Pergamon

Tetrahedron 57 (2001) 5015–5026

TETRAHEDRON

Functionalised organosulfur donor molecules: synthesis of racemic hydroxymethyl-, alkoxymethyl- and dialkoxymethyl-bis(ethylenedithio)tetrathiafulvalenes

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Received 27 November 2000; revised 23 March 2001; accepted 12 April 2001

Abstract—Short synthetic routes to racemic derivatives of bis(ethylenedithio)tetrathiafulvalene carrying one hydroxymethyl (HMET), alkoxymethyl or dialkoxymethyl side chain are reported along with cyclic voltammetry measurements and conversion of HMET to (2:1) radical cation salts.

1. Introduction

The discovery of superconductivity in the perrhenate radical cation salt of the organosulfur donor bis(ethylenedithio)-tetrathiafulvalene, ET, **1**[1] has led to the preparation of an enormous range of further radical cation salts[2] as illustrated by over 300 crystal structures now in Cambridge Structural Database. The salts with the complex anions $[Cu\{N(CN)_2\}Br]^-$ and $[Cu(SCN)_2]^-$ have shown the highest temperatures for the onset of the superconducting state.[3,4] The latter two salts adopt a layered crystal structure[3,4] in which the molecules of ET are packed into sheets with their longest molecular axes perpendicular to the sheet, and sandwiched between layers composed of the polymeric complex anions. Indeed, in this and the various other packing arrangements found for radical cation salts of ET, the ethylene bridges of the ET molecules lie adjacent to the anions. Although a good case has been made for there being weak hydrogen bonding between the two species,[5] the lack of a strong directed attraction leads to orientational disorder for symmetrical anions, and may also be responsible for the high degree of polymorphism shown in the radical cation salts with anions such as triiodide and hexafluorophosphate. Indeed, the large organic cation with its highly delocalised positive charge and the much smaller anions, are not ideal partners. We have started a programme to introduce hydrogen bonding functionality into the radical cation salts. This could involve hydrogen bond formation between a hydroxymethyl group for instance and an inorganic anion, but conversely, a suitable hydrogen bond accepting substituent could be used in combination with an anion with hydrogen bonding potential such as hydrogen phosphate. Introduction of a single substituent on one ethylene bridge of ET creates a stereogenic centre, and we have already reported the syntheses of **2**, HMET, the enantiopure derivative carrying a hydroxymethyl side chain,[6] and **3** the derivative carrying a 2-fluoro-1-hydroxyethyl side chain **3**.[7] Both of these materials are prepared by reaction of the dithiolate **4** with cyclic sulfate esters, a class of reagent we introduced for the synthesis of the chiral tetramethyl derivative **5**.[8] We now report a short synthesis of the racemic modification of HMET **2**, and direct routes to its O-alkylated derivatives **6** and **7**. The procedures reported here make these materials readily available to the synthetic metals research community for further studies. The ET derivative with a methoxymethyl group attached to all four carbons of the ethylene bridges, **8**, has also been prepared as one enantiomer using cyclic sulfate ester methodology, but only in very low yield. Furthermore, the syntheses of ET derivatives **9** and **10** which are substituted with acetal containing functionalities, either a dimethoxymethyl or a 2-dioxolanyl group, are described (Scheme 1).

Keywords: organic conductors; bis(ethylenedithio)tetrathiafulvalenes; radical cation salts; synthesis.

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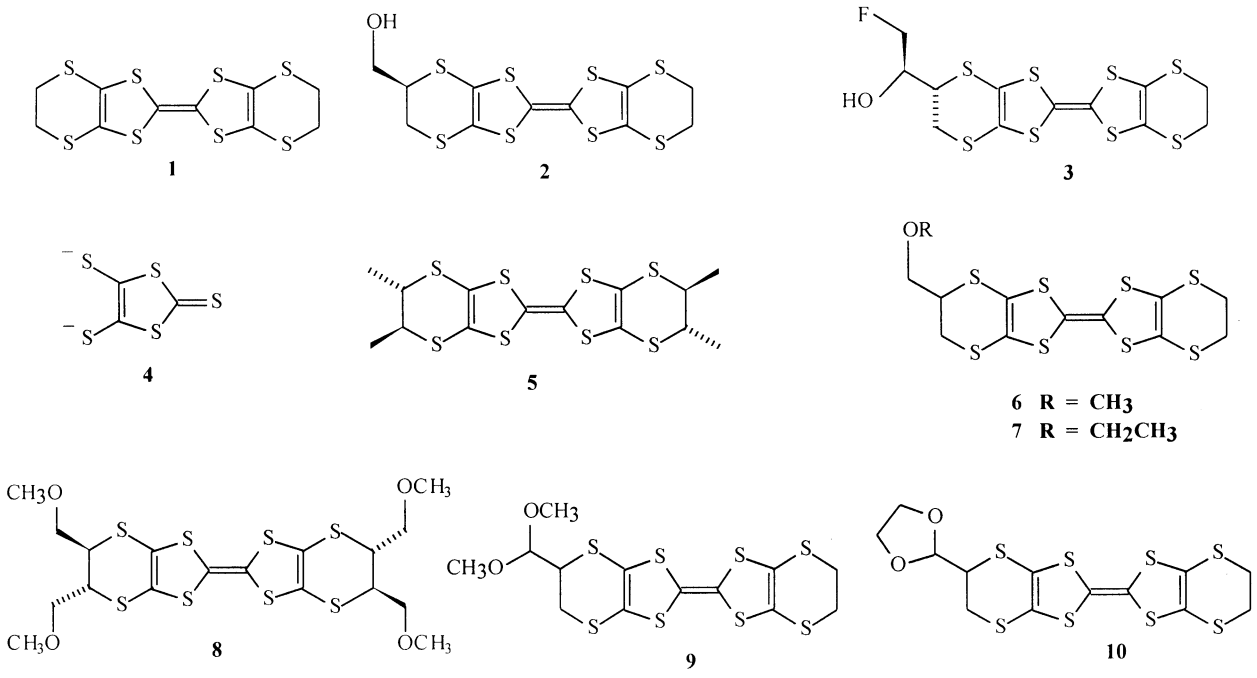
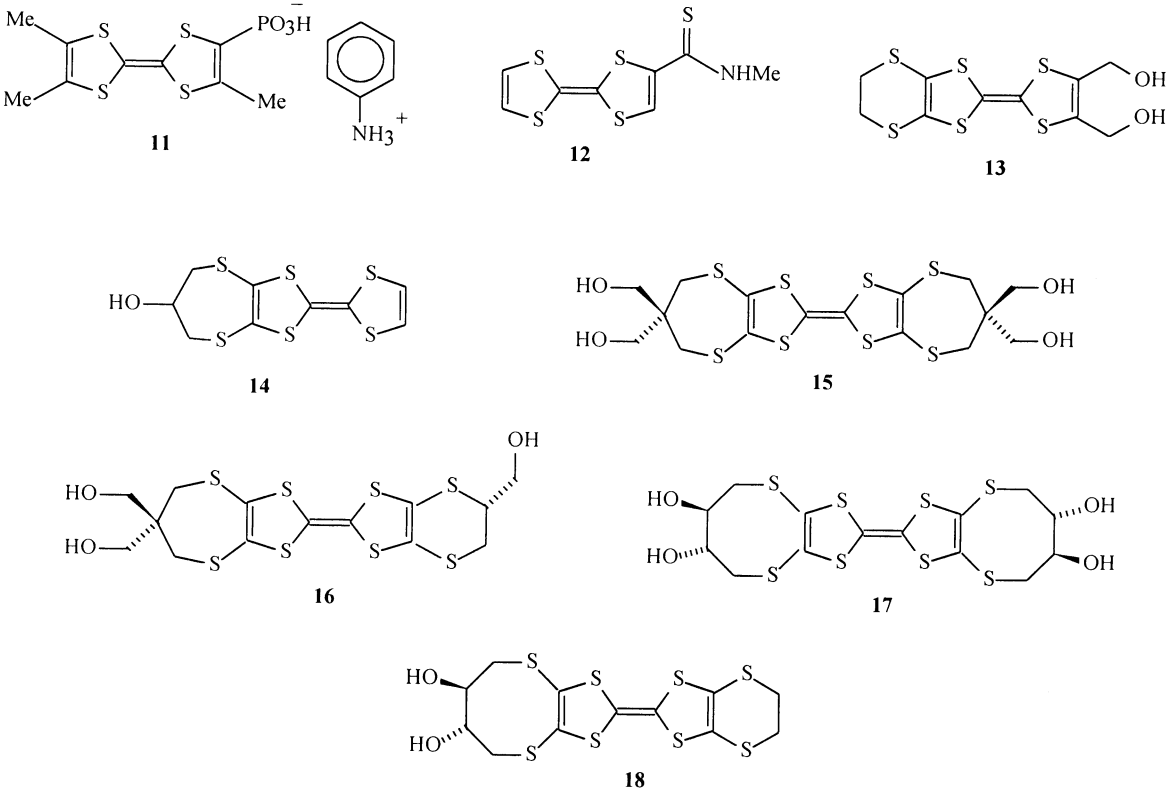
PII: S0040-4020(01)00432-X

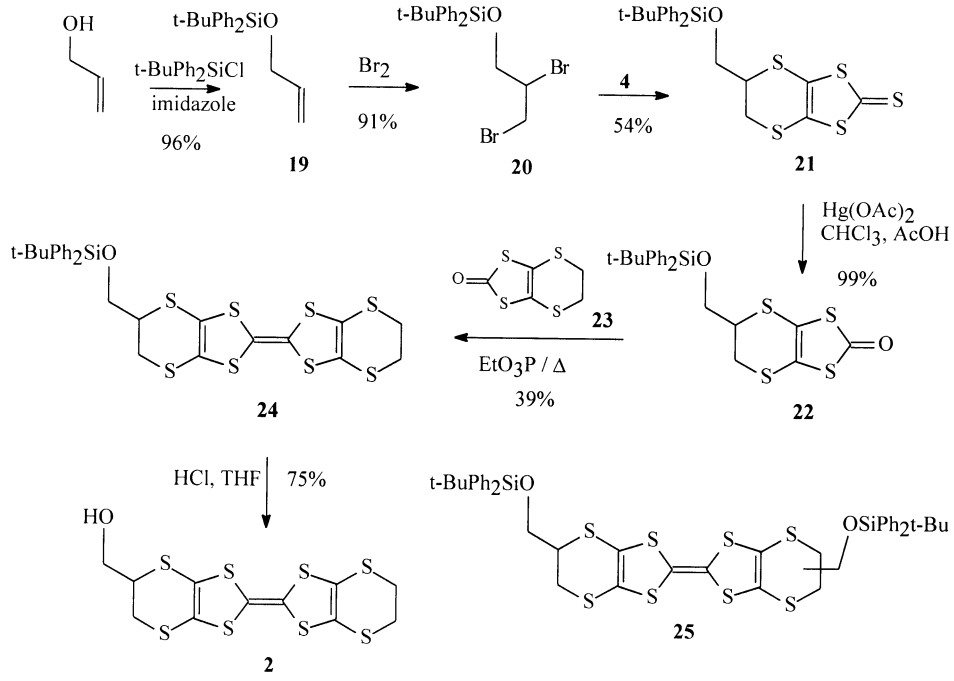


Scheme 1.

