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Synthetic strategies to chiral organosulfur donors related to bis(ethylenedithio)tetrathiafulvalene

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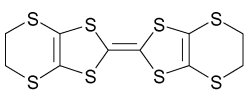
Syntheses of enantiopure organosulfur donors by three different strategies requiring only four–six steps are reported. The key step involves either double substitution of an enantiopure cyclic sulfate ester by a dithiolate, attachment of a chiral diol as a ketal, or completely diastereoselective cycloaddition of 1,3-dithiole-2,4,5-trithione to an enantiopure alkene.

Introduction

Recently Rikken observed electrical magneto-chiral anisotropy in individual (chiral) carbon nanotubes, that is the resistance for current passing through a nanotube in a coaxial magnetic field depends on the current and magnetic field *and* the sense of chirality of the object.[1] This is the first experimental indication of the role of chirality in conduction, this particular effect being predicted in theoretical studies.[2] Recent studies on the radical cation salts of achiral donor **1** known as BEDT–TTF or ET, with $MHg(SCN)_4$ (M = K or Tl) as the counterion suggest that in a magnetic field a chiral surface metal forms, since the electrons can only move in one direction under these conditions.[3,4] Thus, incorporation of chirality into a ET salt may provide new materials suitable for further investigations. Well before these results were known, Dunitz had opened the discussion on whether chirality might have an effect on electrical conduction, and prepared the first chiral organic donor, *S*,*S*,*S*,*S*-tetramethyl–ET **2**,[5] and characterized several of its radical cation salts though they adopted pseudo-centrosymmetric crystal structures.[6] Hilti and Zambounis have reported that the κ-phase perchlorate salt of the enantiopure dimethyl–ET **3** becomes superconducting at 2 K[7] and Sugawara and Kawada have reported the only comparison to date of the crystal packing arrangements of a racemic and enantiopure ET derived salt, for the 2 : 1 PF_6^- salt of **3**.[8] In both modifications each stack contains only one enantiomer, and these molecules lie head over tail, but with a lateral twist of *ca.* 30° in alternate directions along the stack. Ordered PF_6^- ions sit in centrosymmetric pockets in the racemic salt, but in the enantiopure salt the different symmetries of the PF_6^- anion and the chiral pocket lead to the anion being orientationally disordered between two positions. In contrast, Schlueter and collaborators have included chirality in the anion by making a ET salt with racemic $SF_5CHFCF_2SO_3^-$, however the anions were orientationally disordered due to the similar sizes of the H and F atoms at the stereogenic centre.[9] A number of ET salts with racemic *tris*-oxalato-metallate anions are known.[10,11] Of particular note is Day's report of two polymorphs of the racemic salt $ET_4[(H_3O)Cr(C_2O_4)_3]\cdot C_6H_5CN$, one superconducting and one semiconducting.[11] In the former, the ET layer lies between two anion layers containing either all Δ or all Λ enantiomers, but in the latter the anion layers contain an ordered array of both Δ and Λ enantiomers, which is sufficient to alter the packing arrangement of the ET molecules from β″ to pseudo-κ *via* weak hydrogen bonding interactions. Interestingly, the former is prepared from racemic $Cr(C_2O_4)_3^{3-}$, but the latter from enantiopure material which subsequently racemised.

We have reported the synthesis of two new enantiopure donors from chiral pool materials, though the syntheses involve at least ten steps. The hydroxymethyl–ET, *R*-HMET, **7** was prepared from D-mannitol, the key step being double substitution of the enantiopure cyclic sulfate ester **5** by dithiolate **4** to give the thione **6** (Scheme 1).[12] Similarly the 2-fluoro-1-hydroxyethyl–ET **10** was prepared from the thione **9** which was an unexpected product of the reaction of dithiolate **4** and the enantiopure cyclic sulfate ester **8**.[13] We and others have prepared the enantiopure donors **11–13**, which contain one or more outer eight-membered rings each with a pair of chirally disposed hydroxyl groups, from dimethyl L-tartrate,[14–15] and Fourmigué and Avarvari have prepared the enantiopure ligand **14**[16] containing the ethylenedithio–TTF molecular skeleton.

We were interested to expand the range of chiral organosulfur donors available, to provide further systems for use in investigations of the effects of chirality on electro-magnetic properties. Here we report syntheses of three such donors **15–17** as single enantiomers by three different strategies whose key steps are (a) double substitutions of dithiolate **4** on an enantiopure cyclic sulfate ester, (b) attachment of a chiral grouping to an achiral donor and (c) diastereoselective cycloaddition to 1,3-dithiole-2,4,5-trithione. Each strategy has potential for extension to the preparation of a wide range of donors, and further results of the diastereoselective cycloaddition strategy are reported. Rajca has reported syntheses of alternative chiral building blocks such as dodecaphenylenes and helical annelated oligothiophenes for preparing conducting materials, wave guides and molecular glasses.[17,18] There have also been significant advances in preparing chiral conducting polymers[19,20] and nanotubes.[21] Chiral metals may find applications as novel electrode materials for chiral electrochemical analysis, while chiral donors have potential applications in enantioselective chromatographic media. The first chiral single-molecule magnets have been reported recently.[22]



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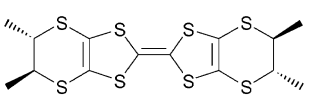

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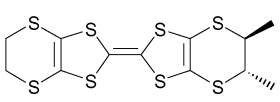

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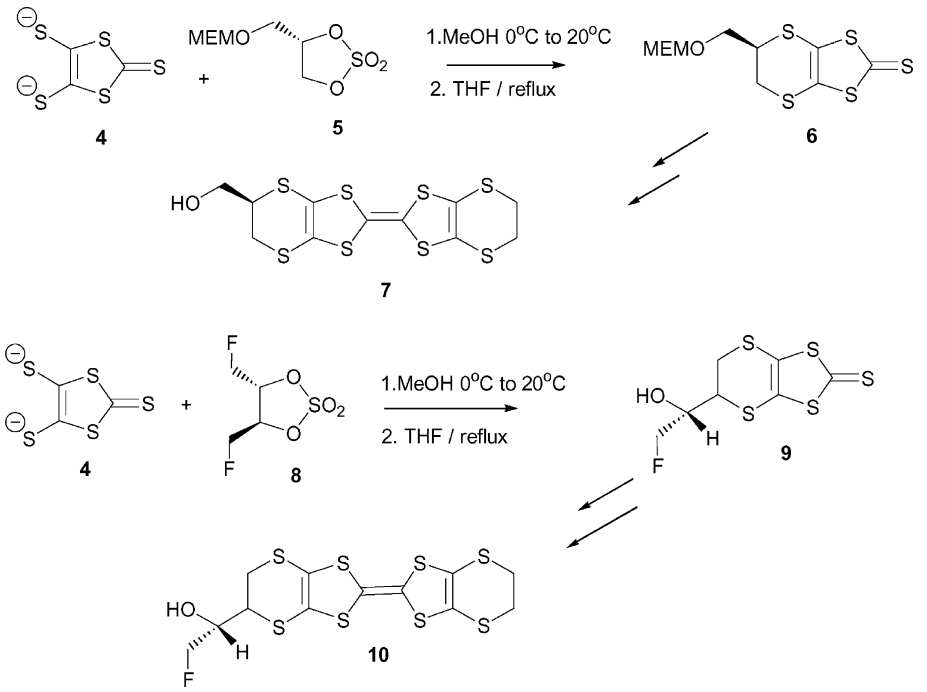
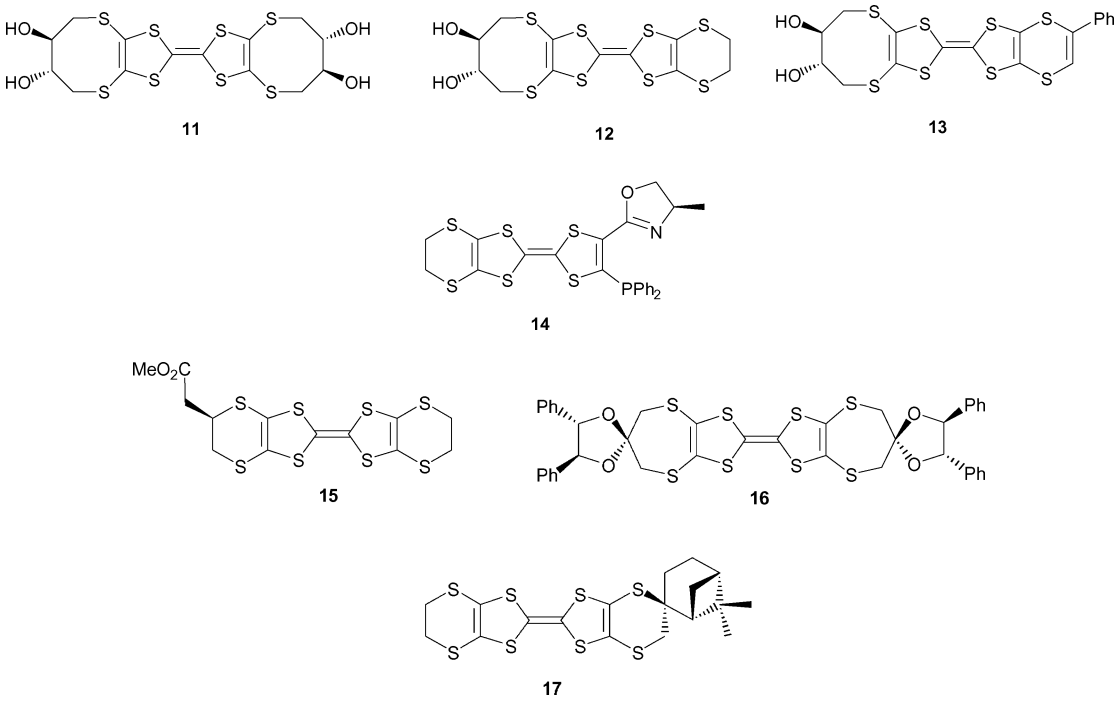


Scheme 1

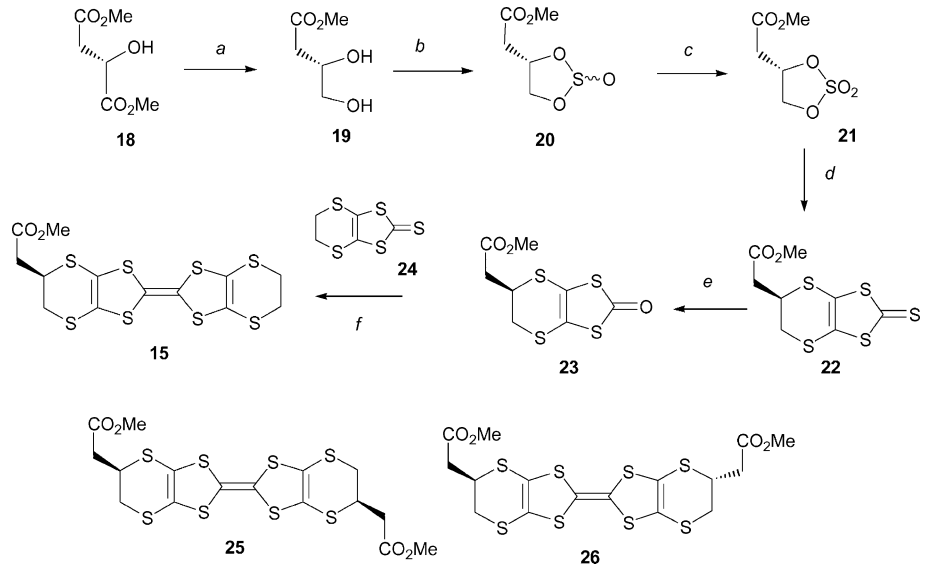


Results and discussion

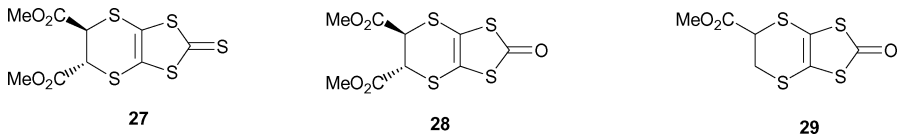
Synthesis of donors 15–17

Since a carboxyl functionality provides opportunities for attachment of further molecular species, as well as functional group interconversions, we identified donor **15** as an important target. Starting from dimethyl L-malate, we have prepared this molecule in six steps, with an overall yield of 10%, requiring four straightforward chromatographic separations. Dimethyl L-malate **18** is reduced regioselectively to the diol **19**,[23] and then converted into its cyclic sulfate ester **21** in two steps *via* the cyclic sulfite ester **20**. A double substitution reaction by the dithiolate **4** gives the bicyclic thione **22** in 35% yield. The thione **22** was converted to the corresponding oxo compound **23** (86%) using mercuric acetate. Cross coupling with a two fold excess of unsubstituted thione **24** in triethyl phosphite gave the donor **15** in 47% yield after chromatographic separation from the homocoupled materials ET **1** and the two inseparable difunctionalised ETs **25** and **26** (Scheme 2). The synthesis of the racemic donor **15** has been effected in just four steps, preparing the thione **22** from dithiolate **4** and methyl 3,4-dibromobutanoate.[24] We avoided direct attachment of the ester group to the ET framework, since the stereogenic centre would be vulnerable to epimerisation in some conditions due to the activating effects of the carbonyl and sulfur atom on the acidity of the hydrogen atom at the stereogenic centre. Furthermore, coupling of the diester functionalised thione compound **27** failed,[25] though heterocoupling of the corresponding oxo compound **28** and homocoupling of oxo compound **29** have been reported.[26]

