.7; H, 7.3%). m/z (DCI) 493 (M^++1); ν_{max}(nujol)/cm^{-1} 1742 (C=O) and 1060 (C=S).

Compound **10**, a yellow solid (395 mg, 56%), m.p. 222°C (sublimes) (from dichloromethane/hexane). (Found: C, 29.7; H, 2.7; N, 3.8. $C_9H_{10}ClNO_2S_5$ requires C, 30.0; H, 2.8; N, 3.9%). m/z (DCI) 360

(M^++1); $\delta_H(CDCl_3)$ 5.30-5.20 (2H, m), 3.63 (2H, m), 3.55 (2H, t, J = 5.5 Hz), 3.08 (2H, m) and 2.79 (2H, m); ν_{max} (nujol)/cm^{-1} 3320 (NH), 1690 (C=O), 1060 (C=S).

Compound **11.** To a suspension of sodium hydride (90 mg of a 60% dispersion in mineral oil, 2.25 mmol) in dry THF (100 mL) cooled to 0°C under nitrogen, was added alcohol **3** (500 mg, 1.97 mmol) and the mixture was stirred at 0°C for 1.5 h. Tosyl chloride (450 mg, 2.36 mmol) was added and the mixture allowed to warm to 20°C overnight. Workup and purification as described for compound **7**, gave compound **11**, an orange solid (595 mg, 74%) m.p. 107-109°C. (Found: C, 38.2; H, 3.0. $C_{13}H_{12}O_3S_6$ requires C, 38.2; H, 3.0%) m/z (DCI) 409 (M^++1); $\delta_H(CDCl_3)$ 7.82 (2H, d, J = 8.26 Hz), 7.39 (2H, d, J = 8.03 Hz), 4.96 (1H, m), 3.02 (2H, m), 2.73 (2H,m), and 2.48 (3H, s); ν_{max} (nujol)/cm^{-1} 1065 (C=S).

Compound **12.** Alcohol **3** (2.3 g, 9.0 mmol) was dissolved in dry DMF (200 mL); imidazole (7.0 g, 0.10 mol) and *tert*-butyl-diphenylsilyl chloride (3.0 g, 0.01 mol) were added and the mixture stirred at 20°C for 16 h. Dichloromethane (250 mL) was then added and the organic layer separated and washed sequentially with ice-cold hydrochloric acid (3M, 3 x 50 mL) and water (50 mL). The organic layer was separated, dried ($MgSO_4$) and solvent evaporated *in vacuo*. The residue was chromatographed on a short silica column eluting with cyclohexane / dichloromethane (1:1 v/v) to yield compound **12** (4.4 g, 98%) as a yellow solid, m.p. 109-111°C. (Found: C, 53.9; H, 5.0. $C_{22}H_{24}OS_5Si$ requires C, 53.7; H, 4.9%) m/z (EI) 492 (M^+); $\delta_H(CDCl_3)$ 7.62-7.48 (10H, m), 4.28 (1H, m), 2.94 (2H, m), 2.77 (2H, m) and 1.04 (9H, s).

Compound **13.** To a solution of alcohol **3** (500 mg, 1.97 mmol) and methyl iodide (0.12 mL, 1.97 mmol) in toluene (50 ml), was added sodium shavings (200 mg, excess) and the mixture was heated at reflux for 24 h. Filtration removed excess sodium, and aqueous work-up of the filtrate, followed by chromatography on a silica column (eluent toluene) gave compound **13** as a yellow solid (27 mg, 5%); m.p. 76-79°C. (Found: C, 31.1; H, 2.9. $C_7H_8OS_5$ requires C, 31.3; H, 3.0%). m/z (DCI) 269 (M^++1); $\delta_H(CDCl_3)$ 3.79 (1H, m), 3.45 (3H, s), 3.06 (2H, m) and 2.61 (2H, m); ν_{max} (nujol)/cm^{-1} 1060 (C=S).

Compound **14.** Compound **15** (200 mg, 0.22 mmol) was dissolved in THF (50 mL) under nitrogen; tetrabutylammonium fluoride (270 mg, 0.44 mmol) was added and the mixture was stirred at 20°C for 2 h. Solvent was removed *in vacuo* and the resulting orange solid was washed with methanol and ether to yield compound **14** (80 mg, 80%); m.p. >230°C (decomp.). (Found: C, 32.4; H, 3.0. $C_{12}H_{12}O_2S_8$ requires C, 32.4; H, 2.7%). m/z (DCI) 445 (M^++1); $\delta_H[(CD_3)_2SO]$ 5.61 (1H, d, J=5.0 Hz), 5.52 (1H, d, J=5.0 Hz), 3.93 (2H, m), 2.93 (4H, m) and 2.49 (4H, m); ν_{max} (nujol)/cm^{-1} 3300 (OH).