Introduction of hydrogen bonding functionality into TTF derivatives has been achieved in several other laboratories using various functional groups, e.g. a hydrogen phosphate group in **11**,[9] a thioamide in **12**[10] and hydroxy functionalities in **13** and **14**,[11,12] though none of these molecules have chiral structures. In our own work we have made TTF derivatives with fused 1,4-dithiepine rings bearing hydroxymethyl side chains such as **15** and **16**[13] and with fused 1,4-dithiocene rings bearing hydroxyl functionalities such as **17** and **18**, the latter three having chiral structures (Scheme 2).[14]



Scheme 2.



Scheme 3.

2. Results and discussion

2.1. Synthesis of the racemic hydroxymethyl derivative of ET 2

The synthesis of racemic **2** started from inexpensive allyl alcohol by protection of its hydroxyl group with a *t*-butyldiphenylsilyl group to give **19**. Subsequent treatment with one equivalent of bromine provided the dibromo compound **20**. Both reactions take place in yields of over 90%. Treatment of **20** with the disodium salt of dithiolate **4**[15,16] in THF at room temperature for 12 h, furnished the bicyclic thione **21** in 54% yield after chromatography. Reaction of the thione **21** with mercuric acetate in chloroform and acetic acid led to replacement of the exocyclic sulfur atom with oxygen to give oxo compound **22** in almost quantitative yield. Cross coupling of oxo compound **22** with the related unsubstituted oxo compound **23** in triethyl phosphite led to the production of a 39% yield of the racemic monosubstituted-ET derivative **24**, after chromatographic separation from unsubstituted ET **1** and disubstituted material **25** (which may be present in up to four diastereoisomeric forms: two racemic and two meso forms), both arising from self coupling reactions of starting materials. Removal of the *t*-butyldiphenylsilyl protecting group by treatment with either tetrabutylammonium fluoride or 20% hydrochloric acid in THF gave racemic **2**. The material is a light orange powder which is sensitive to air oxidation and should be stored under nitrogen (Scheme 3).

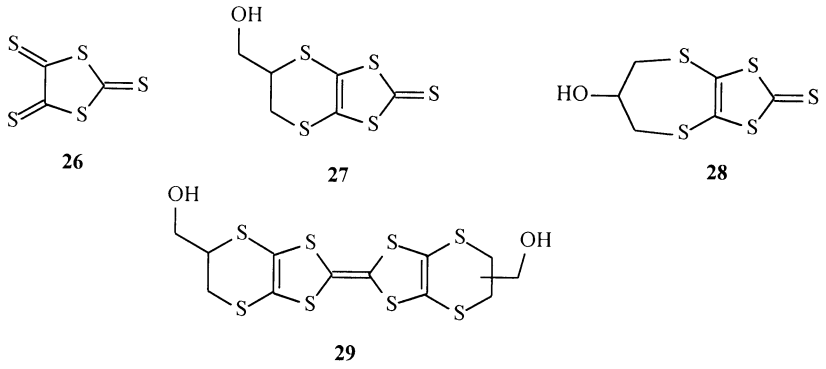
The results of cyclic voltammetric measurements on racemic **2** are given in Table 1 along with data for **1**, **3** and **5** for comparison, and other monosubstituted ET derivatives reported here. The first two oxidation potentials of HMET (0.48 and 0.74 V relative to Ag/AgCl) are similar to those of ET. Electrocrystallisation of **2** in dichloromethane in the presence of various tetrabutylammonium salts (BF_4^-, Cl^-, PF_6^-) produced black microcrystalline radical cation salts. Raman spectra of these compounds showed an absorption, deriving from C=C bond stretchings, in the range 1464–1467 cm^{-1}, typical[17] of ET molecules in radical cation salts of stoichiometry 2:1, and this was supported by chemical analysis data. The Raman spectrum from a 1:1 radical cation salt would show an absorption in the region 1410–1420 cm^{-1}, though the absorption from a 3:2 radical cation salt would be in the same region as that from a 2:1 salt. Further investigations of the electrical and structural properties of the 2:1 radical cation salts of HMET are planned.

Zhang et al. have published very recently their own synthetic route to racemic HMET,[18] which involves cycloaddition of allyl alcohol with the trithione **26**, generated thermally in situ from an oligomer, followed by the same hydroxyl protection strategy as our own. They also

Table 1. Oxidation potentials (V, relative to the AgCl/Ag electrode) measured by cyclic voltammetry

	$E_1^{1/2}$	$E_2^{1/2}$
1[a]	0.44	0.73
(+)-**2**[b]	0.49	0.78
(+/-)-**2**[a]	0.48	0.74
3[b]	0.55	0.82
5[b]	0.56	0.80
6[a]	0.50	0.75
7[a]	0.49	0.74
9[c]	0.41	0.65
10[c]	0.42	0.65

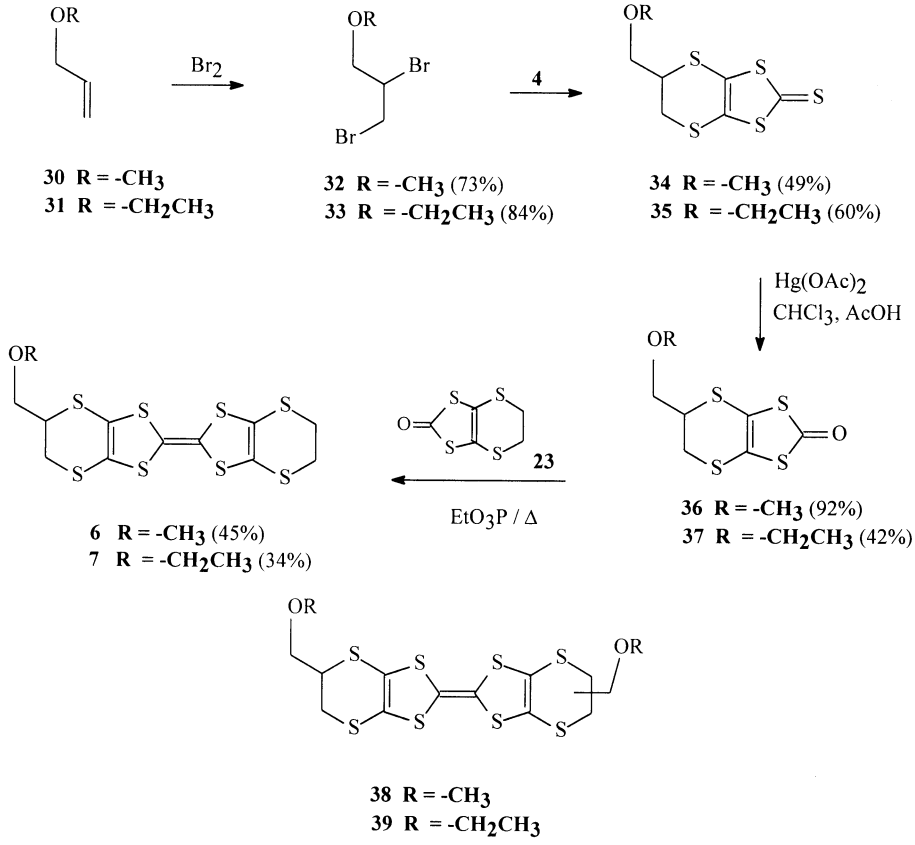
[a] Measured in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate with a scan rate of 20 mV s^{-1}.
[b] Measured in acetonitrile containing 0.02 M tetrabutylammonium hexafluorophosphate with a scan rate of 20 mV s^{-1}.
[c] Measured in acetonitrile containing 0.1 M sodium perchlorate with a scan rate of 100 mV s^{-1}.