The attachment of an enantiopure fragment to a side chain is another approach for introducing chirality, but to avoid production of diastereoisomers, this would have to involve a reaction

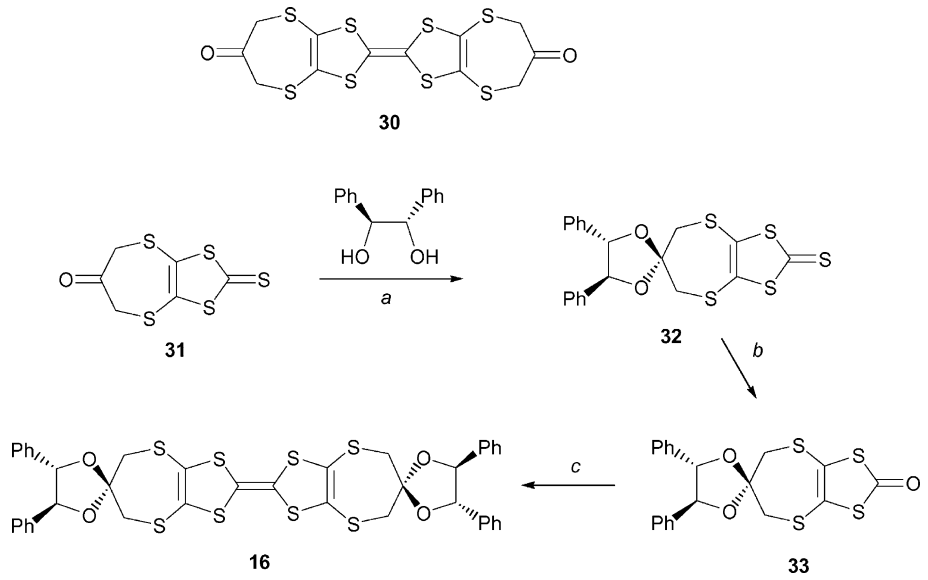


Scheme 2 a) BH_3SMe_2, cat. $NaBH_4$; b) $SOCl_2$, py; c) $NaIO_4$, cat. RuO_2; d) **4**, MeOH, 0 °C, 24 h, then THF 65 °C; e) $Hg(OAc)_2$, $CHCl_3$, AcOH; f) $(EtO)_3P$.

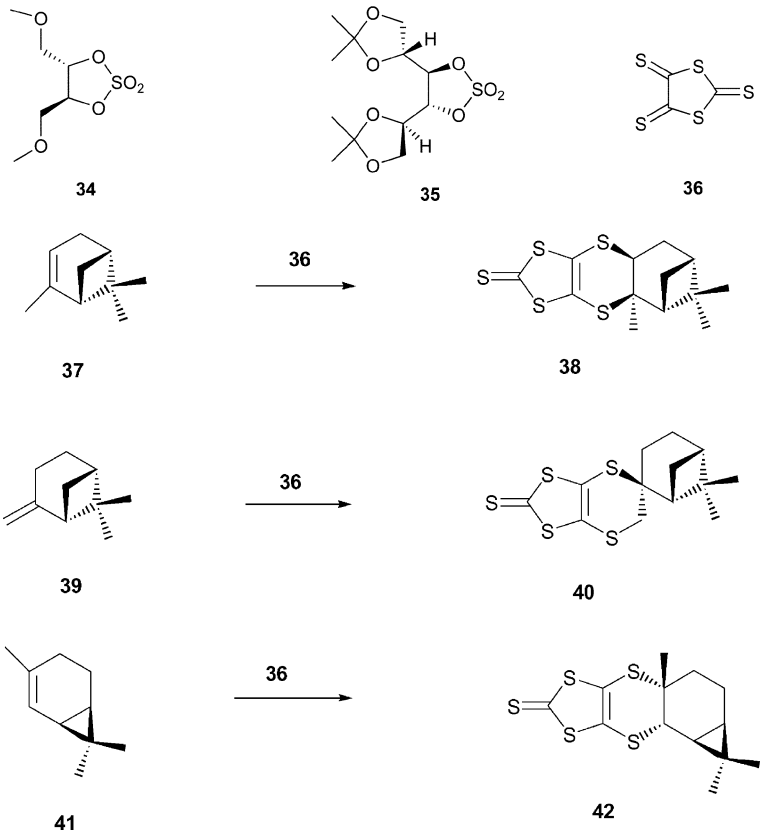


with an enantiopure ET (*e.g.* by ester exchange on donor **15** with an enantiopure alcohol)! However, the achiral donor **30**, which has 2-oxopropylene-1,3-dithio bridges instead of ethylenedithio bridges, is an ideal molecular skeleton since the keto groups can be converted to ketals with an enantiopure diol, for example, to give our second target **16**. This type of molecule is of particular interest, since it offers the possibility of building stacks which must have a continual twist if the chirally disubstituted dioxolane rings on successive donors are to avoid one another. It is known that increasing the size of the outer ring of ET does not alter the oxidation potential too much.[27] Enantiopure diols are available from Sharpless's asymmetric dihydroxylation (AD) methodology. In this case we installed the ketal early in the synthesis by reaction of *S*,*S*-1,2-diphenylethane-1,2-diol[28,29] with the ketone **31**,[30] available from the zinc complex of dithiolate **4** and 1,3-dichloroacetone, to give the ketal **32** in 80% yield. The exchange of thione sulfur for oxygen to give oxo compound **33** was carried out in 95% yield using mercuric acetate in chloroform and a small amount of acetic acid but for just fifteen minutes to avoid hydrolysis of the ketal. Finally the donor **16** was obtained in 37% yield by homo-coupling of oxo compound **33** in triethyl phosphite, corresponding to an overall yield of 28% from the enantiopure diol (Scheme 3).

Although these strategies have considerable scope for preparing further enantiopure donors, we wanted access to more complex ET donors. The double substitution of a cyclic sulfate ester from chiral pool materials has limited potential for the preparation of such materials, since the cyclisation reaction is much less effective when there are two larger substituents on the cyclic sulfate ester. Thus, the double substitution of the cyclic sulfate esters **34** and **35** gave 5% and 0% yields of the thione product.[31,32] Neilands introduced the cycloaddition of the highly insoluble trithione **36** with either electron rich or electron poor alkenes to prepare the thione precursors



Scheme 3 a) $CHCl_3$, cat. TsOH, mol. sieves, reflux; b) $Hg(OAc)_2$, $CHCl_3$, AcOH, 15 min; c) $(EtO)_3P$.



Scheme 4

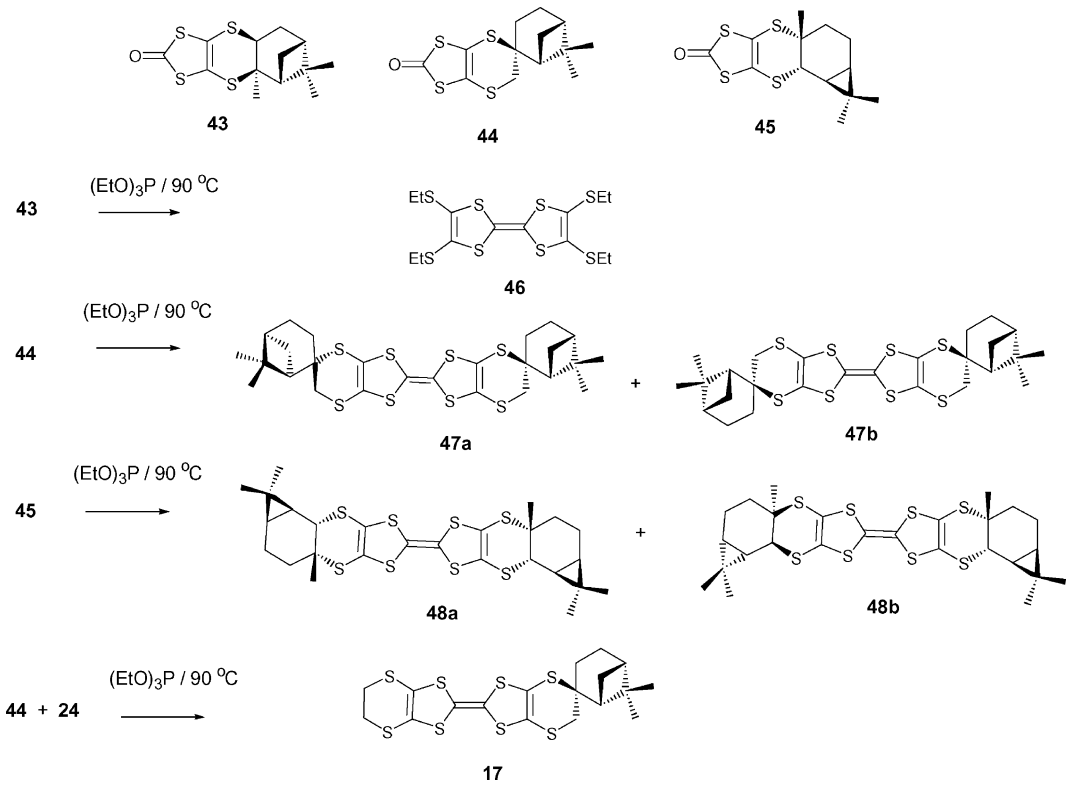
for donor synthesis,[33] and the reaction has been widely used *en route* to preparing many monosubstituted ET derivatives[34] *e.g.* with aminomethyl,[35] or hexadecyl[36] sidechains, as well as disubstituted ET derivatives[37] and donors with fused carbocyclic and heterocyclic rings.[38] Toluene is often the solvent of choice and, with long reaction times, leads to the optimum yields in general. However, the reactions of trithione **36** with enantiopure alkenes have not been investigated. Thus, we examined the reaction with several chiral, sterically hindered, alkenes.

Reaction of trithione **36** with monoterpenes (−)-α-pinene **37**, (−)-β-pinene **39** and (+)-2-carene **41** in refluxing toluene gave the corresponding thiones **38, 40** and **42**, as single diastereoisomers in excellent yields of 80–90%, and with no sign of the second diastereoisomer on chromatographic separation or in the ^{1}H and ^{13}C NMR spectra of the main products (Scheme 4). The molecular structures of these three thiones were measured by single crystal X-ray crystallography.† In each case, the results show that the trithione **36** has attacked exclusively from the less hindered side of the alkene. Details of these interesting structures are discussed later.

Thiones **38, 40** and **42** reacted with mercuric acetate in chloroform and acetic acid to furnish the corresponding oxo compounds **43–45** in high yields of 92–95%. Each oxo compound was heated in triethyl phosphite to form the corresponding homocoupled BEDT–TTF derivatives (Scheme 5). The most strained oxo compound **43**, however, gave a high yield (87%) of tetra(ethylthio)–TTF **46**, the product of Arbusov reactions. This is probably due to the adduct undergoing a retro-cycloaddition in the reaction conditions, as has been observed elsewhere.[39] The other two oxo compounds did yield the desired BEDT–TTF derivatives. After chromatography they still contained ethylated material, suggestive of competing Arbusov reactions, but these products were removed by washing with methanol, to furnish **47** in 46% yield, and **48** in 42% yield. Both products are expected to be mixtures of two diastereoisomers (**a** and **b**). However, the less substituted donor **17**, as a single diastereoisomer, was obtained by cross coupling the oxo compound **44** with the unsubstituted thione **24** in triethyl phosphite. Indeed this chiral donor **17** was isolated in a very respectable yield of 42% after separation from homocoupled donors and ethylated material by chromatography and washing in methanol. Although donor **17** has a somewhat bulky *spiro* substituent, which might be envisaged to disfavour pi stacking of the organosulfur residues, it should be noted that the donor DOET **49** which contains a dioxane ring at more or less right angles to the organosulfur plane, still can form stacks and its 4 : 1 salt with $Hg_2Cl_6^{2-}$ is metallic down to 4 K![40] The size of the substituent leads to the molecules lying head to tail in stacks, with the dioxane rings lying outside the stack. The 2 : 1 AsF_6^- salt of the structurally related donor DODHT **50** also shows head to tail stacks, though with shorter S ⋯ S contacts between stacks than within them. Nevertheless, under pressure this material becomes a metal-like conductor which shows superconductivity below 3.3 K.[41] Furthermore, donor DO–MET **51** forms a 2 : 1 salt with AsF_6^- which is metallic down to 2 K in which the donors pack head to head with a shift on the long molecular axis so that the axial dioxolanes lie outside the stack.[42] Our initial attempts to cross couple the oxo compound **45**, derived from 2-carene, and the unsubstituted thione **24** were unsuccessful, due to difficulties in separating the cross coupled donor from the products of Arbusov reactions.