Compound **15.** Thione **12** (4.0 g, 8.5 mmol) or ketone **18** (4.0 g, 8.1 mmol) were suspended in triethylphosphite (10 mL) under nitrogen and the mixture was slowly heated to 130°C and then held at that temperature for 45 min. The mixture was cooled to 20°C and chromatographed on a silica column, eluting with cyclohexane/toluene (4:1 v/v) to yield compound **15**, as an orange solid (1.3 g, 33% from thione **12**; 1.8 g, 50%, from ketone **18**) m.p. 201-202°C (from methanol/ dichloromethane). (Found: C, 57.4; H, 5.3. $C_{44}H_{48}O_2S_8Si_2$ requires, C, 57.4; H, 5.2%); m/z (EI) 920 (M^+); $\delta_H(CDCl_3)$ 7.61 (8H, m), 7.40 (12H, m), 4.16 (2H, m), 2.70 (4H, m), 2.48 (4H, m) and 1.06 (18H, s).

Compounds **16** and **17.** General Procedure. Diol **14** was suspended in dry toluene (50 mL) under nitrogen, and excess acetyl chloride or 4-bromobutyryl chloride was added followed by imidazole (1.0 g). The mixture was refluxed for 16 h. After hot filtration of the precipitate, the toluene is removed *in vacuo* and the residue purified by chromatography on a silica column, eluting with dichloromethane. There was obtained:

Compound **16**, from diol **14** (220 mg) and acetyl chloride (5 mL) as an orange solid (180 mg, 69%), m.p. >230°C; (Found: C, 36.3; H, 3.0. $C_{16}H_{16}O_4S_8$ requires C, 36.4; H, 3.0); m/z (EI) 528 (M^+); $\delta_H(CDCl_3)$ 5.30 (2H, m), 2.92 (4H, m), 2.60 (4H, m) and 2.08 (6H, s).

Compound **17**, from diol **14** (140 mg) and 4-bromobutyryl chloride (3 mL), as an orange solid (100 mg, 43%); m.p. 224-225°C (from toluene). (Found: C, 32.4; H, 3.1%). $C_{20}H_{22}Br_2O_4S_8$ requires, C, 32.4; H, 3.0%.) m/z (CI) 742 (M^+); $\delta_H(CDCl_3)$ 5.30 (2H, m), 3.61 (4H, t, J=6.5 Hz), 2.55 (4H, m), 2.92 (4H, m), 2.51 (4H, m) and 2.10 (4H, m); ν_{max} (nujol)/cm^{-1} 1733 (C=O).

Compound **18**. Thione **12** (4.5 g, 9.0 mmol) was dissolved in a mixture of chloroform (75 mL) and acetic acid (25 mL). Mercuric acetate (7.0 g, excess) was added and the mixture was stirred at 20°C for 16 h whence a white precipitate was removed by filtration, and washed with dichloromethane. The filtrate and the dichloromethane washings were combined and washed sequentially with saturated sodium hydrogencarbonate (3 x 100 mL) and water (100 mL), and then dried ($MgSO_4$) and evaporated *in vacuo* to yield a colourless oil which crystallised upon storage *in vacuo*. There was obtained compound **18** (4.3 g, 100%) m.p. 119-120°C. (Found: C, 55.2; H, 4.9; $C_{22}H_{24}O_2S_4Si$ requires C, 55.5; H, 5.0%) m/z (DCI) 477 (M^++1); $\delta_H(CDCl_3)$ 7.63 (4H, m), 7.46 (6H, m), 4.20 (1H, m), 2.82 (2H, m), 2.61 (2H, m) and 1.04 (9H, s); ν_{max} (nujol)/cm^{-1} 1668 (C=O).