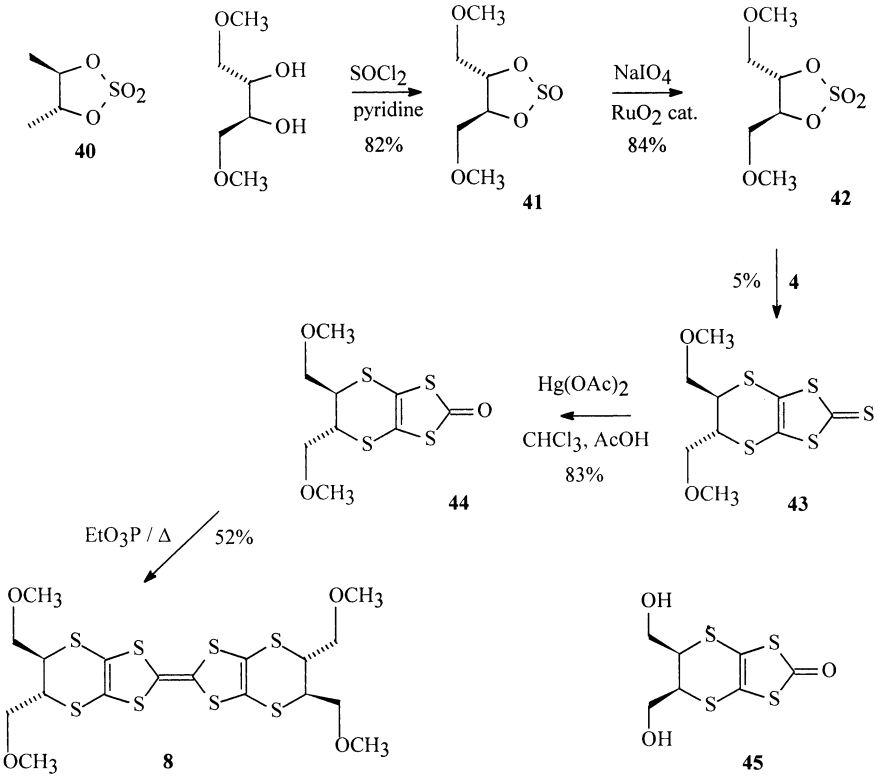
Scheme 4.

report the preparation by electrocrystallisation of a 2:1 radical cation perchlorate salt from HMET. The two synthetic routes are comparable. Their synthesis consists of six steps from the zinc complex of dithiolate **4** and allyl alcohol, has an overall yield of ca 8%, and involves three chromatographic purifications, while our own synthesis from the same starting materials requires an extra step (conversion of the zinc complex to the disodium salt of the dithiolate), has slightly better overall yield, ca 11%, and involves the same number of chromatographic purifications. Either route should be feasible for inter-disciplinary researcher workers in the field of organic metals to accomplish (Scheme 4).

Kumar et al. have reported the synthesis of the racemic hydroxymethyl substituted thione **27**, the unprotected form of **22**, from reaction of the zinc complex of dithiolate **4** with 2,3-dibromopropanol.[19] However, when the disodium salt of **4** was used in basic media rather than the zinc complex, the isomeric thione **28** containing a hydroxy-substituted dihydro-1,4-dithiepine ring was produced. They report the self coupling reaction of thione **27** in triethyl phosphite gives **29**, as a mixture of up to four stereoisomers, though the total yield is only 5%. The need for superconducting materials to have a well-ordered structure suggests that the use of a single diastereoisomer of the organosulfur donor for formation of radical cation salts is preferable, though of course it cannot be ruled out that one stereoisomer from a mixture may preferably form crystalline material. We have made the hydroxymethyl substituted thione **27** in



Scheme 5.



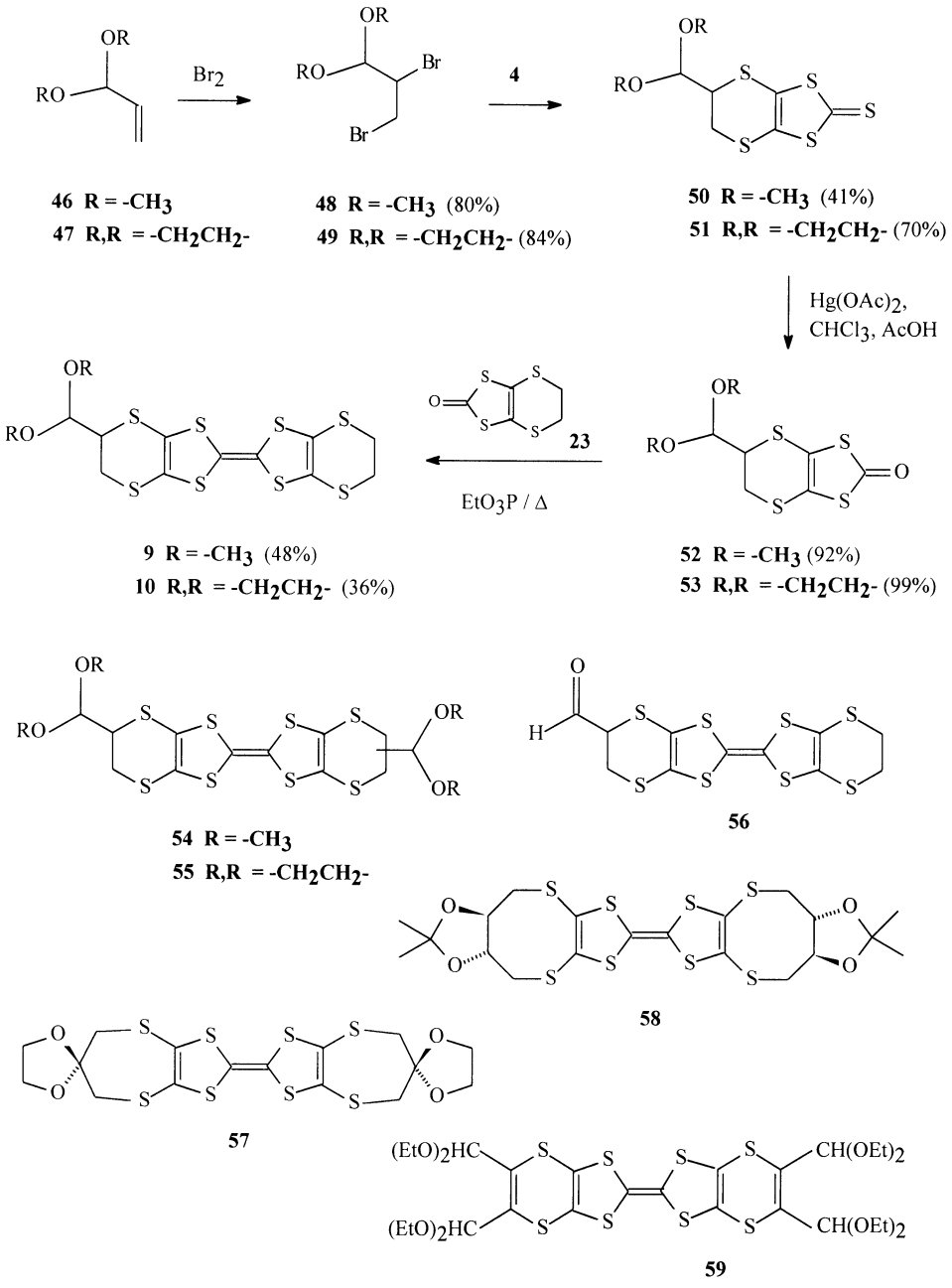
Scheme 6.

the same way, but found separation from unreacted dibromopropanol (which is reported to be carcinogenic) not to be straightforward. For this reason, we preferred to install the protecting group at the start of the synthesis, and remove it after the coupling step.

2.2. Synthesis of alkoxymethyl derivatives of ET 6–8

Although O-alkylated derivatives could in principle be prepared by ether formation from HMET **2**, only five synthetic steps are required if the alkyl group is introduced to allyl alcohol in the first step instead of the *t*-butyldiphenylsilyl protecting group. Thus, 3-methoxypropene **30**, prepared from allyl alcohol, was brominated to give **32**, and then reacted with the zinc complex of dithiolate **4** in acetonitrile to give the thione **34** in 49% yield. Exchange of the thione sulfur atom of **34** for oxygen using mercuric acetate in acetic acid and chloroform gave oxo compound **36** in 92% yield. In the final step oxo compound **36** was coupled with the unsubstituted oxo material **23** to yield the racemic cross-coupled methoxymethyl-ET derivative **6** in 45% yield after chromatography. A later band gave a mixture of stereoisomers of **38** from self coupling of the substituted oxo compound **36**. The racemic ethoxyethyl-ET derivative **7** was prepared from commercially available allyl ethyl ether in just four steps. In this case, 2,3-dibromo-1-ethoxypropane **33** was prepared and reacted with the disodium salt of dithiolate **4** to give the thione **35** in 60% yield. This procedure is preferable to reaction with the zinc complex of dithiolate **4**, which had been used to prepare **34**, since the reaction is cleaner and gives a better yield. Exchange of the thione sulfur atom in **35** for oxygen gave oxo compound **37**, which was coupled with the unsubstituted oxo material **23** to give the ethoxymethyl-ET **7** in 34% yield along with self coupled materials **1** and **39**. The oxidation potentials for donors **6** and **7** have similar values to those of HMET **2** (Scheme 5).

Tetrasubstituted derivatives of ET are attractive targets since they offer the potential for interaction with anions at either 'end' of the molecule, however, their syntheses are more problematic, requiring two substitution reactions at secondary carbon atoms. Interestingly, the racemic forms of these materials, e.g. the tetramethyl derivative **5**, can only be prepared by preparation of both enantiomers separately and then making a 1:1 mixture. It is a rare case of the enantiomer being easier to synthesize than the racemate! Synthesis of enantiomerically pure tetramethyl-ET **5** involves reaction of the cyclic sulfate ester **40** with the disodium salt of dithiolate **4** to give a reasonable yield (30%) of the bicyclic thione, and is completed by self coupling in triethyl phosphite.[20] However, when the size of substituents on the cyclic sulfate ester is increased smaller yields are obtained in the cyclisation step. The cyclic sulfate ester **42** which has two chirally disposed methoxymethyl substituents was prepared from the corresponding enantiopure diol[21] by conversion to the cyclic sulfite ester **41** with thionyl chloride and pyridine and subsequent oxidation with sodium periodate and a catalytic amount of ruthenium(IV) oxide.[6] However, reaction of this cyclic sulfate ester with the disodium salt of dithiolate **4** gave only ca 5% of thione **43**. Nevertheless, this could be converted to the tetramethoxymethyl-ET derivative **8** by exchange of thione sulfur for oxygen to give **44** and then self coupling in triethyl phosphite. With larger substituents on the cyclic sulfate ester e.g. with two benzyloxymethyl