Cyclic voltammetry measurements on the enantiopure donors **15–17** and the homocoupled donors **47** and **48** showed two reversible oxidation potentials (Table 1). The ET derivative **15** shows oxidation peaks typical of a ET system and identical to those for its racemate,[24] while those ET derivatives derived from β-pinene and 2-carene consistently show lower oxidation potentials (by *ca.* 0.06 V). We note that in the donor **52** lower oxidation potentials were also observed. We speculated tentatively that this may be due to oxidation of associated ET moieties. The donor **16** with outer seven-membered rings shows

† CCDC reference numbers 230195, 264422 and 264423. See http://www.rsc.org/suppdata/ob/b5/b502437d/ for crystallographic data in CIF or other electronic format.



Scheme 5

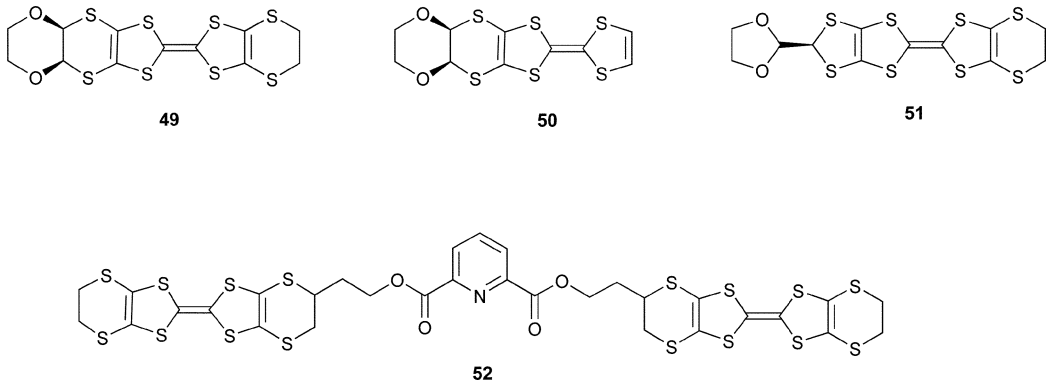


Table 1 Cyclic voltammetry of enantiopure donors, measured in dichloromethane using 0.1 M tetrabutylammonium hexafluorophosphate as the charge carrier

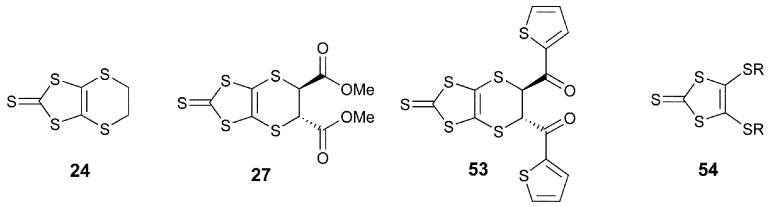
Compound	$E_1^{1/2}$	$E_2^{1/2}$
15	0.50	0.91
16	0.56	0.94
17	0.44	0.85
47a/b	0.44	0.86
48a/b	0.43	0.86

an increase of *ca.* 0.06 V in its first oxidation potential compared to ET systems, due to the change in the conjugation of the outer sulfurs with the TTF system.

Molecular structures of thiones 38, 40, 42

Before describing the structures of the cycloaddition products, it is useful to outline some details of the molecular geometry of simpler substituted dithiolodithiin-thiones. X-Ray crystal structure data for the unsubstituted thione **24** and its substituted derivatives indicate that a range of conformations are possible for the six-membered ring. Thus, the unsubstituted thione **24**[43] and its *trans* 5,6-diphenyl derivative[39,44] show envelope conformations, the 5-(2-pyridyl) substituted derivative[45] prefers the half chair conformation, and the *trans* 5,6-dimethyl derivative[46] an intermediate conformation. However, in **27** and **53** which have two *trans* carbonyl groups,[25,47] the conformations are close to a boat with both sp^3 carbon atoms strongly displaced to the same side of the organosulfur ring system, though in **27** there is also a substantial additional twist (*ca.* 40°, *cf.* 11° in **53**) about the ring C,C bond. A notable feature of the six-membered ring system in all cases is the large bond angles at the sp^3 carbon atoms, (111–118°) which is a consequence of the smaller bond angles at sulfur. Without the constraints of a six-membered ring, the bis(alkylthio)dithioles **54** show a range of conformations in the solid state, with both in-plane and strongly out of plane orientations for alkyl groups.[48]

The molecular structures of the cycloaddition adducts will be discussed in order of increasing strained structures. The results are shown with selected geometric data in Figs. 1–5. The structure of the carene adduct **42** shows that the trithione has attacked the carene ring system on the face opposite to the dimethylated cyclopropane ring (Fig. 1). The cyclohexane and dithiin rings are fused along the C4–C5 bond. The cyclohexane adopts an envelope conformation with C4 at the flap displaced by 0.712(7) Å from the plane defined by the other five ring carbon atoms in the opposite direction to the fused cyclopropane ring.



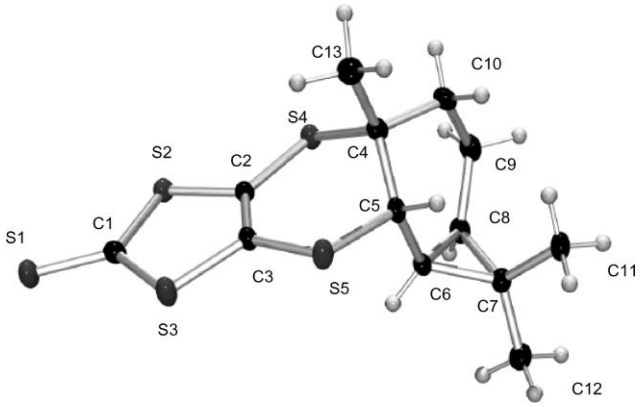


Fig. 1 Molecular structure of carene adduct **42**. Selected molecular geometry: C2–C3 1.350(2), C2–S4 1.7470(17), C3–S5 1.7375(18), C4–S4 1.8393(18), C4–C5 1.541(2), C4–C10 1.538(2), C5–S5 1.8183(18), C5–C6 1.514(2), C6–C7 1.524(2), C7–C8 1.511(3), C8–C9 1.513(3), C9–C10 1.535(3), C2–S4–C4 100.46(8), C3–S5–C5 100.78(8), S4–C4–C5 111.37(12), S4–C4–C10 105.64(12), C5–C4–C10 107.08(15), S5–C5–C4 113.40(12), S5–C5–C6 112.06(12), C4–C5–C6 113.59(14), C6–C7–C11 120.61(15), C6–C7–C12 117.58(16), C5–C6–C8 118.03(14), C8–C7–C11 119.87(16), C8–C7–C12 116.23(16), C6–C8–C9 120.60(15), C8–C9–C10 115.34(15), C4–C10–C9 114.73(15)°.

The dithiin ring adopts an approximate half chair conformation with the two sp^2 C atoms and the two S atoms in plane, and C4 and C5 deviating from the plane defined by the five coplanar sulfur atoms by 0.526(5) Å and 0.323(9) Å respectively. Thus the cyclohexane ring lies nearly perpendicular to the organosulfur system, reminiscent of the structure of the donor with a fused 1,4-dioxane ring, DOET, **49**.[49] The methyl group at the ring fusion, C13, lies in a pseudo-equatorial position with respect to the cyclohexane ring, and lies well away from the other atoms. In contrast, methyl group C11 from the cyclopropyl group lies over the cyclohexane ring, and there is some steric strain with the two pseudo-axial hydrogen atoms from C5 and C10. This is manifested in the methyl group being pushed away so that the C11–C7 bond makes angles of 119.87(16)° and 120.61(15)° with the cyclopropyl bonds C7–C8 and C7–C6 respectively, while the bond to the other geminal methyl group C12–C7 makes smaller angles with these two bonds (116.23(16)° and 117.58(16)°). There are no substantial extensions of the two sp^3 C–S bond lengths at the fusion of the rings: C4–S4 1.8393(18) Å and C5–S5 1.8183(18) Å, *cf.* 1.811–1.825 Å in unsubstituted thione **24** and its *trans* dimethyl and diphenyl analogues, taking into consideration that C4 is a quaternary centre. In adducts **38** and **40**, these bond lengths are significantly longer.

The crystals of the β-pinene adduct **40** contain two unique molecules per asymmetric unit. The molecules have similar geometries, except in the particular half chair conformations adopted by the dithiin rings. Data for molecule 1 are discussed, with data for molecule 2 in parentheses. The molecular structure shows that the trithione has attacked the double bond from the less hindered side which contains the unsubstituted methylene bridge to form an adduct with a spiro junction between the carbocyclic system and the dithiin ring (Figs. 2 and 3). Five carbon atoms of the bicyclo[3.1.1]heptane ring system adopt an almost perfect planar arrangement, while the other two carbons of the skeleton, C9 and C11, are displaced from this plane by −1.073(3) Å (−1.064(4) Å) and 1.076(3) Å (1.080(4) Å). The dithiin ring system adopts an approximate half chair conformation in which the two sp^2 C atoms and the two S atoms lie in a plane and C4 and C5 deviate by 0.407(4) Å and −0.489(3) Å (0.560 (4) and −0.328(3) Å) respectively from this plane. The position of the larger displacement is different in the two molecules. The spiro centre results in the best planes of the carbocyclic skeleton and the dithiin ring being in a roughly perpendicular orientation to one another. The structure has little conformational freedom apart from the flexing of the dithiin ring. The spiro centre results in a reduction in the normally wide bond angle at the sp^3 carbon in the dithiin ring to 107.4(2)° (107.9(2)°) at C5, compared to 115.3(3)° (114.4(2)°) at C4. The C–S bond to the spiro centre C5–S5 1.858(3) Å (1.858(3) Å) is particularly long, especially when compared to the C4–S4 bond which involves a methylene carbon 1.808(3) Å (1.816(4) Å). Sulfur atom S5 is attached to a quaternary carbon and experiences additional steric pressure from the methylene bridge (S5–H9b 2.72(4) Å (2.62(3) Å)).

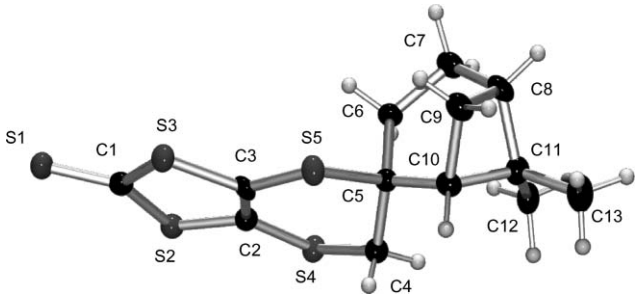


Fig. 2 Molecular structure of β-pinene adduct **40**, molecule 1. Selected geometry for molecules 1 (and 2): C2–C3 1.353(4) (1.349(4)), C2–S4 1.739(3) (1.747(3)), C3–S5 1.755(3) (1.744(3)), C4–S4 1.808(3) (1.816(4)), C5–S5 1.858(3) (1.858(3)), C4–C5 1.536(4) (1.535(5)), C5–C6 1.555(5) (1.554(5)), C5–C10 1.535(5) (1.533(5)), C6–C7 1.554(5) (1.552(5)), C7–C8 1.518(5) (1.528(6)), C8–C9 1.545(5) (1.538(5)), C8–C11 1.552(5) (1.547(5)), C9–C10 1.547(5) (1.557(5)), C10–C11 1.576(4) (1.571(4)), C2–S4–C4 99.85(16) (99.07(16)), C3–S5–C5 101.70(15) (102.71(15)), S4–C4–C5 115.3(3) (114.4(2)), S5–C5–C4 107.4(2) (107.9(2)), S5–C5–C6 111.0(2) (110.3(2)), S5–C5–C10 102.1(2) (103.2(2)), C4–C5–C6 113.3(3) (113.5(3)), C4–C5–C10 110.9(3) (109.6(3)), C6–C5–C10 111.5(3) (111.7(3)), C5–C6–C7 115.7(3) (115.6(3)), C6–C7–C8 113.3(3), (113.3(3)), C7–C8–C9 108.1(3) (108.7(3)), C7–C8–C11 112.2(3) (110.9(3)), C9–C8–C11 88.0(3) (88.1(3)), C8–C9–C10 86.5(2) (86.6(3)), C5–10–C9 108.6(3) (108.2(3)), C5–C10–C11 113.4(3) (113.3(3)), C9–C10–C11 87.1(2) (86.6(2)), C8–C11–C10 85.3(2) (85.9(2)), C8–C11–C12 117.7(3) (119.0(3)), C8–C11–C13 111.8(3) (112.2(3)), C10–C11–C12 122.8(3) (122.0(3)), C10–C11–C13 110.5(3) (109.9(3)), C12–C11–C13 107.3(3) (106.8(3))°.

