Chemistry of Insect Antifeedants from *Azadirachta indica* (Part 13[1]): On the Use of the Intramolecular Diels–Alder Reaction for the Construction of *trans*-Fused Hydrobenzofuran Fragments for Azadirachtin Synthesis

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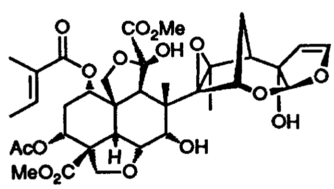
This paper describes a detailed analysis of the influence of various substituents on the stereochemical outcome of the intramolecular Diels–Alder cyclisation of a number of ether-linked trienes. In particular, the role of diene planarity in governing reaction synchronicity and related twist asynchronicity is delineated. Additionally, the controlling influence of a large dimethyl(phenyl)silyl substituent on the dienophile portion of the triene is also explored. A detailed transition-state analysis is given together with X-ray structures for compounds **41** and **46**.

During our synthetic studies towards the potent insect antifeedant azadirachtin **1**,[2] we have had cause to examine in detail several aspects of an intramolecular Diels–Alder (IMDA) reaction necessary for the eventual construction of the decalin portion of this molecule.[1,3]



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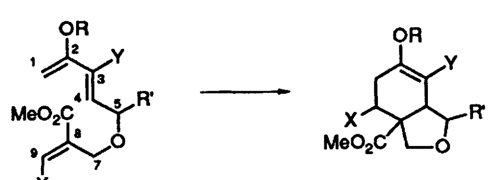
Here we discuss in full the factors which control this key reaction, particularly the role of dimethyl(phenyl)silyl substitution on the dienophile and the effects of substituent changes on the diene.

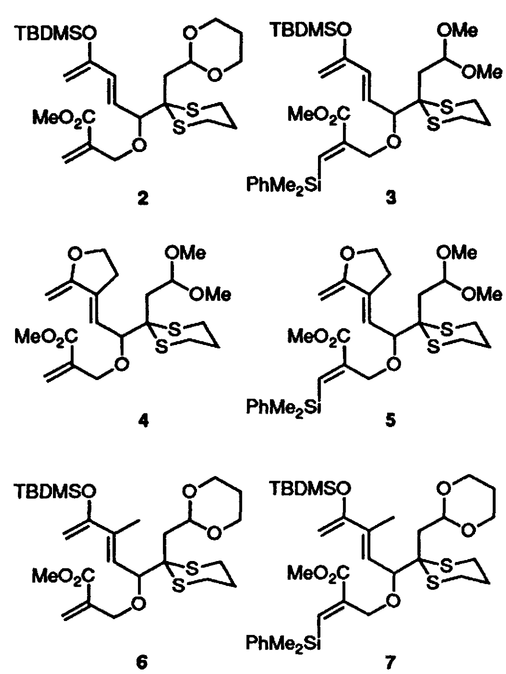
In recent years the IMDA reaction has been recognised as one of the most powerful and versatile methods for the preparation of polycyclic systems. Indeed, much has already been discovered regarding the factors which control this important reaction.[4] In this work we will focus on a variant of the IMDA reaction in which the precursor trienes have two carbon atoms and one oxygen atom in the tether along with a large side-chain substituent, R′. Additionally, an electron-donating moiety at C(2) and an electron-withdrawing one at C(8) facilitate asynchronous peripheral bond formation (Scheme 1). Furthermore, we have examined the effect of changes in the terminal C(9) dienophile substituent, X and the diene C(3) substituent, Y.



Scheme 1

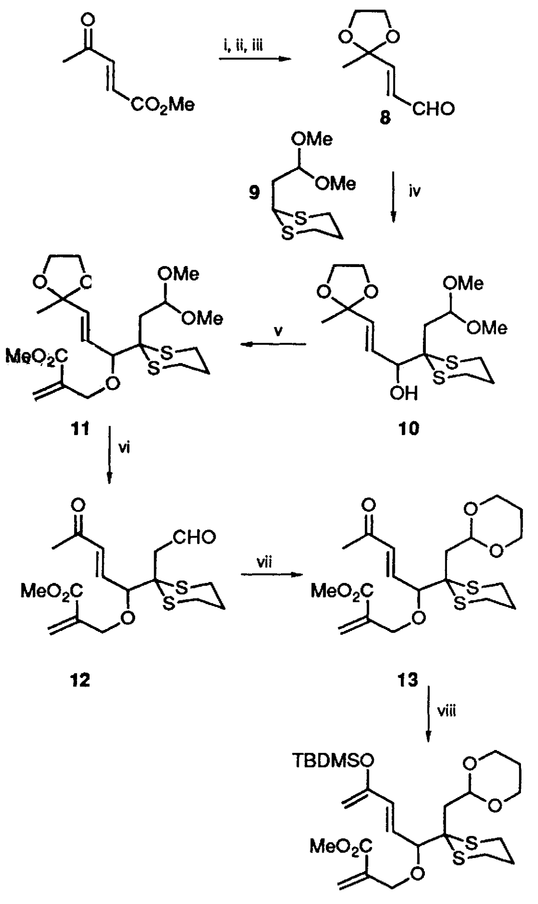
This example of the IMDA reaction achieves the formation of two rings and up to three stereogenic centres in one operation and, therefore, requires very careful transition-state analysis in order to make reliable predictions regarding the relative stereochemistry of the products. Any analysis must encompass a range of controlling factors including, *endo versus exo* reaction modes,[5] the effect of a large C(5) group in the tether and consequential $A_{1,3}$ strain,[6] transannular and other steric interactions, $A_{1,2}$ strain and related diene twisting about the C(2)–C(3) bond. As a result of the triene substitution pattern, asynchronicity leading to advanced peripheral-bond formation and the impact of twist asynchronicity[7] associated with the various transition states must also be considered.