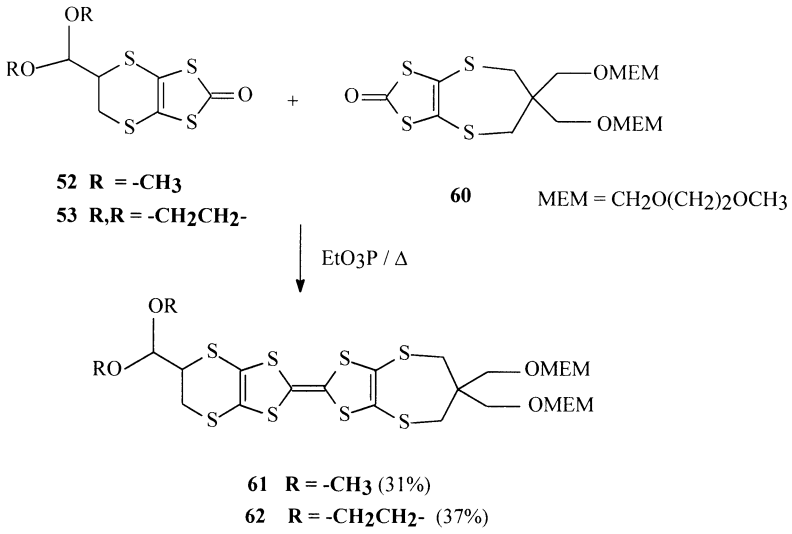


Scheme 7.

groups, the reaction with dithiolate **4** failed completely. Other workers have reported the synthesis of the *cis* di-(hydroxymethyl) thione **45**, and its conversion to an unseparated mixture of two stereoisomers of the tetrakis-(hydroxymethyl) derivative of ET (Scheme 6).[22]

2.3. Synthesis of dialkoxymethyl derivatives of ET 9–10

With a view to preparing the ET derivative substituted with an aldehyde group, **56**, we have prepared the corresponding acetals **9** and **10** by cross coupling methodologies. Thus, the dimethyl acetal and ethylene acetal of acrolein **46** and **47** were brominated to give **48** and **49**, and these were reacted with the disodium salt of the dithiolate **4** to give the thiones **50** and **51** in 41 and 70% yields, respectively. Both acetal groups are diastereotopic, due to their attachment to stereogenic centres. Thus in the ^{13}C NMR spectrum there are small differences between the two methoxy carbon resonances (δ: 55.4 and 54.7) and between the two carbon resonances of the ethylene group (δ: 65.8 and 65.6). Exchange of the thiocarbonyl sulfur atom for oxygen in the usual way gave the oxo compounds **52** and **53** in yields of over 90%. Finally, cross coupling of each compound with the unsubstituted oxo compound **23** gave the monosubstituted ET derivatives **9** and **10** in reasonable yields (48 and 36%), along with ET and the disubstituted materials **54** and **55** as mixtures of diastereoisomers. Attempts to convert the acetal groups in the organosulfur donors **9** and **10** to the aldehyde **56** have been unsuccessful to date. For example, treatment with 20% hydrochloric acid and THF at room temperature did not hydrolyse the acetal, though under more vigorous conditions the substrate was consumed.



Scheme 8.

The hydrolysis of ketals in related organosulfur donors has been difficult, thus bis-ketal **57**[23] required refluxing in 15% sulphuric acid in THF, and **58** could not be cleanly deprotected.[14] The cyclic voltammograms of the derivatives **9** and **10** show two oxidation peaks, with $E^{1/2}$ values typical of ET derivatives (Table 1). Several related organosulfur donors containing vinyl aldehyde groups[24] and the tetraacetal **59** have been reported (Scheme 7).[25]

Since these synthetic routes to ET derivatives make the central double bond at the end of the synthesis, access to an increasing range of monosubstituted oxo compounds such as **36**, **37**, **52**, and **53** opens up access to further unsymmetrically substituted organosulfur donors, providing that the second component in the synthesis has a C_2 axis, for example an enantiopure *trans* disubstituted 1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-one or a 6,6-disubstituted 1,3-dithiolo-[4,5-*b*]1,4-dithiepin-2-one such as **60**. Thus, cross coupling of **52** or **53** with **60** yielded **61** and **62** after separation from self coupled products (Scheme 8).

3. Conclusions

A series of monosubstituted derivatives of ET have been prepared by short synthetic routes, and the intermediate oxo compounds prepared in the course of this work are now available for cross coupling reactions with other dithiolones to prepare further novel donors. Further studies to prepare and investigate the radical cation salts of the donors described here are to be undertaken. The availability of HMET **2** now provides a molecule with a side arm for linking the ET moiety to other systems, or alternatively the ET moiety can be built up from an appropriately substituted allyl ether, and opens many possibilities. If more than one molecule of HMET is to be attached to another molecular species, the use of the single enantiomer form will avoid the formation of more than one diastereoisomer of product. Since HMET is available now in both enantiopure[6] and racemic forms, there is an opportunity for investigations of the effects of a chiral environment on the electrical properties of the corresponding radical cation salts.

4. Experimental

4.1. General

NMR spectra were measured on a JEOL GX 270 machine at 270 MHz for ^{1}H and at 67.8 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard, and measured in ppm. downfield from TMS, unless otherwise stated. Coupling constants (*J*) are given in Hz. IR spectra were recorded on a ATI Mattson Genesis Series FTIR machine as liquid films or nujol mulls. Reflective Raman spectra were measured with a Renishaw System 1000 Ramascope using a He–Ne laser (λ=632.8 nm) with 10 μm slits and ×50 objective lens. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre. Flash chromatography was performed on 40–63 silica gel (Merck). Cyclic voltammograms were measured with a PAR 263/273 electrochemical system using a platinum foil anode (ca 2 cm^2) and over the range 20–1000 mV; measurements were made on acetonitrile solutions (0.1 mM), using tetra *n*-butylammonium perchlorate (0.1 M) or tetra *n*-butylammonium hexafluorophosphate (0.1 M, unless indicated otherwise) under an atmosphere of nitrogen, using a Ag/AgCl reference electrode. 3-Methoxypropene was prepared by a literature method.[26]

4.1.1. 3-(*t*-Butyldiphenylsilyloxy)prop-1-ene, 19. To a solution of allyl alcohol (0.52 g, 9.0 mmol) in dry DMF (20 ml) was added sequentially imidazole (6.80 g, 100 mmol) and *t*-butyldiphenylsilyl chloride (2.75 g, 10 mmol). After stirring at room temperature for 20 h, water (90 ml) and dichloromethane (40 ml) were added, the dichloromethane layer separated, and the aqueous layer extracted twice more with dichloromethane (2×40 ml). The combined organic solution was washed sequentially with ice-cold HCl (3 M, 3(50 ml) and water (50 ml) and dried over $MgSO_4$. Removal of the solvent

under reduced pressure afforded the silylated product **19** (2.60 g, 96%) as a colourless oil: δ_H: 7.65 (4H, m, Ar-H_4), 7.38 (6H, m, Ar-H_6), 5.91 (1H, ddt, J=17.0, 10.4, 4.3 Hz, 2-*H*), 5.38 (1H, ddt, J=17.0, 1.9, 1.9 Hz, 1-*H* (*trans* to 2-H)), 5.11 (1H, ddt, J=10.4, 1.9, 1.9 Hz, 1-*H* (*cis* to 2-H)), 4.20 (2H, m, 3-H_2), 1.07 (9H, s, 3×CH_3); δ_C: 136.9, 135.5, 129.6 and 127.6 (Ar-C_{12}), 133.6 (2-*C*), 113.8 (1-*C*), 64.6 (3-*C*), 26.8 (3×*C*H_3), 19.3 (*C*(CH_3)$_3$); ν_{max} (evaporated film): 3470, 3070, 2934, 1590, 1468, 1428, 1112, 822 cm^{-1}; found C, 77.4; H, 8.4%, $C_{19}H_{24}OSi$ requires C, 77.0; H, 8.2%; *m/z* (CI): 314 ([M+NH_3+H]$^+$, 65), 297 ([M+H]$^+$, 100), 239 (M−C(CH_3)$_3$, 19%); HRMS: (CI) found [M+H]$^+$ 297.1684, [$C_{19}H_{24}OSi$+H]$^+$ requires 297.1675.

4.2. General method for brominations

To a stirred solution of the alkene in chloroform (ca 1 M) maintained at 0°C was added slowly, dropwise, a solution of bromine (1 equiv.) in chloroform (ca 1 M). The resultant mixture was stirred for a further 30 min at that temperature, after which time it was allowed to warm to room temperature and stirred for a further 3 h. The solution was washed twice with aqueous sodium thiosulfate solution and twice with water, dried over $MgSO_4$, and the solvent removed in vacuo to afford the product.

4.2.1. 3-(*t*-Butyldiphenylsilyloxy)-1,2-dibromopropane, 20. Colourless oil (9.81 g, 91%), δ_H: 7.68 (4H, m, Ar-H_4), 7.39 (6H, m, Ar-H_6), 4.20 (1H, m, 2-*H*), 4.09 (1H, dd, J=11.3, 3.8 Hz, 3-H_α), 4.00–3.91 (2H, m, 3-H_β and 1-H_α), 3.83 (1H, dd, J=10.2, 4.7 Hz, 1-H_β), 1.09 (9H, s, 3×CH_3); δ_C: 135.6, 135.5, 129.8 and 127.8 (Ar-C_{12}), 64.6 (3-*C*), 51.5 (2-*C*), 32.6 (1-*C*), 26.7 (3×*C*H_3), 19.3 (*C*(CH_3)$_3$); ν_{max} (evaporated film): 3070, 2934, 2860, 1468, 1428, 1112, 702 cm^{-1}; found C, 49.9; H, 5.2%, $C_{19}H_{24}Br_2OSi$ requires C, 50.0; H, 5.3%; *HRMS*: (CI) found [M+NH_3+H]$^+$ 472.0307, [$C_{19}H_{24}OSiBr_{2+}NH_{3+}$H]$^+$ requires 472.0307.

4.2.2. 1,2-Dibromo-3-methoxypropane, 32. Slightly yellow liquid (36.3 g, 73%): δ_H: 4.26 (1H, m, 2-*H*), 3.80 (4H, m, 1-,3-H_2), 3.45 (3H, s, CH_3); δ_C: 73.4 (3-*C*), 59.2 (*C*H_3), 48.9 (2-*C*), 32.9 (1-*C*); ν_{max} (neat): 2988, 2930, 2828, 2740, 1452, 1382, 1324, 1260, 1210, 1118, 1016, 958, 922, 876, 668 cm^{-1}.