Compound **23**. Ketone **18** (3.45 g, 7.25 mmol) and ketone **19** (1.52 g, 7.24 mmol) were suspended in triethylphosphite (8 mL) and the mixture was warmed to 130°C with stirring under nitrogen, whereupon dissolution of the ketones was complete. After 2 h at 130°C the deep red reaction mixture was cooled to 20°C and chromatographed on a silica column, eluting with cyclohexane / toluene (3:1 v/v) to yield the product as an orange solid. Compound **23**, which could not be completely separated from self-coupled products (t.l.c. and mass spectroscopic evidence) even after repeated chromatography, was obtained (*ca.* 1.43 g, 30%) m/z (DCI) 655 (M^++1); $\delta_H(CDCl_3)$ 7.62 (4H, m), 7.41 (6H, m), 4.12 (1H, m), 2.72 (2H, m), 2.49 (2H, m), 2.38 (6H, s) and 1.06 (9H, s).

Compound **24.** To a solution of compound **23** (1.43 g, 2.18 mmol) in THF (80 mL), tetrabutylammonium fluoride trihydrate (1.38 g, 4.37 mmol) was added and the reaction mixture was stirred at 20°C for 16 h under nitrogen. Water (50 mL) was then added and the mixture was extracted with dichloromethane (2 x 80 mL). The combined extracts were washed with water, dried ($MgSO_4$) and evaporated. Chromatography of the residue on a silica column, eluting with dichloromethane gave compound **24** as an orange solid (610 mg, 67%) m.p. 143-144°C (from dichloromethane / hexane). (Found: C, 31.6; H, 2.8. $C_{11}H_{12}OS_8$ requires, C, 31.7; H, 2.9%); m/z (DCI) 417 (M^++1); $\delta_H(CDCl_3)$ 4.39 (1H, m), 3.47 (1H, broad), 2.82 (4H, m) and 2.41 (6H, s).

Compounds **25** and **26** - General Procedure To a solution of compound **24** (200 mg, 0.48 mmol) in dry dichloromethane (80 mL) was added either acryloyl chloride (0.05 mL, 0.61 mmol) or 2-chloroethylisocyanate (0.05 mL, 0.59 mmol) followed by dry triethylamine (0.13 mL, 0.93 mmol) and the mixture was stirred at 20°C for 16 h. Water (50 mL) was then added and the mixture extracted with dichloromethane (2 x 50 mL). The combined extracts were washed with water, dried ($MgSO_4$) and evaporated. The residue was chromatographed on a silica column, eluting with dichloromethane to yield the product. There was obtained:

Compound **25**, a yellow solid (70 mg, 31%), m.p. 156-157°C (from dichloromethane / hexane). (Found: C, 35.5; H, 3.0. $C_{14}H_{14}O_2S_8$ requires C, 35.7; H, 3.0%); m/z (DCI) 471 (M^++1); δ_H ($CDCl_3$) 6.45, 6.11 and 5.90 (3H, ABX, J_{AX} = 16.96 J_{BX} = 10.67 and J_{AB} = *ca.* 1 Hz), 5.30 (1H, m), 2.95 (2H, m), 2.67 (2H, m) and 2.41 (6H, s).

Compound **26**, a yellow solid (200 mg, 80%), m.p. 219-221°C (from dichloromethane/hexane). (Found: C, 32.0; H, 3.0; N, 2.7. $C_{14}H_{16}ClNO_2S_8$ requires C, 32.3; H, 3.1; N, 2.7%) m/z (DCI) 522 (M^++1); δ_H ($CDCl_3$) 5.16 (2H, m), 3.62 (2H, m), 3.54 (2H, t, J = 5.45 Hz), 2.95 (2H, m), 2.64 (2H, m) and 2.41 (6H, s).

Compound **27** was prepared analogously to compound **23**, from ketone **18** (1.0 g) and thione **21** (268 mg). Final purification was achieved by preparative t.l.c. (silica, eluent cyclohexane) to yield an orange solid (365 mg, 32%), m.p. 95-96°C. (Found: C, 53.3; H,4.6. $C_{25}H_{26}OS_6Si$ requires C, 53.4; H, 4.6%); m/z (DCI) 563 (M^++1); δ_H($CDCl_3$) 7.62 (4H, m), 7.41 (6H, m), 6.33 (2H, s) 4.13 (1H, m), 2.72 (2H, m), 2.49 (2H, m) and 1.06 (9H, s).

Compound **28** was prepared from **27**, analogously to compound **24**, and isolated as an orange solid (495 mg, 70%), m.p.190-192°C. (Found: C, 33.3; H, 2.4. $C_9H_8OS_6$ requires C, 33.3; H, 2.5%); m/z (DCI) 325 (M^++1); δ_H($CDCl_3$) 6.32 (2H, s), 4.39 (1H, m), 3.48 (1H, broad) and 2.83 (4H, m).
Alternatively, compound **28** was obtained from **42** as follows: to a solution of compound **42** (500mg, 1.6 mmol) in dry THF (40 mL), lithium aluminium hydride (excess) was added and the mixture was stirred at 20°C for 1 h. Aqueous workup followed by extraction of the product into dichloromethane, which was dried ($MgSO_4$) evaporated and chromatographed on a silica column (eluent, dichloromethane : hexane, 1:1 v/v) gave compound **28** (400 mg, 80%).