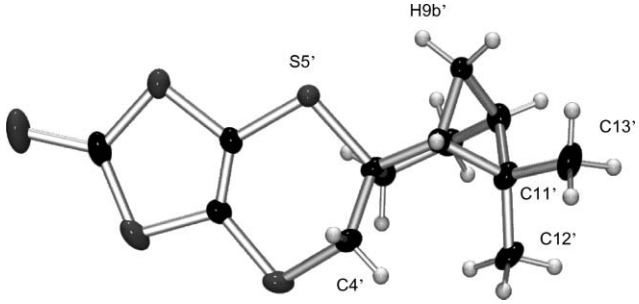


Fig. 3 View of **40**, molecule 2, showing atoms involved in main steric interactions.

There is a steric interaction between the C4 methylene group of the dithiin ring, and the methyl group C12, which are in pseudo-axial positions relative to the carbocyclic system, (C4–C12, 3.260(5) Å (3.276(5) Å)). The main distortion is displacement of the methyl group C12 away from C4 and towards its geminal partner C13, so that the C11–C12 bond makes angles in the range 117.7(3)–122.8(3)° with cyclobutyl bonds C10–C11 and C8–C11, compared to the corresponding angles involving the other geminal methyl group C13 (109.9(3)–112.2(3)°). C4 is not strongly displaced away from C12 primarily due to its confinement in a ring. The steric pressures between C4 and C12 and between S5 and H9b are also reduced by an asymmetric distortion of the cyclobutane ring of the alicyclic skeleton, thus the two bonds nearer to the spiro centre are longer than those on the opposite side of the ring. More notably C10–C11 (1.576(4) Å (1.571(4) Å)) is more than 0.02 Å longer than C8–C11 (1.552(5) Å (1.547(5) Å)) while C9–C10 (1.547(5) Å (1.557(5) Å)) is slightly longer than C8–C9 (1.545(5) Å (1.538(5) Å)).

The structure of the α-pinene adduct **38** is the most remarkable (Fig. 4). Cycloaddition has occurred on the face of the alkene adjacent to the unsubstituted methylene bridge, and opposite to the dimethylated bridge. However, the fusion of the dithiin ring with the bicyclo[3.1.1]heptane ring system and interactions between substituents leads to a very strained structure. The dithiin ring is forced into a boat conformation, which is achieved by flexing about the S4 · · · S5 vector. Thus, the torsion angle about the C4–C5 bond is only 25.6(3)°, and both C4 and C5 are displaced in the same direction from the [S4, C2, C3, S5] plane by 1.415(3) Å and 1.217(3) Å respectively. The bicyclohexane system is also strained by the ring fusion, and atoms C4, C5, C6, C8 and C9 form only an approximate plane (average deviation of atoms from plane: 0.054 Å) which lies at 74.42(11)° to the plane of the five sulfur atoms.

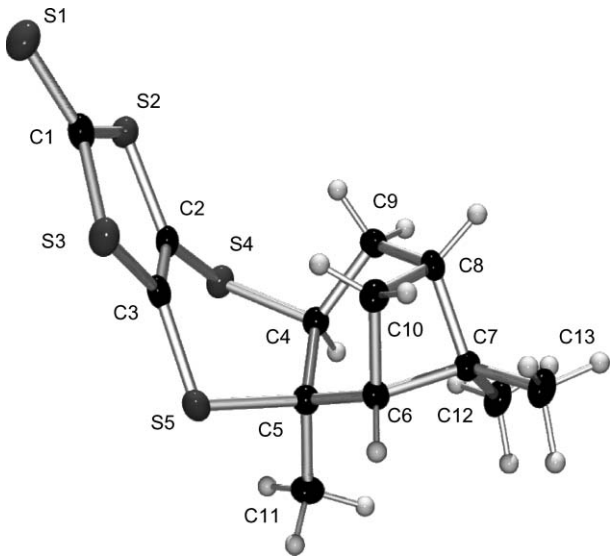


Fig. 4 Molecular structure of α-pinene adduct **38**. Selected molecular geometry: C2–C3 1.349(4), C2–S4 1.740(3), C3–S5 1.734(3), C4–S4 1.833(3), C4–C5 1.552(4), C4–C9 1.551(4), C5–S5 1.880(3), C5–C6 1.530(4), C5–C11 1.531(4), C6–C7 1.582(4), C6–C10 1.561(4), C7–C8 1.556(4), C7–C12 1.527(4), C7–C13 1.537(4), C8–C9 1.528(4), C8–C10 1.538(4), C2–S4–C4 98.72(13), C3–S5–C5 104.41(13), S4–C4–C5 115.8(2), S4–C4–C9 111.6(2), C5–C4–C9 115.3(2), S5–C5–C4 114.2(2), S5–C5–C6 107.56(19), S5–C5–C11 101.1(2), C4–C5–C6 110.9(2), C4–C5–C11 110.9(2), C6–C5–C11 111.9(2), C5–C6–C7 113.2(2), C5–C6–C10 110.1(2), C7–C6–C10 86.4(2), C6–C7–C8 85.1(2), C6–C7–C12 123.4(2), C6–C7–C13 109.2(3), C8–C7–C12 118.5(3), C8–C7–C13 112.7(2), C12–C7–C13 106.8(3), C7–C8–C9 112.4(2), C7–C8–C10 88.1(2), C9–C8–C10 107.4(2), C4–C9–C8 113.1(2), C6–C10–C8 86.4(2)°.

There are two main sources of strain in the structure: the close approach of the unsubstituted methylene bridge at C10 to

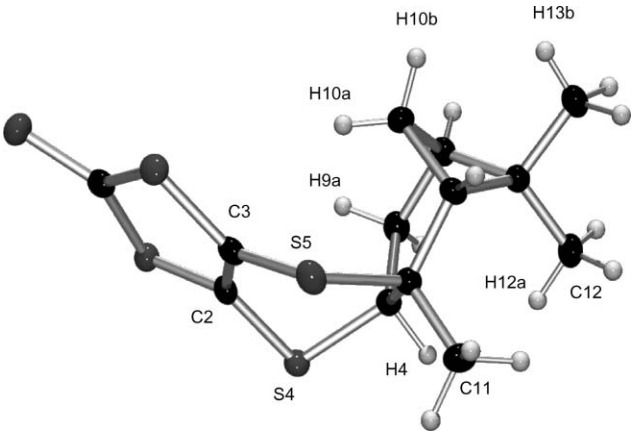


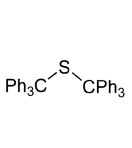
Fig. 5 View of **38** showing atoms involved in main steric interactions.

sulfur atom S5, and the close contact between methyl groups C11 and C12, the former located at the fusion of the two ring systems and the latter on the dimethylated bridge (Fig. 5). The consequences for sulfur atom S5 of steric pressure from C10, are the remarkable elongation of the C5–S5 bond to 1.880(3) Å, the closing of the angle at C5 with the bridgehead methyl group C11 to 101.1(1)° and the short 1,5 interaction S5–H10a of 2.92 Å. The interacting methyl groups are splayed apart, but the C–C separation between the two methyl carbons is only 3.321(5) Å. At the dimethyl bridge at C7, methyl group C12 is pushed towards methyl group C13 so that the bond angles C7–C12 makes with cyclobutyl bonds C7–C6 and C7–C8 are widened to 123.4(2)° and 118.5(3)° while those made by C13–C7 with these bonds are reduced to 109.2(3)° and 112.7(2)°.

The organosulfur ring system lies *anti* to the bridgehead methyl group C11, and there are additional close contacts between the heterocyclic system and the bicyclohexane system, notably a 1,5 interaction C2–H9a 2.79 Å and a 1,6 interaction C3–H10a 2.69 Å. The outward splaying of the bridgehead methyl group is sufficient to disfavour the *syn* conformation. There are further close intramolecular contacts from the dimethylated bridge to methine hydrogen atom H4 and to the methylene bridge: H12a–H4 (2.06 Å) and H13b–H10b (2.08 Å). Steric pressure from methyl group C11 and the heterocyclic system lead to an asymmetric distortion of the cyclobutane ring, with bonds C6–C7 and C6–C10 being very long for C,C single bonds (1.582(4) and 1.561(4) Å) and longer than the other two bonds to the bridging carbons: C8–C7 and C8–C12 (1.556(4) and 1.538(4) Å). The exceptionally long C6–C7 bond is involved in relieving the steric pressure between the methyl groups C11 and C12.

Since both sp^3 C–S bonds at the ring junction are elongated by the steric strain, (1.880(3) and 1.833(3) Å), it is not surprising that the oxo compound prepared from this adduct is prone to a retro Diels Alder reaction. Longer C–S bonds are not common and occur only if there is exceptional strain, as in bis(triphenyl)sulfide **55** (C–S: 1.891 and 1.916 Å)[50] and the tetrathiaprotoadamantane **56** (C–S: 1.914 and 1.844 Å)[51] or where the carbon is attached to one or more additional heteroatoms, especially nitrogen, as in thiazolidine **57** or the 2-(dimethylamino)thiazolidinone derivative **58**.[52,53]

Among the analogous dithiolodithiines, only the diketone **53** shows such long bonds (1.864 and 1.879 Å). The considerable strain experienced at C5 in the α-pinene adduct **38** at the ring fusion is shown by the ^{13}C NMR shifts of C5 and C4 at δ 71.4 and 51.2. In comparison for the β-pinene adduct, the equivalent carbons show shifts of δ 55.4 and 41.1, the former from the quaternary spiro centre and the latter from the methylene group, while in the 2-carene adduct the equivalent methine carbons have shifts of δ 48.0 and 45.4. Further evidence of the strain in the thione **38** are the unexpectedly high ^{13}C NMR shifts for the sp^2 carbons at the fusion of the dithiole and dithiin rings δ 133.0 and 140.7 compared to δ 124.5 and 119.9 in adduct **40**, δ 122.9 and



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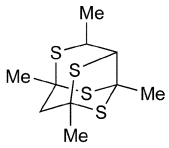

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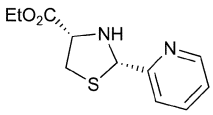

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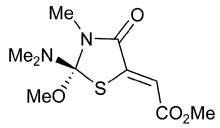

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117.4 in adduct **42** and *ca.* δ 122 in **24** and simple substituted materials. This relates partly to the boat conformation of the dithiin ring, since compounds **27** and **53**, which take the boat conformation in the solid state, show higher sp^2 C resonances of δ 129.9 and 128.3, while the envelope conformation allows more electron donation from one dithiin S atom into the double bond. For the dithiin sp^2 C atoms in the bis(alkylthio)1,3-dithioles **54** (*e.g.* R = Et, *n*-octyl) the corresponding carbons have a chemical shift of *ca.* 136 ppm.[54]

Conclusion

Three short synthetic strategies for preparing enantiopure organosulfur donors are reported. All three donors have potential for developing access to a wider range of materials, either by reaction with the carbonyl group of **15**, or use of alternative enantiopure diols in the syntheses of donors analogous to **16**. Of particular significance is the total diastereoselectivity of the cycloaddition of trithione **36** to selected enantiopure alkenes, which we now intend to extend to other less structurally complex alkenes.

Experimental

General

NMR spectra were measured on a JEOL JNM-EX270 spectrometer 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. IR spectra were recorded on a PerkinElmer Spectrum RX 1 FT-IR spectrometer. Optical rotation data were measured on a PerkinElmer 21 polarimeter. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre. Chemical analysis data were obtained from Mr T. Spencer, University of Nottingham. Flash chromatography was performed on 40–63 silica gel (Merck). Cyclic voltammetry was performed with a μAutolab Type II apparatus.

Dimethyl *S*-3,4-dihydroxybutanoate 19[23]. Dimethyl L-malate **18** (3.07 g, 21.6 mmol) was reduced with $BH_3{\cdot}SMe_2$ and 5 mol% of $NaBH_4$ in THF as in the literature to give diol **19** after flash chromatography as a pale yellow oil (1.96 g, 77.2%); ^{1}H NMR: 3.89 (1H, m, 3-*H*), 3.48 (3H, s, OCH_3), 3.40 (1H, dd, J = 11.4, 3.7 Hz, 4-H_α), 3.28 (1H, dd, J = 11.4, 6.4 Hz, 4-H_β), 2.29 (2H, d, J = 6.5 Hz, 2-H_2); ^{13}C NMR: 172.2 (*C*=O), 68.3 (3-*C*), 65.2 (4-*C*), 51.3 (O*C*H$_3$), 37.5 (2-*C*); ν_{max}/cm^{-1} (thin film): 3389, 2955, 1732, 1439, 1287, 1171, 1042; $^{293}[\alpha]_D = -24.91$ (c = 1.06, $CHCl_3$).