4.2.3. 1,2-Dibromo-3-ethoxypropane, 33. Colourless liquid (11.94 g, 84%): δ_H: 4.18 (1H, m, 2-*H*), 3.76 (4H, m, 1-, 3-H_2), 3.52 (2H, q, J=7.0 Hz, CH_2CH$_3$), 1.16 (3H, t, J=7.0 Hz, CH_3); δ_C: 71.4 (3-*C*), 66.7 (*C*H_2CH$_3$), 49.4 (2-*C*), 33.4 (1-*C*), 15.0 (*C*H_3); ν_{max} (evaporated film): 2976, 2872, 1444, 1378, 1356, 1260, 1232, 1124 and 988 cm^{-1}.

4.2.4. 1,2-Dibromo-3,3-dimethoxypropane, 48. Addition of bromine at −70°C, then by the general method to give **48** as a colourless oil (18.0 g, 80%) bp 70–71°C, 0.1 mmHg. δ_H: 4.54 (1H, d, J=4.4 Hz, 3-*H*), 4.21 (1H, m, 2-*H*), 3.79 (2H, m, 1-H_2), 3.50 and 3.48 (6H, 2×s, 2×OCH_3); δ_C: 103.7 (3-*C*), 55.8 and 55.5 (2×O*C*H_3), 51.3 (2-*C*), 33.1 (1-*C*); ν_{max}: 2992, 2934, 2832, 1446, 1357, 1311, 1239, 1196, 1114, 1066, 966, 876, 575, 476 cm^{-1}.

4.2.5. 2-(1′-,2′-Dibromoethyl)-1,3-dioxolane, 49. Addition of bromine at −70°C then by the general method to give **49** as a colourless liquid (11.0 g, 84%) bp 88°C. δ_H: 5.22 (1H, d, J=6.4 Hz, 2-*H*), 4.26 (1H, ddd, J=7.7, 6.4, 2.9 Hz, 1′-*H*), 4.11 (2H, m, 4α-,5α-*H*), 3.99 (2H, m, 4β-,5β-*H*), 3.79 (2H, m, 2′-H_2); δ_C: 101.8 (2-*C*), 65.9 and 65.8 (4-,5-*C*), 52.7 (1′-*C*), 31.5 (2′-*C*); ν_{max}: 2963, 2887, 1472, 1425, 1378, 1279, 1230, 1154, 1121, 1066, 1033, 947, 911, 882, 732, 606 cm^{-1}; HRMS: (EI) found [M−H]$^+$ 256.8811, $C_5H_7O_2Br_2$ requires 256.8813.

4.3. General method for preparation of substituted 5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-thiones

To a stirred solution of the disodium salt of dithiolate **4**[15,16] in dry THF (ca 0.5 M) under nitrogen at 0°C was added a solution of the dibromo compound (1 equiv.) in THF (ca 0.5 M) at room temperature. After stirring for 12 h, the solvent was removed under reduced pressure and the residue was extracted with dichloromethane, washed three times with water, dried over $MgSO_4$ and concentrated in vacuo and purified.

4.3.1. 5-(*t*-Butyldiphenylsilyloxy)methyl-5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-thione, 21. Purification by flash chromatography (hexane/ethyl acetate (10:1)) afforded **21** (4.97 g, 54%) as a yellow solid; mp 100–102°C. δ_H: 7.66 (4H, m, Ar-H_4), 7.37 (6H, m, Ar-H_6), 3.98–3.75 (3H, 2×m, CH_2OSiR_3 and 5-*H*), 3.31 (1H, dd, J=13.5, 5.8 Hz, 6-H_α), 3.19 (1H, dd, J=13.5, 2.8 Hz, 6-H_β), 1.08 (9H, s, 3×CH_3); δ_C: 207.1 (*C*=S), 135.3, 132.3, 129.9 and 127.7 (Ar-C_{12}), 123.7 and 121.9 (3a-, 7a-*C*), 64.6 (*C*H_2OSiR_3), 45.1 (5-*C*), 31.1 (6-*C*), 26.7 (3×*C*H_3), 19.1 (*C*(CH_3)$_3$); ν_{max}: 1109, 1062, 1025, 893, 821, 737, 704, 604 cm^{-1}; *m/z*: (CI) 493 ([M+H]$^+$, 20), 492 (M$^+$, 20), 435 (65), 239 (35), 161 (100), 117 (43), 105 (29), 77 (25%); HRMS: (CI) found [M+H]+493.0278, [$C_{22}H_{24}OS_5Si$+H]$^+$ requires 493.0278.

4.3.2. 5,6-Dihydro-5-ethoxymethyl-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-thione, 35. Purification by flash chromatography (ethyl acetate) afforded **35** as a reddish brown oil (340 mg, 60%): δ_H: 3.81 (1H, m, 5-*H*), 3.78 (2H, m, CH_2OEt), 3.57 (2H, m, OCH_2CH$_3$), 3.33 (2H, m, 6-H_2), 1.21 (3H, t, CH_3); δ_C: 208.0 (*C*=S), 123.7 and 122.3 (3a-, 7a-*C*), 71.3 (*C*H_2OEt), 67.2 (O*C*H_2Me), 43.0 (5-*C*), 31.6 (6-*C*), 15.0 (*C*H_3); *m/z* (CI): 283 ([M+H]$^+$, 100), 282 (M$^+$, 10), 196 (30), 85 (25), 29 (10%); HRMS: (CI) found M$^+$ 281.9335, $C_8H_{10}OS_5$ requires 281.9335.

4.3.3. 5,6-Dihydro-5-dimethoxymethyl-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-thione, 50. Purification by flash chromatography (hexane/dichloromethane 1:1) gave **50** (2.10 g, 41%) as a yellow solid, mp 73°C. δ_H: 4.52 (1H, d, J=7.7 Hz, C*H*(OMe)$_2$), 3.89 (1H, dt, J=7.7, 5.2 Hz, 5-*H*), 3.47 and 3.45 (6H, 2×s, 2×OCH_3), 3.25 (2H, d, J=5.2 Hz, 6-H_2); δ_C: 208.1 (*C*=S), 125.8 and 122.9 (3a-,7a-*C*), 104.4 (C*H*(OMe)$_2$), 55.4 and 54.7 (2×O*C*H_3), 47.6 (5-*C*), 31.0 (6-*C*); $\nu_{max.}$: 1228, 1182, 1113, 1066, 973, 879, 721 cm^{-1}; found C: 31.8, H: 3.4%. $C_8H_{10}O_2S_5$ requires C: 32.2, H: 3.4%.

4.3.4. 5,6-Dihydro-5-(1′-,3′-dioxolan-2′-yl)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-thione, 51. Residual dibromo compound **49** was distilled off by heating in vacuo. Chromatography of the residue (hexane/dichloromethane 5:1) gave **51** (2.01 g,

70%) as a yellow solid, mp 98–100°C. δ_H: 5.16 (1H, d, J=5.8 Hz, 2′-*H*), 4.01 (4H, m, 4′-,5′-H_2), 3.79 (1H, m, 5-*H*), 3.28 (2H, m, 6-H_2); δ_C: 208.0 (*C*=S), 125.7 and 123.5 (3a-,7a-*C*), 103.4 (2′-C), 65.8 and 65.6 (4′-,5′-*C*), 48.8 (5-*C*), 30.8 (6-*C*); ν_{max}: 1225, 1129, 1066, 1036, 1007, 973, 939, 892, 865, 800, 722 cm^{-1}; found C: 32.0, H: 2.8%. $C_8H_8O_2S_5$ requires C: 32.4, H: 2.7%; HRMS: (EI) found M^+ 295.9117. $C_8H_8O_2S_5$ requires 295.9128.

4.3.5. Preparation of 5-(methoxymethyl)-5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-thione, 34. The tetraethylammonium salt of the zinc complex of dithiolate **4**[15] (48.1 g, 0.067 mol) and **32** (23.1 g, 0.1 mol) were stirred together in acetonitrile (1 l) under nitrogen and warmed in an oil bath at 70°C for three days. The mixture was heated to reflux for a further day. The solvent was removed in vacuo, and the residue treated with dichloromethane (300 ml) and filtered to remove salts. After evaporation of solvent, the residue was subjected to Kugelrohr distillation (70°C, 0.02 mmHg) to remove residual **32**. The residue was washed thoroughly with chloroform (5×100 ml) and the washings decanted from an oily phase and combined. After evaporation of the solvent, the residue was purified by flash chromatography (hexane/dichloromethane (2:3)). Three main fractions containing the desired product were collected. The first contained a trace of **32** which was removed by trituration with hexane, the second was pure by TLC, and the third fraction required further chromatography (hexane/ether (1:1)). The combined purified fractions of **34** (13.1 g, 49%) were obtained as a yellow powder, mp 43°C: δ_H: 3.89 (1H, m, 5-*H*), 3.76 (1H, dd, J=9.6, 8.1 Hz, CH_αOMe), 3.58 (1H, dd, J=9.6, 5.9 Hz, CH_βOMe), 3.41 (3H, s, CH_3), 3.31 (2H, d, J=4.8 Hz, 6-H_2); δ_C: 207.6 (2-*C*), 123.6 and 122.1 (3a-,7a-*C*), 73.2 (*C*H_2OMe), 59.2 (*C*H_3), 42.6 (5-*C*), 31.4 (6-*C*); ν_{max}: 1308, 1178, 1112, 1072, 962, 878, 784, 723 cm^{-1}; found C, 31.3; H, 2.8%. $C_7H_8OS_5$ requires C, 31.3; H, 3.0%; *m*/*z*: (EI) 268 (M^+, 75), 196 (15%).

4.3.6. General method for preparation of substituted 5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-ones. To a solution of the thione in chloroform (ca 0.1 M) was added glacial acetic acid (2 ml per 10 ml $CHCl_3$) followed by mercuric acetate (2.5 equiv.) and the reaction mixture was stirred at room temperature for 2 h during which the solution lightened in colour and a white precipitate was obtained. The mixture was filtered, and the filtrate washed sequentially with water, three times with aqueous $NaHCO_3$ and again with water (50 ml) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure.