Compound **29**. To a stirring solution of alcohol **28** (100 mg, 0.31 mmol) and octadecylisocyanate (90 mg, 0.31 mmol) in dry dichloromethane (50 mL), triethylamine (0.14 mL, 1 mmol) was added dropwise over 1 min. The reaction mixture was stirred at 20°C for 3 days, whence water (100 mL) was added. The organic layer was separated, dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product which was chromatographed on a neutral alumina column (eluent, hexane : toluene, 3:1 v/v) to afford compound **29** as a yellow solid (20 mg, 10%), m.p. 129-132°C. (Found: C, 54.1; H, 7.2; N, 2.4%. $C_{28}H_{45}NO_2S_6$ requires C, 54.3; H, 7.3; N, 2.3%); m/z (DCI) 620 (M^++1).

Compound **30**. To a solution of the zinc complex **2** (1.17 g, 1.64 mmol) in dry acetonitrile (100 mL), 1,3-dichloroacetone (0.5 g, 3.94 mmol) was added. The reaction was refluxed under nitrogen with stirring for 2-3 hours after which time the solution had changed from a deep red to an orange colour. Acetonitrile was removed *in vacuo* and the product dissolved in dichloromethane and washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Purification using chromatography on a silica column, eluent dichloromethane, afforded compound **30** as an orange solid (630 mg, 76%), m.p. 153-156°C. (Found: C, 28.8; H, 1.5. $C_6H_4OS_5$ requires C, 28.5; H, 1.6%); m/z (EI) 252 (M^+); δ_H ($CDCl_3$) 3.50 (4H, s); δ_C ($CDCl_3$) 42.71 (CH_2), 138.96 (C=C), 200.24 (C=O) and 208.72 (C=S); ν_{max} (Nujol)/cm^{-1} 1705 (C=O) and 1060 (C=S).

Compound **31**. To a solution of **30** (100 mg, 0.40 mmol) in dry chloroform / glacial acetic acid (30 mL, 3:1 v/v), mercuric acetate (an excess) was added. The reaction was stirred at 20°C under nitrogen for 2 h, after which time a white precipitate had formed. The precipitate was filtered off and washed with dichloromethane. The filtrate was then washed sequentially with water and a solution of sodium hydrogen carbonate, dried ($MgSO_4$), and solvent removed *in vacuo*. Purification using chromatography on a silica column, and dichloromethane as the eluting solvent, afforded the product as a white solid (95 mg), 100%). m.p. 184-187°C (decomp). (Found: C, 30.8; H, 1.9. $C_6H_4O_2S_4$ requires, C, 30.5; H, 1.7%); m/z (EI) 236 (M^+); δ_H ($CDCl_3$) 3.46 (4H, s); δ_C ($CDCl_3$) 42.80 (CH_2), 130.6 (C=C), 187.39 (C=O) and 200.85 (C=O); ν_{max} (Nujol)/cm^{-1} 1700 and 1670 (both C=O).

Compound **32**. To a solution of compound **31** (130 mg, 0.55 mmol) in dry toluene (50 mL), ethylene glycol (0.04 mL, 0.66 mmol) and conc sulphuric acid (3 drops) were added. A Dean-Stark apparatus was assembled, and the reaction refluxed with stirring under nitrogen for 2-3 h. The organic phase was washed with a solution of sodium hydrogen carbonate, dried ($MgSO_4$), and solvent removed *in vacuo* to afford compound **32** as a white solid (130 mg, 84%), m.p. 143-145°C. (Found: C, 34.4; H, 2.8. $C_8H_8O_3S_4$ requires C, 34.3; H, 2.9%); m/z (CI) 280 (M^+); δ_H ($CDCl_3$) 4.03 (4H, s) and 2.75 (4H, s); ν_{max} (Nujol)/cm^{-1} 1670 (C=O).