Methyl (2′-oxo-1,3,2-dioxathiolan-4′-yl)ethanoate 20. Thionyl chloride (0.50 ml, 6.90 mmol) was added dropwise to a solution of diol **19** (0.84 g, 6.27 mmol) and pyridine (1.09 g, 13.8 mmol) in THF (25 ml) at 0 °C. The mixture was allowed to warm to room temperature and left to stir overnight. Pyridinium hydrochloride was filtered off and washed with THF (20 ml). The combined washings and filtrate were evaporated under reduced pressure and the residue partitioned between DCM (50 ml) and water (20 ml). The organic phase was collected and washed consecutively with water (20 ml) and 0.5 M HCl (2 × 20 ml), dried (Na_2SO_4), evaporated and the crude oil purified by flash chromatography (SiO_2, 1 : 1 EtOAc–cyclohexane) to afford cyclic sulfite ester **20** as a light yellow oil (1.11 g, 98.3%) as a mixture of two diastereoisomers; ^{1}H NMR (major isomer): 5.18 (1H, m, 4′-*H*), 4.32 (1H, t, J = 8.9 Hz, 5′-H_α), 4.07 (1H, dd, J = 8.9, 5.6 Hz, 5′-H_β), 3.60 (3H, s, OCH_3), 2.72 (1H, dd, J = 16.5, 6.3 Hz, 2-CH_α), 2.54 (1H, dd, J = 16.5, 7.3 Hz, 2-CH_β); ^{1}H NMR (minor isomer): 5.18 (1H, m, 4′-*H*), 4.72 (1H, dd, J = 8.9, 6.2 Hz, 5′-H_α), 4.60 (1H, dd, J = 8.9, 6.4 Hz, 5′-H_β), 3.60 (3H, s, OCH_3), 2.99 (1H, dd, J = 16.8, 6.4 Hz, 2-CH_α), 2.79 (1H, dd, J = 16.8, 7.2 Hz, 2-CH_β); ^{13}C NMR (major isomer): 169.4 (*C*=O), 76.5 (4′-C), 71.0 (5′-C), 52.1 (O*C*H$_3$), 37.2 (2-*C*); ^{13}C NMR (minor isomer): 169.7 (*C*=O), 76.0 (4′-*C*), 70.7 (5′-*C*), 51.7 (O*C*H$_3$), 38.7 (2-*C*); ν_{max}/cm^{-1} (thin film): 2955, 2860, 1734, 1281, 1212, 1123, 1070, 954, 743; HRMS (ES): found 198.0432 (M + H)$^+$, $C_5H_8O_5S$ requires 198.0431 (M + H)$^+$; $^{293}[\alpha]_D = -7.92$ (c = 1.06, $CHCl_3$).

Methyl *S*-(2′,2′-dioxo-1,3,2-dioxathiolan-4′-yl)ethanoate 21. To a solution of cyclic sulfite ester **20** (0.50 g, 2.77 mmol) in DCM (10 ml) at 0 °C were added a solution of $NaIO_4$ (1.10 g, 5.11 mmol) in water (10 ml) and ruthenium dioxide (2–3 mg). The mixture was stirred to ensure full mixing of the phases until an apple-green colouration appeared. After 10 min, the organic layer was separated and stirred with several drops of 2-propanol for 15 min. After addition of anhydrous $MgSO_4$, the mixture was stirred for a further 10 min, filtered through Celite and evaporated to furnish cyclic sulfate ester **21** as an orange oil (0.56 g, 93.7%); ^{1}H NMR: 5.26 (1H, m, 4′-*H*), 4.85 (1H, dd, J = 9.2, 6.2 Hz, 5′-H_α), 4.45 (1H, dd, J = 9.2, 7.2 Hz, 5′-H_β), 3.70 (3H, s, OCH_3), 3.03 (1H, dd, J = 17.1, 6.4 Hz, 2-CH_α), 2.84 (1H, dd, J = 17.1, 7.4 Hz, 2-CH_β); ^{13}C NMR: 168.4 (*C*=O), 77.9 (4′-*C*), 72.5 (5′-*C*), 52.3 (O*C*H$_3$), 36.5 (2-*C*); ν_{max}/cm^{-1} (thin film): 2912, 1719, 1402, 1378, 1243, 1189, 1051; $^{293}[\alpha]_D = -18.89$ (c = 0.27, MeOH).

Methyl *R*-(5′,6′-dihydro-2′-thioxo-1,3-dithiolo[4,5-*b*]-1, 4-dithiin-5′-yl) ethanoate 22. 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (1.16 g, 2.86 mmol) was added to a solution prepared from sodium metal (0.14 g, 6.29 mmol) and dry methanol (40 ml) under nitrogen and the mixture stirred for 1 h at room temperature. A solution of cyclic sulfate ester **21** (0.56 g, 2.86 mmol) in dry methanol (5 ml) was added to the reaction mixture at 0 °C and stirring continued overnight at room temperature. The solvent was removed *in vacuo* and replaced with dry THF (40 ml), and the mixture refluxed for 5 h under nitrogen. The solvent was evaporated and the residue partitioned between DCM (100 ml) and water (50 ml). The organic phase was collected, washed with water (50 ml), dried ($MgSO_4$) and evaporated to yield a brown oil. Kugelrohr distillation removed methyl benzoate, and the residue was purified by flash chromatography (SiO_2, 2 : 1 chloroform–cyclohexane) to furnish thione **22** as a yellow oil (0.30 g, 35.5%); ^{1}H NMR: 4.12 (1H, m, 5′-*H*), 3.75 (3H, s, OCH_3), 3.45 (1H, dd, J = 13.5, 2.9 Hz, 6′-H_α), 3.26 (1H, dd, J = 13.5, 5.7 Hz, 6′-H_β), 2.92 (2H, d, J = 7.2 Hz, 2-H_2); ^{13}C NMR: 207.8 (*C*=S), 170.5 (*C*=O), 122.5, 121.3 (3′a-, 7′a-*C*), 52.3 (O*C*H$_3$), 39.3 (2-*C*), 38.2 (5′-*C*), 34.0 (6′-*C*); ν_{max}/cm^{-1} (thin film): 1732, 1486, 1437, 1408, 1361, 1296, 1242, 1220, 1173, 1061, 1032, 979, 891, 756; *m/z*: (APCI) 297 ([M + H]$^+$, 100), 197 ([C_3S_5 + H]$^+$, 45), 121 (5); HRMS (EI): found M$^+$ 295.9117, $C_8H_8O_2S_5$ requires 295.9122; $^{293}[\alpha]_D = +183$ (c = 0.15, $CHCl_3$).

Methyl *R*-(5′,6′-dihydro-2′-oxo-1,3-dithiolo[4,5-*b*]-1, 4-dithiin-5′-yl) ethanoate 23. To a solution of thione **22** (0.21 g, 0.71 mmol) in $CHCl_3$ (10 ml) and glacial acetic acid (3 ml) was added mercuric acetate (0.34 g, 1.06 mmol). After 2 h stirring

at room temperature, the mixture was filtered, and the solution was washed consecutively with saturated $NaHCO_3$ solution (3 × 20 ml) and H_2O (20 ml), dried (Na_2SO_4) and evaporated to afford oxo compound **23** as a brown oil (0.17 g, 85.6%); ^{1}H NMR: 4.09 (1H, m, 5′-*H*), 3.75 (3H, s, OCH_3), 3.45 (1H, dd, J = 13.4, 3.0 Hz, 6-H_α), 3.20 (1H, dd, J = 13.4, 5.8 Hz, 6-H_β), 2.89 (2H, d, J = 6.9 Hz, 2-H_2); ^{13}C NMR: 188.6 (S_2C=O), 170.5 (*C*=O), 113.3, 112.1 (3a′-, 7a′-*C*), 52.2 (O*C*H_3), 40.0 (2-*C*), 39.3 (5′-*C*), 35.2 (6′-*C*); ν_{max}/cm^{-1} (thin film): 2955, 1733, 1677, 1625, 1505, 1436, 1410, 1363, 1298, 1222, 1171, 1013, 984, 892, 764; *m*/*z* (EI): 280 (M^+, 74), 252 (32), 221 (24), 152 (44), 149 (53), 120 (100); HRMS (EI): found M^+ 279.9355, $C_8H_8O_3S_4$ requires 279.9351; $^{293}[\alpha]_D$ = +104 (c = 0.204, $CHCl_3$).

Methyl *R*-ET-ethanoate 15. A mixture of oxo compound **23** (0.12 g, 0.46 mmol) and the unsubstituted thione **24** (0.10 g, 0.64 mmol) was heated in triethyl phosphite (5 ml) to 90 °C under N_2 for 5 h to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 1 : 1 cyclohexane–DCM) to yield the donor **15** as an orange oil (0.10 g, 47.2%); ^{1}H NMR: 4.03 (1H, m, 5-*H*), 3.71 (3H, s, OCH_3), 3.31 (1H, dd, J = 13.3, 3.1 Hz, 6-H_α), 3.28 (4H, s, 5′, 6′-CH_2), 3.13 (1H, dd, J = 13.3, 5.4 Hz, 6-H_β), 2.84 (2H, d, J = 7.2 Hz, CH_2C=O); ^{13}C NMR: 170.7 (*C*=O), 113.8, 113.5, 112.7, 112.0, 111.3 (sp^2-*C*), 52.1 (O*C*H_3), 39.4 (5-*C*(CO)), 38.6 (5-*C*), 34.7 (6-*C*), 30.1 (5′, 6′-*C*); ν_{max}/cm^{-1} (KBr): 1733, 1434, 1408, 1359, 1290, 1220, 1170, 1006, 979, 917, 888, 773; HRMS (EI): found M^+ 455.8602, $C_{13}H_{12}O_2S_8$ requires 455.8603. Found: C, 34.0; H, 2.6%; $C_{13}H_{12}O_2S_8$ requires C, 34.1; H, 2.6%; $^{293}[\alpha]_D$ = +12.5 (c = 0.16, $CHCl_3$).

***S*,*S*-1,2-Diphenylethane-1,2-diol.** The diol was prepared following the literature procedure[29] using AD-mix-α, and isolated in 70% with [α] −91.5° (c = 1.0 in ethanol), corresponding to an optically pure product.[28]

(4′*S*,5′*S*) 4′,5′-Diphenyl-1′,3′-dioxolane-spiro[2′.6]-5,6-dihydro-7*H*-1,3-dithiolo[4,5-*b*]1,4-dithiepin-2-thione 32. Ketone **31**[26] (0.63 g, 2.50 mmol) and *S*,*S*-1,2-diphenylethane-1,2-diol (0.64 g, 3.00 mmol) and a few crystals of tosic acid were refluxed together in chloroform (100 ml) under a Soxhlet extractor which contained molecular sieves, for 24 h. The reaction mixture was washed with saturated sodium hydrogen carbonate solution (2 × 30 ml) and water (2 × 30 ml) and dried (Na_2SO_4). Chromatography, eluting with chloroform, gave the thione **32** (0.85 g, 75.9%) as a pale yellow solid; mp 162–163 °C; ^{1}H NMR: 7.30 (6H, m, Ar-H_6), 7.17 (4H, m, Ar-H_4), 4.84 (2H, s, 4′-, 5′-*H*), 3.25 (2H, br d, J = 14.5 Hz, 5-, 7-H_α), 3.07 (2H, br d, J = 14.5 Hz, 5-, 7-H_β); ^{13}C NMR: 210.2 (*C*=S), 138.6 br (3a-, 8a-*C*), 134.9, 128.9, 128.7, 126.6 (Ar-C_{12}), 108.7 (6-*C*), 86.2 (4′-, 5′-*C*), 41.2 (5-, 7-*C*); υ_{max} (KBr): 1496, 1260, 1110, 1090, 1052, 1032, 767, 746, 730, 700, 538; *m*/*z* (APCI): 449 ([M + H]$^+$, 100), 417 (10), 282 (28); HRMS (ES): found [M + H]$^+$ 448.9822, $C_{20}H_{16}O_2S_5$ + H requires 448.9827; $[\alpha]_D^{20}$ = −56.2° (c = 0.21 in DCM).