4.3.7. 5-(*t*-Butyldiphenylsilyloxy)methyl-5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-one, 22. Purification by flash chromatography (hexane/ethyl acetate (10:1)) afforded the product **22** as a pale yellow oil (3.81 g, 99%): δ_H: 7.67 (4H, m, Ar-H_4), 7.39 (6H, m, Ar-H_6), 3.99 (1H, dd, J=12.1, 9.9 Hz, *C*H_αOSiR$_3$), 3.83 (1H, m, 5-*H*),3.82 (1H, dd, J=12.1, 5.7 Hz, CH_βOSiR$_3$), 3.32 (1H, dd, J=13.3, 5.5 Hz, 6-H_α), 3.23 (1H, dd, J=13.3, 3.2 Hz, 6-H_β), 1.07 (9H, s, 3×CH_3); δ_C: 188.7 (*C*=O), 135.5, 132.7, 130.0 and 127.9 (Ar-C_{12}), 114.4 and 112.7 (3a-, 7a-*C*), 64.9 (*C*H_2OSiR$_3$), 47.1 (5-*C*), 32.3 (6-*C*), 26.8 (3×*C*H_3), 19.3 (*C*(CH$_3$)$_3$); ν_{max} (evaporated film): 2958, 2858, 1678, 1590, 1468, 1262, 1112, 868 and 704 cm^{-1}; HRMS: (CI) found $[M+NH_3+H]^+$ 494.0772, $[C_{22}H_{24}O_2S_4Si+NH_{3+}H]^+$ requires 494.0772.

4.3.8. 5-Methoxymethyl-5,6-dihydro-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-one, 36. Evaporation gave the oxo compound **36** as an oil which slowly solidified (3.90 g, 92%), mp 34°C, δ_H: 3.90 (1H, m, 5-*H*), 3.77 (1H, dd, J=9.6, 8.1 Hz, CH_αOMe), 3.57 (1H, dd, J=9.6, 5.9 Hz, CH_βOMe), 3.40 (3H, s, CH_3), 3.32 (2H, m, 6-H_2); δ_C: 188.5 (*C*=O), 114.0 and 112.7 (3a-,7a-*C*), 73.3 (*C*H_2OMe), 59.1 (*C*H_3), 44.3 (5-*C*), 32.4 (6-*C*); found C, 33.1; H, 3.0%. $C_7H_8O_2S_4$ requires C, 33.3; H, 3.2%.

4.3.9. 5,6-Dihydro-5-ethoxymethyl-1,3-dithiolo[4,5-*b*]1,4-dithiin-2-one, 37. Purification by flash chromatography (hexane/ethyl acetate 4:1) afforded **37** (0.90 g, 42%) as a pale yellow oil: δ_H: 3.91 (1H, m, 5-*H*), 3.79 (1H, dd, J=9.6, 8.5 Hz, CH_αOEt), 3.61 (1H, dd, J=9.6, 5.7 Hz, CH_βOEt), 3.55 (2H, apparent dq, *AB*X$_3$ system from OCH_2Me), 3.33 (2H, m, 6-H_2), 1.21 (3H, t, J=6.9 Hz, CH_3); δ_C: 188.7 (*C*=O), 114.2 and 112.7 (3a-, 7a-*C*), 71.3 (*C*H_2OEt), 67.0 (O*C*H_2CH$_3$), 44.6 (5-*C*), 32.5 (6-*C*), 15.0 (*C*H$_3$); ν_{max} (evaporated film): 2974, 1674, 1500, 1412, 1376, 1294, 1110, 890, 766 cm^{-1}; found C, 36.3; H, 3.7% $C_8H_{10}S_4O_2$ requires C, 36.1; H, 3.8%; *m*/*z* (CI): 284 ($[M+NH_4]^+$, 50), 266 (M^+, 100%).

4.3.10. 5,6-Dihydro-5-dimethoxymethyl-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-one, 52. Purification by flash chromatography (hexane/ethyl acetate 5:1) gave **52** (1.50 g, 92%) as a pale yellow solid, mp 38–39°C. δ_H: 4.53 (1H, d, J=7.7 Hz, C*H*(OMe)$_2$), 3.94 (1H, dt, J=7.7, 5.3 Hz, 5-*H*), 3.46 and 3.43 (6H, 2×s, 2×OCH_3), 3.25 (2H, d, J=5.3 Hz, 6-H_2); δ_C: 188.5 (*C*=O), 116.1 and 113.3 (3a-,7a-*C*), 104.1 (C*H*(OMe)$_2$), 54.9 and 54.3 (2×O*C*H$_3$), 49.1 (5-*C*), 31.6 (6-*C*); $\nu_{max.}$: 1682, 1623, 1507, 1309, 1227, 1189, 1102, 1081, 1065, 965, 878, 875, 764, 666 cm^{-1}; found C: 33.8, H: 3.6%. $C_8H_{10}O_3S_4$ requires C: 34.0, H: 3.6%.

4.3.11. 5,6-Dihydro-5-(1′-,3′-dioxolan-2′-yl)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-one, 53. Evaporation of solvent gave **53** (1.00 g, 99%) as a pale yellow solid, mp 90–92°C, δ_H: 5.16 (1H, d, J=6.1 Hz, 2′-*H*), 4.00 (4H, m, 4′-,5′-H_2), 3.84 (1H, m, 5-*H*), 3.30 (2H, m, 6-H_2); δ_C: 188.8 (*C*=O), 116.2 and 114.1 (3a-,7a-*C*), 103.4 (2′-C), 65.7 and 65.6 (4-,5′-*C*), 50.5 (5-*C*), 31.6 (6-*C*); $\nu_{max.}$: 1694, 1625, 1500, 1222, 1133, 1032, 1007, 948, 908, 889, 863, 607 cm^{-1}; found C: 34.0, H: 2.9%. $C_8H_8O_3S_4$ requires C: 34.3, H: 2.9%; *m*/*z*: (EI) 280 (M^+, 25), 88 (50), 76 (47), 73 ([1,3-dioxolan-2-yl]$^+$,100%).

4.4. General procedure for preparation of substituted ET derivatives

A mixture of oxo compounds was heated in triethyl phosphite to 80°C under nitrogen for 2 h to give an orange solution. Triethyl phosphite was removed by distillation in vacuo, and the residue was stirred with chloroform for 10 min and filtered to remove ET. The products were separated by chromatography.

4.4.1. 5-(*t*-Butyldiphenylsilyloxy)methyl-5,6-dihydro-2-(5′,6′-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiin-2′-ylidene)-1,3-dithiolo[4,5-*b*]-1,4-dithiin, 24. From an equimolar

mixture of **22** and **23**. Purified by flash chromatography (hexane/ethyl acetate 5:1), collecting the band with R_f 0.52 gave **24** (0.38 g, 39%), as an orange solid, mp 54–56°C. δ_H: 7.62 (4H, m, Ar-*H*$_4$), 7.41 (6H, m, Ar-*H*$_6$), 3.94 (1H, dd, *J*=10.4, 11.8 Hz, C*H*$_\alpha$OSiR$_3$), 3.76 (2H, m, C*H*$_\beta$OSiR$_3$ and 5-*H*), 3.29 (4H, s, 5′-, 6′-*H*$_2$), 3.28 (1H, dd, *J*=13.2, 4.7 Hz, 6-*H*$_\alpha$), 3.18 (1H, dd, *J*=13.2, 3.3 Hz, 6-*H*$_\beta$), 1.06 (9H, s, 3×C*H*$_3$); δ_C: 135.3, 132.6, 129.8 and 127.7 (Ar-*C*$_{12}$), 114.6, 113.6 and 113.2 (3a-,3a′-7a-,7a′-*C*), 111.7 (2a-,2a′-*C*), 64.9 (*C*H$_2$OSiR$_3$), 45.6 (5-*C*), 31.8 (6-*C*), 30.0 (5′- and 6′-*C*), 26.7 (3×*C*H$_3$), 19.1 (*C*(CH$_3$)$_3$); found C, 49.6; H, 4.3%. $C_{27}H_{28}OSiS_8$ requires C, 49.7; H, 4.3%; ν_{max}: 1284, 1106, 1001, 915, 820, 770, 737, 700, 608 cm^{-1}; *m*/*z* (CI): 653 ([M+H]$^+$, 4), 387 (7), 297 ([Ph$_2$SiC(CH$_3$)$_3$-OCH$_2$CH=CH$_2$+H]$^+$, 54), 256 ([Ph$_2$SiC(CH$_3$)$_3$OH]$^+$, 51), 239 (36), 236 (42), 196 (83), 45 (100%).

4.4.2. 5-Methoxymethyl-5,6-dihydro-2-(5′,6′-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiin-2′-ylidene)-1,3-dithiolo[4,5-*b*]-1,4-dithiin, 6. From a 4:3 molar ratio of **23** and **36**. Flash chromatography (hexane/dichloromethane 1:1) gave some ET. Further elution (hexane/dichloromethane 1:2) gave **6** (1.44 g, 45%) as a red oil which solidified on prolonged drying in vacuo, mp 91–92°C: δ_H: 3.79 (1H, m, 5-*H*), 3.69 (1H, dd, *J*=9.5, 8.2 Hz, C*H*$_\alpha$OMe), 3.51 (1H, dd, *J*=9.5, 5.6 Hz, C*H*$_\beta$OMe), 3.38 (3H, s, C*H*$_3$), 3.28 (4H, s, 5′-,6′-*H*$_2$), 3.20 (2H, d, *J*=4.7 Hz, 6-*H*$_2$); δ_C: 114.3, 113.7 and 113.4 (3a-, 3a′-, 7a-, 7a′-*C*), 111.7 and 111.4 (2-, 2′-*C*), 73.5 (*C*H$_2$OMe), 59.1 (*C*H$_3$), 43.0 (5-*C*), 32.1 (6-*C*), 30.1 (5′-, 6′-*C*); ν_{max} (CHCl$_3$ solution): 3002, 2930, 2830, 1412, 1290, 1190, 1114, 960, 914 cm^{-1}; found C, 33.4; H, 2.8%. $C_{12}H_{12}OS_8$ requires C, 33.6; H, 2.8%; *m*/*z* (EI): 428 (M$^+$, 65), 400 (20), 356 (37), 236 (100%). Elution with dichloromethane gave a mixture of stereoisomers of bis(3-methoxypropylene-1,2-dithio)tetrathiafulvalene **38** (0.57 g, 33%), mp 117°C, δ_H: 3.79 (m, C$_2$C*H*S), 3.69(m, C*H*$_\alpha$OMe), 3.51 (m, C*H*$_\beta$OMe), 3.38 (OC*H*$_3$), 3.20 (m, SC*H*$_2$); δ_C: 114.3, 114.2, 113.4, 111.7, 111.7, 111.6 (sp^2 *C*), 73.5 (*C*H$_2$OMe), 59.1 (*C*H$_3$), 43.0 (C$_2$*C*HS), 32.1 (*C*H$_2$S); ν_{max} (CHCl$_3$ solution): 2998, 2932, 2830, 1452, 1410, 1382, 1318, 1206, 1114, 960, 914 cm^{-1}; *m*/*z* (EI): 472 (M$^+$, 30), 400 (25), 236 (38), 208 (100%).