Compound **33**. Compound **32** (0.75 g, 2.68 mmol) was placed in triethylphosphite (8 mL) and the mixture heated slowly upon which dissolution occurred. The reaction mixture was refluxed with stirring under nitrogen for 2 h. The solution was allowed to cool and methanol added. The precipitated solid was filtered off and purified by chromatography on a silica column with dichloromethane as the eluting solvent to afford compound **33** as a yellow solid (465 mg, 66%), m.p. > 230°C. (Found: C, 36.0; H, 2.9. $C_{16}H_{16}O_4S_8$ requires C, 36.3; H, 3.1); m/z (DCl) 529 (M^++1); δ_H ($CDCl_3$) 3.93 (8H, s) and 2.53 (8H, s).

Compound **34**. A solution of compound **33** (100 mg, 0.19 mmol) in THF (75 mL) was acidified with conc sulphuric acid (10 mL) and the reaction mixture refluxed with stirring under nitrogen for 16 h. The solution was allowed to cool and the precipitated solid filtered and washed with methanol to afford compound **34** as an orange solid (75 mg, 87%); m.p. >340°C (Found: C, 32.5; H, 1.7. $C_{12}H_8O_2S_8$ requires C, 32.7; H, 1.8%); m/z (DCl) 441 (M^++1), δ_H [$(CD_3)_2SO$] 3.46 (8H, s); ν_{max} (Nujol)/cm^{-1} 1705 (C=O).

Compounds **36-39**. General Procedure. A mixture of compound **32** (1 mol equiv) and either ketone **19** or **20** (1 mol equiv) or thione **21** or **22** (3 mol equiv) were refluxed in triethylphosphite (*ca* 5 mL) with stirring under nitrogen for 2 h. The solution was cooled to 20°C and dichloromethane was added. The organic phase was separated, washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. The residue was chromatographed on a silica column; initially the eluent was hexane/dichloromethane (3:1 v/v) which was gradually changed to hexane/ dichloromethane (1:1 v/v) to afford the required products. There was obtained:

Compound **36** [from compound **32** (300 mg, 1.07 mmol) and compound **19** (225 mg, 1.07 mmol)] an orange solid (90 mg, 18%), m.p. 152-154°C. (Found: C, 34.0; H, 3.2. $C_{13}H_{14}O_2S_8$ requires C, 34.0; H, 3.1%); m/z (DCl) 459 (M^++1); δ_H ($CDCl_3$) 4.06 (4H, s), 2.72 (4H, s) and 2.41 (6H, s).

Compound **37** [from compound **32** (400 mg, 1.43 mmol) and compound **20** (300 mg, 1.44 mmol)] an orange solid (165 mg, 25%), m.p. 226-228°C (Found: C, 34.0; H, 2.5. $C_{13}H_{12}O_2S_8$ requires C, 34.2; H, 2.6); m/z (DCl) 457 (M^++1); δ_H ($CDCl_3$) 4.07 (4H, s), 3.29 (4H, s) and 2.72 (4H, s).

Compound **38** [from compound **32** (250 mg, 0.89 mmol) and compound **21** (360 mg, 2.69 mmol)] an orange solid (120 mg, 37%) m.p. 200-203°C. (Found: C, 35.8; H, 2.8. $C_{11}H_{10}O_2S_6$ requires C, 36.0; H, 2.7%); m/z (DCl) 367 (M^++1); δ_H [$(CD_3)_2CO$] 6.66 (2H, s), 4.05 (4H, s) and 2.87 (4H, s).

Compound **39** [from compound **32** (160 mg, 0.57 mmol) and compound **22** (280 mg, 1.73 mmol)] an orange solid (45 mg, 20%) m.p. 218-220°C. (Found: C, 39.4; H, 3.6. $C_{13}H_{14}O_2S_6$ requires C, 39.6; H, 3.6%); m/z (DCl) 395 (M^++1); δ_H ($CDCl_3$) 4.05 (4H, s), 2.70 (4H, s) and 1.93 (6H, s).

Compounds **40-43** - General Procedure. A solution of ketal **36-39** dissolved in THF was acidified with concentrated sulfuric acid and the mixture refluxed with stirring for 16 h. Water was added and the product extracted into dichloromethane. The organic layer was separated, washed with $NaHCO_3$ solution, dried ($MgSO_4$) and the solvent removed *in vacuo*. The products were purified by chromatography on a silica column with hexane / dichloromethane mixtures as the eluting solvent. There was obtained:

Compound **40** [from compound **36** (60 mg, 0.13 mmol) in THF (30 mL) and conc sulfuric acid (4 mL)] as an orange solid (50 mg, 92%) m.p. 175-178°C. (Found: C, 31.9; H, 2.5. $C_{11}H_{10}OS_8$ requires C, 31.9; H, 2.4%) m/z (DCl) 415 (M^++1); δ_H ($CDCl_3$) 3.35 (4H, s) and 2.43 (6H, s); ν_{max} (nujol)/cm^{-1} 1700 (C=O).