(4′*S*,5′*S*) 4′,5′-Diphenyl-1′,3′-dioxolane-spiro[2′.6]-5,6-dihydro-7*H*-1,3-dithiolo[4,5-*b*]1,4-dithiepin-2-one 33. Mercuric acetate (0.74 g, 2.32 mmol) was added to a solution of thione **32** (0.69 g, 1.55 mmol) in chloroform (30 ml) and acetic acid (10 ml) and stirred for 15 min. The mixture was filtered, and the solution washed with saturated sodium hydrogen carbonate solution (2 × 20 ml) and water (2 × 20 ml) and dried over anhydrous magnesium sulfate. Evaporation gave the oxo compound **33** as a cream solid (0.49 g, 73.6%); mp 98–99 °C; ^{1}H NMR: 7.27 (6H, m, Ar-H_6), 7.15 (4H, m, Ar-H_4), 4.81 (2H, s, 4′-, 5′-*H*), 3.20 (2H, br d, J = 14.5 Hz, 5-, 7-H_α), 3.02 (2H, br d, J = 14.5 Hz, 5β-, 7-H_β); ^{13}C NMR: 188.8 (*C*=O), 134.9, 128.9, 128.6, 126.6 (Ar-C_{12}), 128.3 (3a-, 8a-*C*), 108.2 (6-*C*), 86.2 (4′-, 5′-*C*), 41.3 (5-, 7-*C*); υ_{max} (KBr): 1670, 1617, 1496, 1455, 1390, 1262, 1239, 1102, 1011, 751, 730, 699, 532; *m*/*z* (APCI): 433 ([M + H]$^+$, 100), 239 (14), 238 (15), 237 (17); HRMS (ES): found [M + NH_4]$^+$ 450.0327, $C_{20}H_{17}O_3S_4$ + NH_4 requires 450.0321; $[\alpha]_D^{20}$ = − 68.1° (c = 0.88 in DCM).

Bis(4′*S*,5′*S*-4′,5′-diphenyl-1′,3′-dioxolane-spiro[2′.2]propan-1,3-dithio)TTF 16. The oxo compound **33** (0.39 g, 0.89 mmol) was heated in triethyl phosphite (10 ml) at 90 °C under nitrogen for 5 h. The triethyl phosphite was removed by kugelrohr distillation. Chromatography of the residue eluting with DCM gave the donor **16** (0.14 g, 37%); mp 149–153 °C (from chloroform); ^{1}H NMR: 7.25 (12H, m, Ar-H_{12}), 7.14 (8H, m, Ar-H_8), 4.76 (4H, s, 2 × 4′-, 5′-*H*), 3.02 (4H, br d, J = 14.5 Hz, 2 × 5-, 7-H_α), 2.92 (4H, br d, J = 14.5 Hz, 2 × 5-, 7-H_β); ^{13}C NMR: 135.1, 128.7, 128.6, 126.6 (Ar-C_{24}), 112.0 (2 × 3a-, 8a-*C*) and 106.2 (2 × 2-*C*), 86.0 (2 × 4′-, 5′-*C*), 41.1 (2 × 5-, 7-*C*); υ_{max} (KBr): 1604, 1496, 1453, 1390, 1283, 1260, 1238, 1211, 1187, 1100, 1012, 902, 764, 753, 731, 698, 647, 532; *m*/*z* (APCI): 833 ([M + H]$^+$, 100), 449 (30), 417 (17), 361 (19); found C, 57.7; H, 3.9% $C_{40}H_{32}O_4S_8$ requires C, 57.6; H, 3.9%; $[\alpha]_D^{20}$ = − 99.3° (c = 0.6 in DCM).

(4a*R*,5*R*,7*S*,8a*S*)-4a,5,6,7,8,8a-Hexahydro-5,7-methano-4a,6,6-trimethyl-1,3-dithiolo[4,5-*b*][1,4]benzodithiin-2-thione 38. A suspension of trithione **36** (1.00 g, 5.1 mmol) in a solution of (−)-α-pinene **37** (0.35 g, 2.5 mmol) and toluene (75 ml) was heated to reflux for 13 h. The reaction mixture was filtered hot and the filtrate was collected, evaporated and purified by chromatography on silica eluting with cyclohexane to yield thione **38** as a yellow brown solid (0.71 g, 83%); mp 139–140 °C; ^{1}H NMR: 3.69 (1H, dd, J = 7.7, 9.5 Hz, 8a-*H*), 2.39 (1H, ddd, J = 3.6, 9.5, 14.1 Hz, 8-H_α), 2.24 (1H, ddd, J = 2.2, 6.1, 10.9 Hz, 10-H_α), 2.15 (1H, t, J = 5.8 Hz, 5-*H*), 1.88 (1H, m, 7-*H*), 1.66 (1H, ddd, J = 2.3, 7.7, 14.1 Hz, 8-H_β), 1.48 (3H, s, 6-(CH_3)$_\alpha$), 1.23 (3H, s, 6-(CH_3)$_\beta$), 1.23 (1H, m, 10-H_β), 1.00 (3H, s, 4a-CH_3); ^{13}C NMR: 210.7 (2-*C*), 140.4 (3a-*C*), 133.3 (9a-*C*), 70.9 (4a-*C*), 56.0 (5-*C*), 51.1 (8a-*C*), 42.4 (6-*C*), 39.5 (7-*C*), 36.4 (8-*C*), 29.8 (10-*C*), 29.4 (6-(*C*H_3)$_\alpha$), 27.7 (6-(*C*H_3)$_\beta$), 23.5 (4a-*C*H_3); ν_{max}/cm^{-1} (KBr): 2910, 1465, 1443, 1385, 1373, 1268, 1225, 1057, 1043, 1021, 918, 898, 792, 574, 512; *m*/*z* (ES): 333 [M + H]$^+$ (100%); found C, 46.9; H, 5.0% $C_{13}H_{16}S_5$ requires C, 47.0; H, 4.9%; $[\alpha]_D^{20}$ = +26.3° (c = 0.3, DCM).

(4a*R*,5*R*,7*S*,8a*S*)-4a,5,6,7,8,8a-Hexahydro-5,7-methano-4a,6,6-trimethyl-1,3-dithiolo[4,5-*b*][1,4]benzodithiin-2-one 43. To a solution of thione **38** (0.17 g, 0.51 mmol) in chloroform (10 ml) were added mercuric acetate (0.24 g, 0.75 mmol) and glacial acetic acid (1.5 ml). A white precipitate formed immediately. After stirring for 2 h, the mixture was filtered and the solid residue washed with chloroform. The combined filtrates were collected and neutralised with aqueous sodium carbonate. The organic layer was collected and washed with water, brine and dried ($MgSO_4$). Concentration *in vacuo* yielded oxo compound **43** as a pale yellow oil (0.15 g, 94%); ^{1}H NMR: 3.72 (1H, dd, J = 7.4, 9.4 Hz, 8a-*H*), 2.42 (1H, m, 8-H_α), 2.31 (1H, m, 10-H_α), 2.13 (1H, t, J = 5.9 Hz, 5-*H*), 1.94 (1H, m, 7-*H*), 1.74 (1H, ddd, J = 2.3, 7.4, 14.0 Hz, 8-H_β), 1.52 (3H, s, 6-(CH_3)$_\alpha$), 1.28 (3H, s, 6-(CH_3)$_\beta$), 1.28 (1H, t, J = 5.3 Hz, 10-H_β), 1.05 (3H, s, 4a-CH_3); ^{13}C NMR: 190.0 (2-*C*), 131.1 (3a-*C*), 124.2 (9a-*C*), 71.7 (4a-*C*), 55.9 (5-*C*), 51.5 (8a-*C*), 42.3 (6-*C*), 39.5 (7-*C*), 36.4 (8-*C*), 29.8 (10-*C*), 29.3 (6-(*C*H_3)$_\alpha$), 27.7 (6-(*C*H_3)$_\beta$), 23.6 (4a-*C*H_3); ν_{max}/cm^{-1} (thin film): 2922, 2870, 1674, 1621, 1472, 1449, 1387, 1375, 1270, 1126, 1013, 921, 880, 792, 752; *m*/*z* (ES): found [M + H]$^+$ 317 (100%); $[\alpha]_D^{20}$ = +35.2° (c = 0.3, DCM).

(1′*R*,5*S*,5′*S*)-Spiro[6′,6′-dimethyl-bicyclo[3.1.1]heptane]-2′,5-[5,6-dihydro-[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione] 40. A suspension of trithione **36** (7.00 g, 40 mmol) in a mixture of (−)-β-pinene (2.70 g, 20 mmol) and toluene (500 ml) was refluxed for 24 h. The reaction mixture was filtered hot and the solid residue was washed with chloroform. The combined filtrates were evaporated and the residue purified by column chromatography on silica eluting with cyclohexane to yield

thione **40** as a yellow solid (5.31 g, 80%); mp 99–100 °C; ^{1}H NMR: 3.40 (1H, d, $J = 13.6$ Hz, 6-H_α), 3.29 (1H, d, $J = 13.6$ Hz, 6-H_β), 2.41 (1H, m, 7′-H_α), 2.28 (1H, m, 1′-*H*), 2.16 (1H, m, 3′-H$_\alpha$), 1.98–2.12 (4H, m, 3′-H_β, 5′-*H*, 4′-H_2), 1.59 (1H, d, $J =$ 10.6 Hz, 7′-H_β), 1.30 (3H, s, 6′-(CH_3)$_\alpha$), 1.07 (3H, s, 6′-(CH_3)$_\beta$); ^{13}C NMR: 208.1 (2-*C*), 124.5, 119.9 (3a-, 7a-*C*), 55.4 (5-*C*), 50.5 (1′-*C*), 41.1 (6-*C*), 40.3 (5′-*C*), 40.2 (6′-*C*), 30.5 (3′-*C*), 29.4 (7′-*C*), 27.8 (6′-(*C*H$_3$)$_\alpha$), 25.3 (4′-*C*), 23.4 (6′-(*C*H$_3$)$_\beta$); ν_{max}/cm^{-1} (KBr): 2909, 1484, 1461, 1404, 1060, 921, 887, 515, 465; *m/z* (ES): found [M + H]$^+$ 333 (100%); found C, 47.0; H, 4.8%; $C_{13}H_{16}S_5$ requires C, 47.0; H, 4.9%; $[\alpha]_D^{20} = -8.7°$ ($c = 0.3$, DCM).

(1′*R*,5*S*,5′*S*)-Spiro[6′,6′-dimethyl-bicyclo[3.1.1]heptane]-2′,5-[5,6-dihydro-[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-one] 44. To a solution of the thione **40** (1.15 g, 36 mmol) in chloroform (20 ml) were added mercuric acetate (1.6 g, 5 mmol) and glacial acetic acid (5 ml). A white solid precipitated almost immediately. The reaction mixture was stirred for 2 h, filtered and the solid residue washed with chloroform. The combined filtrates were collected and neutralised with aqueous sodium carbonate, the organic layer collected and washed with water and dried ($MgSO_4$). Concentration *in vacuo* yielded **44** as a pale oil (1.15 g, 95%); ^{1}H NMR: 3.42 (1H, d, $J = 13.6$ Hz, 6-H_α), 3.34 (1H, d, $J = 13.6$ Hz, 6-H_β), 2.41 (1H, m, 7′-H_α), 2.32 (1H, m, 1′-*H*), 1.97–2.25 (5H, m, 3′-,4′-H_2, 5′-*H*), 1.59 (1H, d, $J =$ 10.6 Hz, 7′-H_β), 1.30 (3H, s, 6′-(CH_3)$_\alpha$), 1.06 (3H, s, 6′-(CH_3)$_\beta$); ^{13}C NMR: 180.2 (2-*C*), 114.2, 110.2 (3a, 7a-*C*), 56.8 (5-*C*), 50.8 (1′-*C*), 42.6 (6-*C*), 40.4 (5′-*C*), 40.3 (6′-*C*), 30.7 (3′-*C*), 29.4 (7′-*C*), 27.9 (6′-(*C*H$_3$)$_\alpha$), 25.3 (4′-*C*), 23.5 (6′-(*C*H$_3$)$_\beta$); ν_{max}/cm^{-1} (KBr): 2916, 1680, 1638, 1503, 1461, 1384, 1369, 1213, 917, 891, 756; *m/z* (ES): found [M + H]$^+$ 317 (100%); HRMS (EI): found M$^+$ 316.0072, $C_{13}H_{16}OS_4$ requires 316.0078; $[\alpha]_D^{20} = -36.0°$ ($c = 0.3$, DCM).

(1″*R*,5*S*,5″*S*)-Spiro[6″,6″-dimethyl-bicyclo[3.1.1]heptane]-2″,5-ET 17. A mixture of oxo compound **44** (0.20 g, 0.63 mmol), unsubstituted thione **24** (0.30 g, 1.3 mmol) and freshly distilled triethyl phosphite (10 ml) was heated to 90 °C for 12 h. The reaction mixture was concentrated and purified by column chromatography on silica eluting with cyclohexane to yield an orange solid. The dried solid was finely divided and stirred with dry methanol (10 ml) for 24 h. The orange solid was collected and washed with further methanol and dried to yield donor **17** (0.12 g, 42%); mp 172–174 °C (dec.); ^{1}H NMR: 3.31 (1H, d, $J = 13.4$ Hz, 6-H_α), 3.28 (4H, s, 5″-, 6″-H_2), 3.19 (1H, d, $J =$ 13.4 Hz, 6-H_β), 2.39 (1H, m, 7′-H_α), 2.24 (1H, t, $J = 5.4$ Hz, 1′-*H*), 1.95–2.14 (5H, m, 3′-, 4′-H_2, 5′-*H*), 1.61 (1H, d, $J =$ 10.6 Hz, 7′-H_β), 1.29 (3H, s, 6′-(CH_3)$_\alpha$), 1.05 (3H, s, 6′-(CH_3)$_\beta$); ^{13}C NMR: 114.7, 113.9, 113.8, 112.6, 110.2 (sp^2-*C*), 55.6 (5-*C*), 50.7 (1′-*C*), 41.7 (6-*C*), 40.5 (5′-*C*), 40.3 (6′-*C*), 30.4 (3′-*C*), 30.2 (5″-, 6″-*C*), 29.6 (7′-*C*), 27.9 (6′-(*C*H$_3$)$_\alpha$), 25.4 (4′-*C*), 23.6 (6′-(*C*H$_3$)$_\beta$); ν_{max}/cm^{-1} (KBr): 2924, 1508, 1458, 1401, 1382, 1363, 1261, 1230, 1188, 1003, 907, 878, 772; found C, 44.2; H, 4.4%; $C_{18}H_{16}S_8$ requires C, 43.9; H, 4.1%; $[\alpha]_D^{20} = -35.7°$ ($c =$ 0.3, DCM).