4.4.3. 5-Ethoxymethyl-5,6-dihydro-2-(5′,6′-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiin-2′-ylidene)-1,3-dithiolo[4,5-*b*]-1,4-dithiin, 7. From a 3:2 molar ratio of **23** and **37**. Flash chromatography (hexane/dichloromethane (1:1)) afforded **7** as a brown/red solid (0.27 g, 34%): mp 73–75°C: δ_H: 3.73 (2H, m, 5-*H* and C*H*$_\alpha$OEt), 3.54 (3H, m, OC*H*$_2$Me and 5-C*H*$_\beta$OEt), 3.29 (4H, s, 5′-, 6′-*H*$_2$), 3.20 (2H, m, 6-*H*$_2$), 1.19 (3H, t, *J*=6.3 Hz, C*H*$_3$); δ_C: 114.4, 113.9 and 113.4 (3a-,3a′-,7a-,7a′-*C*), 111.8 and 111.7 (2-, 2′-*C*), 71.5 (*C*H$_2$OEt), 67.0 (OC*H*$_2$Me), 43.3 (5-*C*), 32.3 (6-*C*), 30.2 (5′-, 6′-*C*), 15.1 (*C*H$_3$); ν_{max} (evaporated film): 2970, 2868, 1408, 1374, 1288, 1110, 918, 772 cm^{-1}; found C, 35.2; H, 3.1%, $C_{13}H_{14}S_8O$ requires C, 35.3; H, 3.1%. A further fraction yielded **39** (0.11 g, 24%).

4.4.4. 5,6-Dihydro-5-dimethoxymethyl-2-(5′,6′-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiiin-2′-ylidene)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin, 9. From an equimolar mixture of oxo compounds **23** and **52**. Flash chromatography (hexane/dichloromethane 1:5) eluted some ET first. The second fraction gave the desired cross coupled product **9** (0.12 g, 48%) as a pale orange solid, mp 170°C. δ_H: 4.48 (1H, d, *J*=8.0 Hz, C*H*(OMe)$_2$), 3.80 (1H, m, 5-*H*), 3.46 and 3.42 (6H, 2×s, 2×OC*H*$_3$), 3.29 (4H, s, 5′-,6′-*H*$_2$), 3.14 (2H, m, 6-*H*$_2$); δ_C: 116.6, 114.4 and 113.8 (3a-,3a′-,7a-,7a′-*C*), 112.1 and 111.9 (2-,2′-*C*), 104.9 (*C*H(OMe)$_2$), 55.5 and 54.5 (2×O*C*H$_3$), 47.9 (5-*C*), 31.8 (6-*C*), 30.2 (5′-,6′-*C*); ν_{max}: 1288, 1259, 1183, 1114, 1051, 967, 907, 800, 770 cm^{-1}; found C: 33.6, H: 3.0%. $C_{13}H_{14}O_2S_8$ requires C: 34.0, H: 3.1%; *m*/*z* (EI) 458 (M$^+$, 100), 430 ([M−CH$_2$CH$_2$]$^+$, 25), 356 ([M−CH$_2$CHCH$_2$(OMe)$_2$]$^+$,45). The final band gave a mixture of stereoisomers of bis(3,3-dimethoxypropylene-1,2-dithio)tetrathiafulvalene **54** (0.08 g, 52%) as an orange solid, mp 168°C. δ_H: 4.49 (br. d, C*H*(OMe)$_2$), 3.80 (m, SC*H*C$_2$), 3.45 and 3.42 (2×s, OC*H*$_3$), 3.14 (m, SC*H*$_2$); δ_C: 116.61, 116.56, 114.35, 114.26, 112.24, 112.21 (sp^2-*C*), 104.82 (*C*H(OMe)$_2$), 55.43 and 54.47 (O*C*H$_3$), 47.93 and 47.88 (S-*C*HC$_2$), 31.76 and 31.71 (S*C*H$_2$); ν_{max}: 1303, 1227, 1183, 1146, 1114, 1053, 965, 915, 769 cm^{-1}; HRMS: (EI) found M$^+$ 531.9113, $C_{16}H_{20}O_4S_8$ requires 531.9127.

4.4.5. 5,6-Dihydro-5-(1″,3″-dioxolan-2″-yl)-2-(5′,6′-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiiin-2′-ylidene)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin, 10. From an equimolar mixture of **23** and **53**. Flash chromatography (hexane/dichloromethane 2:1) eluted some ET first. The second fraction gave the desired cross coupled product **10** (0.40 g, 36%) as an orange-yellow solid, mp 128–130°C. δ_H: 5.11 (1H, d, *J*=6.3 Hz, 2″-*H*), 3.97 (4H, m, 4″-,5″-*H*), 3.69 (1H, m, 5-*H*), 3.29 (4H, s, 5′-,6′-*H*$_2$), 3.22 (2H, m, 6-*H*$_2$); δ_C: 116.8, 115.1 and 113.8 (3a-, 3a′-, 7a-, 7a′-*C*), 111.8 (2-,2′-*C*), 103.9 (2″-*C*), 65.7 and 65.5 (4″-,5″-*C*), 49.4 (5-*C*), 31.6 (6-*C*), 30.2 (5′-,6′-*C*); ν_{max}: 1288, 1240, 1123, 1029, 971, 903, 769 cm^{-1}; found C: 34.1, H: 2.8%. $C_{13}H_{12}O_2S_8$ requires C: 34.2, H: 2.7%. The final band gave a mixture of stereoisomers of bis(3-(1,3-dioxolan-2-yl)ethylene-1,2-dithio)tetrathiafulvalene **55** (0.41 g, 30%) as an orange solid, mp 144–146°C. δ_H: 5.10 (d, *J*=6.3 Hz, C*H*O$_2$), 3.97 (m, OC*H*$_2$C*H*$_2$O), 3.68 (m, SC*H*C$_2$), 3.17 m, SC*H*$_2$); δ_C: 116.6 and 115.0 (3a-,3a′-,7a-, 7a′-*C*), 112.2 (2-,2′-*C*), 103.8 (*C*HO$_2$), 65.7 and 65.5 (OC*H*$_2$C*H*$_2$O), 49.3 (S*C*HC$_2$), 31.6 (S*C*H$_2$); ν_{max}: 1125, 1108, 1059, 1024, 977, 938, 908, 771 cm^{-1}; HRMS: (EI) found M$^+$ 527.8797, $C_{16}H_{16}O_4S_8$ requires 527.8814.

4.4.6. 6,6-Di(methoxyethoxymethoxymethyl)-5,6-dihydro-2-(5′-dimethoxymethyl-5′,6′-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiiin-2′-ylidene)-7*H*-1,3-dithiolo[4,5-*b*]-1,4-dithiepine, 61. From an equimolar mixture of **52** and **60**. Flash chromatography (hexane/ethyl acetate 2:1) eluted some ET first. The second fraction gave the cross coupled material **61** (0.12 g, 31%) as an orange solid, mp 88–90°C, δ_H: 4.66 (4H, s, 2×OC*H*$_2$O), 4.45 (1H, d, *J*=8.0 Hz, C*H*(OMe)$_2$), 3.76 (1H, m, 5′-*H*), 3.68 (4H, s, 2×*C*H$_2$OMEM), 3.57 (8H, m, 2×OC*H*$_2$C*H*$_2$O), 3.43 and 3.41 (6H, 2×s, CH(OC*H*$_3$)$_2$), 3.36 (6H, s, 2×OC*H*$_3$), 3.11 (2H, m, 6′-*H*$_2$), 2.72 (4H, s, 5- and 7-*H*$_2$); δ_C: 128.4 (3a-,8a-*C*), 115.5, 114.2 and 113.3 (2′-,3a′-,7a′-*C*), 108.9 (2-*C*), 103.8 (*C*H(OMe)$_2$), 94.7 (2×OCH$_2$O), 70.7 and 65.9 (2×OC*H*$_2$C*H*$_2$O), 68.5 (2×*C*H$_2$OMEM), 58.0 (2×O*C*H$_3$), 54.4 and 53.5 (CH(O*C*H$_3$)$_2$), 46.9 (5′-*C*), 43.2 (5-, 7-*C*), 36.0 (6-*C*), 30.7

(6′-*C*); ν_{max}: 1114, 1061, 1039, 984, 960, 897, 846 cm^{-1}; HRMS: (EI) found M^+ 708.0179, $C_{24}H_{36}O_8S_8$ requires 708.0176.