Compound **41** [from compound **37** (140 mg, 0.31 mmol) in THF (100 mL) and conc sulfuric acid (10 mL)] a yellow solid, (120 mg, 95%), m.p. 218-220°C. (Found: C, 31.8; H, 1.8. $C_{11}H_8OS_8$ requires C, 32.0; H, 2.0%); m/z (DCl) 413 (M^++1); δ_H ($CDCl_3$) 3.34 (4H, s) and 3.30 (4H, s); ν_{max} (Nujol)/cm^{-1} 1710 (C=O).

Compound **42** [from compound **38** (70 mg, 0.19 mmol) in THF (50 mL) and conc sulfuric acid (5 mL)] as an orange solid (58 mg, 94%) which exhibits two distinct crystalline forms: needles, m.p. 186-187°C (dec) and cubes, m.p. 179-182°C (dec). (Found: C, 33.7; H, 1.7. $C_9H_6OS_6$ requires C, 33.5; H, 1.9%); m/z (DCl) 323 (M^++1); δ_H ($CDCl_3$) 6.35 (2H, s) and 3.34 (4H, s); ν_{max} (Nujol /cm^{-1}) 1700 (C=O).

Compound **43** [from compound **39** (40 mg, 0.10 mmol) in THF (25 mL) and conc sulfuric acid (3 mL)] as a red solid (33 mg, 93%); m.p. 220-222°C (Found: C, 37.8; H, 3.0. $C_{11}H_{10}OS_6$ requires C, 37.7; H, 2.9%); m/z (DCl) 351 (M^++1); δ_H ($CDCl_3$) 3.33 (4H, s) and 1.96 (6H, s).

Compound **44** was obtained from compound **43** (60 mg, 0.17 mmol) in dry THF (60 mL) and lithium aluminium hydride (an excess) as detailed for compound **28**. Purification involved silica column chromatography, eluent dichloromethane, to give the product (55 mg, 90%) as a dark orange solid, m.p. 207-210°C. (Found: m/z (DCl) 353 (M^++1); δ_H ($CDCl_3$) 4.39 (1H, m), 3.48 (1H, broad s), 2.81 (4H, m) and 1.94 (6H, s); ν_{max} (Nujol)/cm^{-1} 3400 (broad, OH).
Compound **45**. Compound **18** (1.0 g, 2 mmol) and compound **32** (0.6 g, 2 mmol) were suspended together in triethylphosphite (10 mL) following the procedure reported for compound **23**. Column chromatography on silica, with dichloromethane / hexane (1:1 v/v) as eluent, cleanly separated compound **45** from the self-coupled products **15** and **33**. Compound **45** was isolated as an orange solid (270 mg, 37%) m.p. >230°C. (Found: C, 49.5; H, 4.4%. $C_{30}H_{32}O_3S_8Si$ requires C, 49.7; H, 4.4%) m/z (EI) 724 (M^+); δ_H ($CDCl_3$) 7.62 (4H, m), 7.41 (6H,m), 4.09 (1H, m), 4.05 (4H, s), 2.70 (6H, m), 2.52 (2H, m) and 1.05 (9H, s).

Crystal Data. Compound **3**: $C_6H_5OS_5$, M = 254.41, triclinic, space group $P\bar{1}$, a = 9.390(6), b = 11.295(6), c = 4.553(4) Å, α = 94.96(7), β = 91.05(6), γ = 78.29(6)°, U = 471.1(6) $Å^3$, Z = 2, D_c = 1.793 g cm^{-3}, F (000) = 260, λ = 0.71069 Å, μ(Mo-Kα) = 11.23 cm^{-1}; R = 0.049; R_w = 0.060.

Crystal Data for Compound **37**: $C_{13}H_{12}O_2S_8$, M = 456.72, monoclinic, space group $P2_1/n$, a = 6.59(1), b =19.865(8), c = 13.947(8) Å, β = 91.68(9), U = 1825(5) $Å^3$, Z = 4, D_c = 1.662 g cm^{-3}, F(000) = 936, λ = 0.71069 Å, μ(Mo-Kα) = 9.44 cm^{-1}; R = 0.058; R_w = 0.063.

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