Homocoupling of 44, preparation of mixture of donors 47a and 47b. A mixture of oxo compound **44** (0.22 g, 0.68 mmol) and freshly distilled triethyl phosphite (5 ml) was heated to 90 °C for 5 h. The reaction mixture was concentrated and purified by column chromatography on silica eluting with cyclohexane to yield an orange solid. This solid was dried, then finely divided before being stirred with dry methanol (10 ml) for 24 h. The mixture was filtered and the orange solid washed with methanol and dried to yield **47a/47b** (0.10 g, 46%); mp 150 °C (dec.); ^{1}H NMR: 3.30 (2H, d, $J = 13.3$ Hz, 2 × 6-H_α), 3.18 (2H, d, $J =$ 13.3 Hz, 2 × 6-H_β), 2.38 (2H, m, 2 × 7′-H_α), 1.96–2.23 (12H, m, 2 × 3′-, 4′-H_2, 1′-,5′-*H*), 1.58 (2H, d, $J = 10.9$ Hz, 2 × 3′-*H*), 1.26 (6H, s, 2 × 6′-(CH_3)$_\alpha$), 1.03 (6H, s, 2 × 6′-(CH_3)$_\beta$); ^{13}C NMR: 113.8, 112.6, 110.2 (sp^2-*C*), 55.6 (2 × 5-*C*), 50.7 (2 × 1′-*C*), 41.8 (2 × 6-*C*), 40.5 (2 × 5′-*C*), 40.3 (2 × 6′-*C*), 30.5 (2 × 3′-*C*), 29.6 (2 × 7′-*C*), 28.0 (2 × 6′-(*C*H$_3$)$_\alpha$), 25.4 (2 × 4′-*C*), 23.6 (2 × 6′-(*C*H$_3$)$_\beta$); ν_{max}/cm^{-1} (KBr): 2978, 2908, 2866, 1463, 1404, 1383, 1364, 1261, 1218, 1005, 919, 884, 771; *m/z* (EI): found [M]$^+$ 600 (10%), 69 (100%); HRMS (EI): found [M]$^+$ 600.0273, $C_{26}H_{32}S_8$ requires 600.0264; $[\alpha]_D^{20} = -35.0°$ ($c = 0.3$, DCM).

(4a*R*,7*R*,8*S*,8a*S*)-4a,5,6,7,8,8a-Hexahydro-7,8-isopropano-4a-methyl-1,3-dithiolo[4,5-*b*][1,4]benzodithiin-2-thione 42. A suspension of trithione **36** (7.00 g, 40 mmol) in a mixture of (+)-2-carene (2.50 g, 18 mmol) and toluene (300 ml) was refluxed for 24 h. The reaction mixture was filtered hot and the solid residue was washed with chloroform. The combined filtrates were collected, evaporated and purified by column chromatography on silica eluting with cyclohexane to yield thione **42** as a yellow solid (5.52 g, 90%); mp 125–126 °C; ^{1}H NMR: 2.53 (1H, d, $J = 5.0$ Hz, 8a-*H*), 1.97 (1H, m, 6-H_α), 1.84 (1H, m, 6-H_β), 1.58 (1H, m, 5-H_α), 1.44 (3H, s, 10-(CH_3)$_\alpha$), 1.40 (1H, m, 5-H_β), 1.02 (3H, s, 10-(CH_3)$_\beta$), 0.97 (3H, s, 4a-CH_3), 0.89 (1H, dd, $J = 9.1$, 5.0 Hz, 8-*H*), 0.77 (1H, m, 7-*H*); ^{13}C NMR: 208.2 (2-*C*), 122.9, 117.4 (3a-, 9a-*C*), 47.9 (4a-*C*), 45.3 (8a-*C*), 31.0 (10-(*C*H$_3$)$_\alpha$), 28.3 (10-(*C*H$_3$)$_\beta$), 36.2 (6-C), 28.9 (8-*C*), 19.8 (7-*C*), 18.6 (10-*C*), 15.6 (5-*C*), 15.4 (4a-*C*H$_3$); ν_{max}/cm^{-1} (KBr): 2917, 2858 1484, 1450, 1376, 1262, 1062, 908, 844, 803, 737, 703; *m/z* (ES): found [M + H]$^+$ 333 (100%); found C, 47.0; H, 4.8%; $C_{13}H_{16}S_5$ requires C, 47.0; H, 4.9%; $[\alpha]_D^{20} = +421.0°$ ($c = 0.3$, DCM).

(4a*R*,7*R*,8*S*,8a*S*)-4a,5,6,7,8,8a-Hexahydro-7,8-isopropano-4a-methyl-1,3-dithiolo[4,5-*b*][1,4]benzodithiin-2-one 45. To a solution of the thione **42** (0.58 g, 1.8 mmol) in chloroform (20 ml) was added mercuric acetate (0.84 g, 2.6 mmol) and glacial acetic acid (3 ml). A white solid precipitated almost immediately. The reaction mixture was stirred for 2 h, filtered and the solid residue washed with chloroform. The combined filtrates were collected and neutralised with aqueous sodium carbonate. The organic layer was collected, washed with water and dried ($MgSO_4$). Concentration *in vacuo* yielded oxo compound **45** as a thick pale yellow oil (0.51 g, 92%); ^{1}H NMR: 2.53 (1H, d, $J = 5.2$ Hz, 8a-*H*), 1.99 (1H, m, 6-H_α), 1.83 (1H, dd, $J = 8.9$, 15.1 Hz, 6-H_β), 1.59 (1H, dd, $J = 7.9$, 14.8 Hz, 5-H_α), 1.50 (3H, s, 10-(CH_3)$_\alpha$), 1.31 (1H, m, 5-H_β), 1.04 (3H, s, 10-(CH_3)$_\beta$), 0.98 (3H, s, 4a-CH_3), 0.96 (1H, m, 8-*H*), 0.82 (1H, m, 7-*H*); ^{13}C NMR: 189.0 (2-*C*), 112.3, 107.1 (3a-, 9a-*C*), 49.1 (4a-*C*), 46.2 (8a-*C*), 30.9 (10-(*C*H$_3$)$_\alpha$), 28.3 (10-(*C*H$_3$)$_\beta$), 36.3 (6-*C*), 28.9 (8-*C*), 19.8 (7-*C*), 18.4 (10-*C*), 15.7 (5-*C*H$_3$), 15.4 (4a-*C*H$_3$); ν_{max} (KBr): 2921, 2862, 1681, 1640, 1504, 1453, 1377, 1126, 906, 731, 649 cm^{-1}; *m/z* (ES): found [M + H]$^+$ 317 (100%); HRMS (ES): found [M + NH$_4$]$^+$ 334.0418, $C_{13}H_{16}OS_4$ + NH$_4$ requires 334.0422; $[\alpha]_D^{20} = -143.0°$ ($c = 0.45$, DCM).

Homocoupling of 45, preparation of mixture of donors 48a and 48b. A mixture of oxo compound **45** (0.20 g, 0.63 mmol) and freshly distilled triethyl phosphite (5 ml) was heated to 90 °C for 5 h. The reaction mixture was concentrated and purified by column chromatography on silica gel eluting with cyclohexane to yield an orange solid. This dried solid was finely divided before being stirred with dry methanol (10 ml) for 24 h. The mixture was filtered and the orange solid washed with further methanol and dried to yield **48a/48b** (0.08 g, 42%); mp >200 °C; ^{1}H NMR: 2.49 (1H, d, $J = 5.0$ Hz, 8a-*H*), 2.00 (1H, m, 6-H_α), 1.83 (1H, m, 6-H_β), 1.58 (1H, m, 5-H_α), 1.43 (3H, s, 10-(CH_3)$_\alpha$), 1.36 (1H, m, 5-H_β), 1.04 (3H, s, 10-(CH_3)$_\beta$), 0.99 (3H, s, 4a-CH_3), 0.90 (1H, dd, $J = 5.0$, 9.0 Hz, 8-*H*), 0.79 (1H, m, 7-*H*); ^{13}C NMR: 112.8, 111.0, 107.3 (sp^2-*C*), 47.9 (2 × 4a-*C*), 45.6 (2 × 8a-*C*), 31.0 (2 × 10-(*C*H$_3$)$_\alpha$), 28.4 (2 × 10-(*C*H$_3$)$_\beta$), 36.1 (2 × 6-*C*), 29.0 (2 × 8-*C*), 19.9 (2 × 7-*C*), 18.3 (2 × 10-*C*), 15.9 (2 × 5-*C*), 15.6 (2 × 4a-*C*H$_3$); ν_{max}/cm^{-1} (KBr): 2919, 2856, 1450, 1376, 1251, 1105, 1080, 1054, 1012, 910, 886, 773; *m/z* (EI): found [M]$^+$ 600 (50%), 463 (50%), 77 (100%); HRMS (EI): found [M]$^+$ 600.0270, $C_{26}H_{32}S_8$ requires 600.0264; $[\alpha]_D^{20} = -68.5°$ ($c = 0.26$, DCM).

X-Ray crystallography of 38, 40 and 42†

The structures were solved by direct methods and refined on F^2 using SHELX-97.[55] All H atoms were found from difference Fourier maps. Non-H atoms were assigned anisotropic displacement parameters. Graphics and geometry calculations were made using PLATON,[56] ORTEP-3[57] and POVRAY.[58]

***Crystal data* for 38.** $C_{13}H_{16}S_5$, $M = 332.6$, monoclinic, $a = 7.2322(2)$, $b = 9.3635(2)$, $c = 11.3961(5)$ Å, $\beta = 106.405(1)^\circ$, $V = 740.31(3)$ Å^3, $P2_1$, $Z = 2$, $T = 120(2)$ K, μ(Mo–Kα) = 0.762 mm^{-1}, $D_c = 1.49$ g cm^{-3}, 3383 unique reflections (R_{int} 0.081). The refinement converged for 3231 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.039$ and $wR_2 = 0.091$, goodness-of-fit = 1.062 and Flack parameter = −0.08(9). Crystals were grown from THF.

***Crystal data* for 40.** $C_{13}H_{16}S_5$, $M = 332.6$, monoclinic, $a = 6.3217(2)$, $b = 13.4551(4)$, $c = 17.5120(5)$ Å, $\beta = 93.0600(16)^\circ$, $V = 1487.43(8)$ Å^3, $P2_1$, $Z = 4$, $T = 120(2)$ K, μ(Mo–Kα) = 0.758 mm^{-1}, $D_c = 1.49$ g cm^{-3}, 6771 unique reflections (R_{int} 0.0612). The refinement converged for 5327 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.041$ and $wR_2 = 0.069$, goodness-of-fit = 0.925 and Flack parameter = 0.03(6). Crystals were grown from cyclohexane–DCM.

***Crystal data* for 42.** $C_{13}H_{16}S_5$, $M = 332.6$, orthorhombic, $a = 7.6090(1)$, $b = 9.7890(2)$, $c = 20.1711(5)$ Å, $V = 1502.43(1)$ Å^3, $P2_12_12_1$, $Z = 4$, $T = 120(2)$ K, μ(Mo–Kα) = 0.751 mm^{-1}, $D_c = 1.47$ g cm^{-3}, 3415 unique reflections (R_{int} 0.053). The refinement converged for 3208 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.025$ and $wR_2 = 0.059$, goodness-of-fit = 1.044 and Flack parameter = −0.03(6). Crystals were grown from cyclohexane–DCM.