4.4.7. 6,6-Di(methoxyethoxymethoxymethyl)-5,6-dihydro-2-(5′-(1″3″-dioxolan-2″-yl)-5′,6′-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiiin-2′-ylidene)-7*H*-1,3-dithiolo[4,5-*b*]-1,4-dithiepine, 62. From an equimolar mixture of **53** and **60**. Flash chromatography (hexane/ethyl acetate 2:3) eluted some ET first. The second fraction gave the cross coupled material **62** (0.14 g, 37%) as an orange oil, δ_H: 5.10 (1H, d, *J*=6.3 Hz, 2″-*H*), 4.70 (4H, s, 2×OCH_2O), 4.98 (4H, 2×m, 4″-, 5″-H_2), 3.91 (1H, m, 5′-*H*), 3.71 (4H, s, 2×CH_2OMEM), 3.61 (8H, 2×m, 2×OCH_2CH_2O), 3.37 (6H, s, 2×OCH_3), 3.18 (2H, m, 6′-H_2), 2.75 (4H, s, 5- and 7-H_2); δ_C: 129.3 (3a-,8a-*C*), 116.5, 115.2 and 114.8 (2′-,3a′-, 7a′-*C*), 109.8 (2-*C*), 103.6 (2″-*C*), 95.6 (2×OCH$_2$O), 71.6 and 66.8 (2×OCH_2CH_2O), 69.5 (2×CH_2OMEM), 65.5 and 65.4 (4″-,5″-*C*), 58.9 (2×OCH_3), 49.2 (5′-*C*), 44.1 (5-, 7-*C*), 36.9 (6-*C*), 31.5 (6′-*C*); ν_{max}: 1302, 1250, 1199, 1115, 1041, 974, 898, 848, 752, 664, 544 cm^{-1}; HRMS: (EI) found M^+ 706.0021, $C_{24}H_{34}O_8S_8$ requires 706.0019.

4.4.8. Preparation of 5,6-dihydro-2-(5′,6′-dihydro-1,3-dithiolo[4,5-*b*]-1,4-dithiin-2′-ylidene)-1,3-dithiolo[4,5-*b*]-1,4-dithiin-5-methanol, (±) 2. Hydrochloric acid (18 ml, 20%) was added dropwise to a solution of **24** (0.20 g, 0.31 mmol) in THF (30 ml) under nitrogen and stirred for 24 h. After neutralisation with sodium hydrogen carbonate, the organic phase was separated, dried over Na_2SO_4, and evaporated. The residue was purified by chromatography on silica eluting with dichloromethane to give racemic HMET **2** (0.098 g, 75%) as a light orange solid; mp 151°C (from ethanol): δ_H: 3.74 (3H, m, CH_2OH and 5-*H*), 3.32 (4H, s, 5′-, 6′-H_2), 3.30 (1H, dd, *J*=13.5, 5.0 Hz, 6-H_α), 3.22 (1H, dd, *J*=13.5, 3.4 Hz, 6-H_β), 1.58 (1H, br, s, O*H*); δ_C: 114.5, 113.5, 113.0 (3a-,3a′-,7a-,7a′-*C*), 111.2 and 111.1 (2-,2′-*C*), 63.9 (*C*H_2OH), 45.5 (5-*C*), 31.7 (6-*C*), 30.1 (5′-, 6′-*C*); ν_{max}: 3400, 2860, 1405, 1260, 1020 and 802 cm^{-1}; found C, 32.0; H, 2.6%. $C_{11}H_{10}S_8O$ requires C, 31.9; H, 2.4%; *m*/*z* (CI): 415 ($[M+H]^+$, 40), 385 (48), 207 (100), 151 (75%).

4.4.9. Radical cation salts of HMET, 2_2 BF_4, 2_2Cl, 2_2PF_6. Radical cation salts were prepared by constant current electrocrystallisation of dichloromethane solutions (50 ml) containing **2** (10 mg) and the appropriate tetrabutylammonium salt (100 mg), at a current flow of 1 μA.

$\mathbf{2}_2{\cdot}BF_4$: Raman ν_4: 1464.0 cm^{-1}; found C, 29.1; H, 2.2; S, 56.4; F, 8.1%. $C_{22}H_{20}O_2S_{16}BF_4$ requires C, 28.8; H, 2.2; S, 56.0; F 8.3%.

$\mathbf{2}_2$Cl: Raman ν_4: 1466.7 cm^{-1}; found C, 30.6; H, 2.4; Cl, 4.2%. $C_{22}H_{20}O_2S_{16}Cl$ requires C, 30.6; H, 2.3; Cl, 4.1%

$\mathbf{2}_2PF_6$: IR ν_{max} (KBr) 3436, 2919, 2837, 2355, 1731, 1625, 1414, 1335, 1267, 1173, 1120, 1079, 843, 668, 556 cm^{-1}; Raman ν_3: 1501.9, ν_4: 1464.0, cm^{-1}; found C, 27.6; H, 2.0; F, 11.0%. $C_{22}H_{20}O_2S_{16}PF_6$ requires C, 27.1; H, 2.1; F 11.7%.

4.4.10. Preparation of *4S*,*5S*-5-Di(methoxymethyl)-1,3,2-dioxathiolane-2,2-dioxide, 42. A solution of 4*S*,5*S*-1,4-dimethoxybutan-2,3-diol (1.20 g, 8.0 mmol), prepared by literature procedures,[21] and dry pyridine (1.3 ml) in anhydrous diethyl ether (25 ml) was stirred at 0°C and treated with thionyl chloride (1.00 g, 8.4 mmol). After stirring for 3 h, the mixture was filtered and washed with water (2×30 ml). The organic extracts were dried over Na_2SO_4 and distillation gave 4*S*,5*S*-5-di(methoxymethyl)-1,3,2-dioxathiolane-2-oxide **41** as a colourless oil (1.28 g, 82%), bp 100°C at 0.03 mmHg, δ_H: 4.93 (1H, m, 4-*H*), 4.51 (1H, m, 5-*H*), 3.76 and 3.66 (4H, 2×m, 2×CH_2OMe), 3.45 and 3.41 (6H, 2×s, 2×OCH_3). This product (1.10 g, 4.6 mmol) was dissolved in dichloromethane (30 ml), ruthenium dioxide (20 mg) added, and the mixture vigorously stirrred with a solution of sodium periodate (2.10 g. 9.8 mmol) in water (15 ml). The solution turned from brown to green sharply after 20 min. After a further 5 min the organic layer was collected, stirred with isopropanol (1 ml) for 15 min, dried over Na_2SO_4 and filtered through Celite. After evaporation of solvent, distillation of the residue gave **42** as a colourless oil (1.01 g, 84%), bp 150°C at 0.02 mm Hg, found C: 34.3, H: 6.1%. $C_6H_{12}O_6S$ requires C: 34.0, H: 5.7%. δ_H: 4.92 (2H, m, 4-,5-*H*), 3.71 (4H, m, 2×CH_2OMe), 3.41 (6H, s, 2×OCH_3).

4.4.11. Preparation of 5*R*,6*R*,-5,6-dihydro-5-,6-di-(methoxymethyl)-1,3-dithiolo[4,5-*b*]-1,4-dithiin-2-thione, 43. Cyclic sulfate ester **42** (0.95 g, 4.5 mmol) was added to a methanol solution (20 ml) of the disodium salt of dithiolate **4** (generated in situ by treatment of a 4,5-di(benzoylthio)-1,3-dithiole-2-thione (1.95 g, 4.8 mmol) with two equivalents of sodium methoxide) at 0°C under nitrogen and left to warm up to room temperature over 12 h. The solvent was evaporated in vacuo and replaced by dry THF (20 ml) and the mixture refluxed for 4 h. The THF was evaporated, the residue partitioned between dichloromethane and water, and the organic layer separated and dried over $MgSO_4$. After evaporation of the solvent, methyl benzoate was removed by distillation in vacuo, and the residue purified by chromatography (hexane/dichloromethane 1:1) to give the product as a yellow solid (71 mg, 5%), mp 67–68°C, δ_H 3.65 (4H, m, 2×CH_2OMe), 3.60 (2H, m, 5-,6-*H*), 3.40 (6H, s, 2×OCH_3); *m*/*z*: (EI) 312 (M^+, 54), 196 (10), 120 (18), 115 (24), 76 (24), 45 (100%).

4.4.12. Preparation of 5*R*,6*R*,5′*R*,6′*R*-5,6-dihydro-2-(5′,6′-dihydro-5′,6′-di(methoxy-methyl)-1,3-dithiolo-[4,5-*b*]1,4-dithiin-2′-ylidene)-5,6-di(methoxymethyl)-1,3-dithiolo[4,5-*b*]1,4-dithiin, 8. Thione **43** (55 mg, 0.18 mmol) was reacted with mercuric acetate (65 mg, 0.20 mmol) in chloroform (10 ml) and acetic acid (10 ml) by the general procedure. The crude oxo product **44** was heated with triethyl phosphite (5 ml) for 3 h. under nitrogen. After distillation of triethyl phosphite in vacuo, chromatography (hexane/ethyl acetate 1:1) of the residue gave the product **8** (21 mg, 43%) as an orange-red solid, mp 106–108°C. δ_H: 3.68 (8H, m, 4×CH_2OMe), 3.52 (4H, m, 5-,5′-,6-, 6′-C*H*), 3.37 (12H, s, 4×OCH_3); δ_C: 111.1 (br, 2-,2′-,3a-, 3a′-,7a-,7a′-*C*), 73.9 (4×*C*H_2OMe), 59.2 (4×OCH_3), 41.9 (5-,5′-,6-,6′-*C*); *m*/*z*: (EI) 560 (M^+, 100), 444 ($[M-(CH_3OCH_2CH),]^+$, 85), 300 (45), 280 (67), *HRMS*: (EI) found M^+ 559.9431, $C_{18}H_{24}O_4S_8$ requires 559.9440; $[\alpha]_D^{293}$=+1200 (*c*=0.05, dichloromethane).

Acknowledgements

We should like to thank the EPSRC Mass Spectrometry Service for data, the EPSRC Chemical Data Service[27] and the EPSRC for a grant (GR/F/86021) and a studentship (R. J. B.). We thank Dr F. Turksoy of the Marmara Research Centre, Turkey for two cyclic voltammetry measurements, and we thank Professor Robin Clark of the Chemistry Dept, University College London for access to the Ramascope and Dr Steven Firth for assistance with the measurements.

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