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References

1 G. L. J. A. Rikken, E. Raupach, V. Krstic and S. Roth, *Mol. Phys.*, 2002, **100**, 1155; V. Krstic, S. Roth, M. Burghard, K. Kern and G. L. J. A. Rikken, *J. Chem. Phys.*, 2002, **117**, 11315.
2 V. Krstic and G. L. J. A. Rikken, *Chem. Phys. Lett.*, 2002, **364**, 51; G. L. J. A. Rikken, J. Folling and P. Wyder, *Phys. Rev. Lett.*, 2001, **87**, art. no. 236602;; Y. Miyamoto, S. G. Louie and M. L. Cohen, *Phys. Rev. Lett.*, 1996, **76**, 2121.
3 J. Singleton, N. Harrison, M. M. Honold, H. Yaguchi, C. Mielke, D. Rickel, I. Deckers, P. H. P. Reinders, F. Herlach, M. Kurmoo and P. Day, *Physica B*, 1998, **246**, 6.
4 M. M. Honold, N. Harrison, M. V. Katsovnik, H. Yaguchi, J. Singleton, C. H. Mielke, N. D. Kushch, M. Kurmoo and P. Day, *Phys. Rev. B*, 2000, **62**, 7908; H. Yaguchi, N. Harrison, M. M. Honold, C. Mielke, J. Singleton, P. J. Gee, D. Rickel, I. Deckers, P. H. P. Reinders, F. Herlach, M. Kurmoo and P. Day, *Physica B*, 1998, **251**, 75.
5 J. D. Dunitz, A. Karrer and J. D. Wallis, *Helv. Chim. Acta*, 1986, **69**, 69.
6 A. Karrer, J. D. Dunitz, J. D. Wallis, B. Hilti, C. W. Mayer, M. Buerkle and J. Pfeiffer, *Helv. Chim. Acta*, 1987, **70**, 942.
7 J. S. Zambounis, C. W. Mayer, K. Hauenstein, B. Hilti, W. Hofherr, J. Pfeiffer, M. Buerkle and G. Rihs, *Adv. Mater.*, 1992, **4**, 33.
8 S. Matsumiya, A. Izuoka, T. Sugawara, T. Taruishi, Y. Kawada and M. Tokumoto, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1949.
9 J. A. Schlueter, B. H. Ward, U. Geiser, H. H. Wang, A. M. Kini, J. Parakka, E. Morales, H. J. Koo, M. H. Whangbo, R. W. Winter, J. Mohtasham and G. L. Gard, *J. Mater. Chem.*, 2001, **11**, 2008; B. R. Jones, I. Olejniczak, J. Dong, J. M. Pigos, Z. T. Zhu, A. D. Garlach, J. L. Musfeld, H. J. Khu, M. H. Whangbo, J. A. Schlueter, B. H. Ward, E. Morales and A. M. Kini, *Chem. Mater.*, 2000, **12**, 2490; B. H. Ward, J. A. Schlueter, U. Geiser, H. H. Wang, E. Morales, J. P. Parakka, Y. S. Thomas, J. M. Williams, P. G. Nixon, R. W. Winter, G. L. Gard, H.-J. Koo and M.-H. Whangbo, *Chem. Mater.*, 2000, **12**, 343.
10 E. Coronado, J. R. Galen-Mascaros, C. J. Gomez-Garcia and C. Laukhin, *Nature*, 2000, **408**, 447.
11 L. Martin, S. S. Turner, P. Day, K. M. A. Malik, S. J. Coles and M. B. Hursthouse, *Chem. Commun.*, 1999, 513; L. Martin, S. S. Turner, P. Day, P. Guionneau, J. A. K. Howard, K. M. A. Malik, M. B. Hursthouse, M. Uriuchi and K. Yakushi, *Inorg. Chem.*, 2001, **40**, 1363.
12 F. Leurquin, T. Ozturk, M. Pilkington and J. D. Wallis, *J. Chem. Soc., Perkin Trans. 1*, 1997, 3173.
13 T. Ozturk, C. R. Rice and J. D. Wallis, *J. Mater. Chem.*, 1995, **5**, 1553.
14 G. A. Horley, T. Ozturk, F. Turksoy and J. D. Wallis, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3225.
15 T. Ozturk, F. Turksoy and E. Ertas, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1999, **153–154**, 417.
16 C. Rethore, M. Fourmigué and N. Avarvari, *Chem. Commun.*, 2004, 1384.
17 R. Shenhar, H. Wang, R. E. Hoffman, L. Frish, L. Avram, I. Willner, A. Rajca and M. Rabinowitz, *J. Am. Chem. Soc.*, 2002, **124**, 4685; A. Rajca, H. Wang, P. Bolshov and S. Rajca, *Tetrahedron*, 2001, **57**, 3725.
18 M. Miyasaka, M. Pink, A. Rajca, S. Rajca, *Chem.–Eur. J.*, accepted; A. Rajca, H. Wang, V. Pawitranon, T. J. Brett and J. J. Stezowski, *Chem. Commun.*, 2001, 1060; A. Rajca, H. Wang, M. Pink and S. Rajca, *Angew. Chem., Int. Ed.*, 2000, **39**, 4481.
19 Q.-S. Hu, D. Vitharana, G.-Y. Liu, V. Jain, M. W. Wagaman, L. Zhang, T. R. Lee and L. Pu, *Macromolecules*, 1996, **29**, 1082.
20 P. A. McCarthy, J. Huang, S.-C. Yang and H.-L. Wang, *Langmuir*, 2002, **18**, 259.
21 Y. Yang and M. Wan, *J. Mater. Sci.*, 2002, **12**, 897.
22 P. Gerbier, N. Domingo, J. Gomez-Segura, D. Ruiz-Molina, D. B. Amabilino, J. Tejada, B. E. Williamson and J. Veciana, *J. Mater. Chem.*, 2004, **14**, 2455.
23 S. Saito, T. Ishikawa, A. Kuroda and T. Moriwake, *Tetrahedron*, 1992, **48**, 4067.
24 R. J. Brown, G. Cameresa, J.-P. Griffiths, P. Day and J. D. Wallis, *Tetrahedron Lett.*, 2004, **45**, 5103.
25 T. Ozturk, D. C. Povey and J. D. Wallis, *Tetrahedron*, 1994, **50**, 11205.
26 W.-C. Wu and Y.-J. Shen, *Youji Huaxue*, 1999, **19**, 587; G. C. Papavassiliou, G. A. Mousdis, S. Y. Yiannopoulos, V. C. Kakoussis and J. S. Zambounis, *Synth. Met.*, 1988, **27**, B373–B378.
27 V. Khodorkovski, A. Edzifna and O. Neilands, *J. Mol. Electron.*, 1989, **5**, 33; M. Minzuno, A. F. Garito and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1978, 18; S. Ikegawa, K. Miyawaki, T. Nogami and Y. Shirota, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2770.
28 K. B. Sharpless, W. Amberg, Y. L. Bennani, G. A. Crispino, J. Hartung, K.-S. Jeong, H. L. Kwong, K. Morikawa, Z.-M. Wang, D. Xu and X.-L. Zhang, *J. Org. Chem.*, 1992, **57**, 2768.
29 E. N. Jacobsen, I. Marko, W. S. Mungall, G. Schroder and K. B. Sharpless, *J. Am. Chem. Soc.*, 1988, **110**, 1968.
30 M. R. Bryce and G. J. Marshallsay, *Tetrahedron Lett.*, 1991, **32**, 6033; G. J. Marshallsay, M. R. Bryce, G. Cooke, T. Joergensen, J. Becher, C. D. Reynolds and S. Wood, *Tetrahedron*, 1993, **49**, 6849.
31 N. Saygili, R. J. Brown, P. Day, R. Hoelzl, P. Kathirgamanathan, E. E. R. Mageean, T. Ozturk, M. Pilkington, M. M. B. Qayyum, S. S. Turner, L. Vorwerg and J. D. Wallis, *Tetrahedron*, 2001, **57**, 5015.
32 J. D. Wallis, unpublished work.
33 O. Y. Neilands, Y. Y. Katsens and Y. N. Kreitsberga, *Zh. Org. Khim.*, 1989, **25**, 658.
34 W. Xu, D. Zhang, H. Li and D. Zhu, *J. Mater. Chem.*, 1999, **9**, 1245; B. Y. Khodorkovskii, G. Pukitis, A. Y. Puplovskii, A. Edzina and O. Y. Neilands, *Khim. Geterotsikl. Soedin.*, 1990, 131; L. M. Goldenberg, V. Y. Khodorkovsky, J. Y. Becker, P. J. Lukes, M. R. Bryce, M. C. Petty and J. Yarwood, *Chem. Mater.*, 1994, **6**, 1426; A. M. Kini, J. P. Parakka, U. Geiser, H.-H. Wang, F. Rivas, E. DiNino, S. Thomas, J. D. Dudek and J. M. Williams, *J. Mater. Chem.*, 1999, **9**, 883.
35 J.-P. Griffiths, A. A. Arnal, G. Appleby and J. D. Wallis, *Tetrahedron Lett.*, 2004, **45**, 2813.
36 B. Y. Khodorkovskii, G. Pukitis, A. Y. Puplovskii, A. Edzina and O. Y. Neilands, *Khim. Geterotsikl. Soedin.*, 1990, 131.
37 A. M. Kini, J. P. Parakka, U. Geiser, H.-H. Wang, F. Rivas, E. DiNino, S. Thomas, J. D. Dudek and J. M. Williams, *J. Mater. Chem.*, 1999, **9**, 883.
38 R. Medne, J. Kacens, I. Kraupsa and O. Y. Neilands, *Khim. Geterotsikl. Soedin.*, 1991, **10**, 1317; G. G. Abashev, E. V. Shklyaeva, V. S. Russkikh and S. Krol, *Mendeleev Commun.*, 1997, 127.
39 D.-Y. Noh, H.-J. Lee, J. Hong and A. E. Underhill, *Tetrahedron Lett.*, 1996, **37**, 7603.

40 A. I. Kotov, L. I. Buravov, V. V. Gritsenko, A. A. Bardin, S. V. Konvalikhin, O. A. Dyachecko, E. B. Yagubskii, K. V. Van and M. Mizuno, *Synth. Met.*, 2001, **120**, 861.
41 H. Nishikawa, T. Morimoto, T. Kodama, I. Ikemoto, K. Kikuchu, J. Yamada, H. Yoshino and K. Murata, *J. Am. Chem. Soc.*, 2002, **124**, 730.
42 J. Yamada, R. Oka, T. Mangetsu, H. Akutsu, S. Nakatsuji, H. Nishikawa, I. Ikemoto and K. Kikuchi, *Chem. Mater.*, 2001, **13**, 1770.
43 S. Larsen, T. Thorsteinsson, S. Bowadt, T. K. Hansen, K. S. Varma, J. Becher and A. E. Underhill, *Acta Chem. Scand.*, 1991, **45**, 709.
44 Q. Fang, W.-T. Yu, J.-H. Xu, H. Lei and M.-H. Jiang, *Acta Crystallogr.*, 1994, **50**, 1519; M. B. Hursthouse, D. E. Hibbs, A. E. Underhill, CCDC, private communication, 2003.
45 H. J. Nam, H.-J. Lee and D.-Y. Noh, *Polyhedron*, 2004, **23**, 115.
46 J. D. Wallis and J. D. Dunitz, *Acta Crystallogr., Sect. C*, 1988, **44**, 1037.
47 P. J. Skabara, I. M. Serebryakov, D. M. Roberts, I. F. Perepichka, S. J. Coles and M. B. Hursthouse, *J. Org. Chem.*, 1999, **64**, 6418.
48 Z. H. Chohan, R. A. Howie, J. L. Wardell and S. M. S. V. Wardell, *J. Chem. Crystallogr.*, 1999, **29**, 1165; C. Wang, M. R. Bryce, A. S. Batsanov and J. A. K. Howard, *Chem.–Eur. J.*, 1997, **3**, 1679; C. Jia, D. Zhang, W. Xu and D. Zhu, *Org. Lett.*, 2001, **3**, 1941.
49 J. Yamada, S. Tanaka, H. Anzai, T. Sato, H. Nishikawa, I. Ikemoto and K. Kikuchi, *J. Mater. Chem.*, 1997, **7**, 1311.
50 G. A. Jeffrey and A. Robbins, *Acta Crystallogr., Sect. B*, 1980, **36**, 1820.
51 G. A. Tolstikov, B. M. Lerman, L. I. Umanskaya, Y. Y. Struchkov and D. S. Yufit, *Russ. Chem. Bull.*, 1985, 597.
52 H. Brunner, D. Mijolovic and M. Zabel, *Synthesis*, 2001, 1671.
53 A. P. K. Orrell and J. D. Wallis, *J. Chem. Soc., Perkin Trans. 2*, 1984, 227.
54 K. B. Simonsen, N. Svenstrup, J. Lau, O. Simonsen, P. Mork, G. J. Kristensen and J. Becher, *Synthesis*, 1996, 407.
55 G. M. Sheldrick, *SHELX97, Program for the solution and refinement of crystal structures*, University of Gottingen, Germany, 1997.
56 L. Farrugia, *PLATON (A. L. Spek, University of Utrecht) for Windows*, University of Glasgow, 2004.
57 C. K. Johnson and M. N. Burnett, *ORTEPIII Report ORNL-6895*, Oak Ridge National Laboratory, Tennessee, USA.
58 POVRAY, Persistence of Vision Ray Tracer graphics program, www.povray.org.