Before examining the pertinent IMDA reactions, preparation of the precursor trienes **2**–**7** was necessary. Trienes **5** and **6** had been synthesized during previous studies[1,8] and it was envisaged that the remaining examples could be prepared by adopting existing procedures. As these routes mirror closely those already described they are presented in schematic form for the sake of brevity.

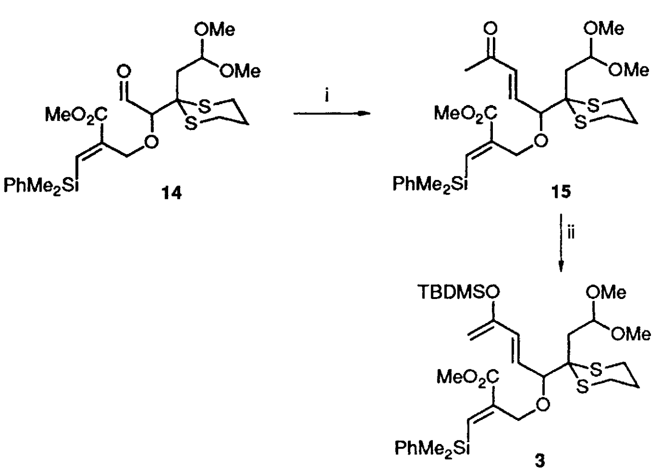


Results and Discussion

In general, one of two strategies was adopted for triene synthesis involving construction of the latent diene carbon framework either prior to or following etherification, as in Schemes 2 and 5, and Schemes 3 and 4 respectively. For details of the synthesis of the β-silicon-substituted acrylate **23** the reader is directed to the preceding paper[1] and for the substituted dithiane **9** to our

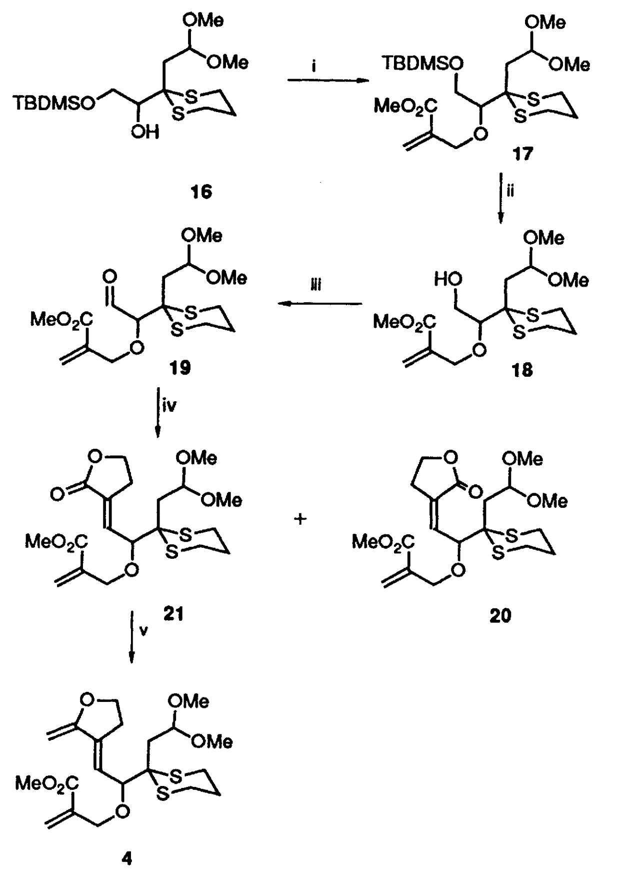


Scheme 2 *Reagents and conditions:* i, ethylene glycol, PPTS, benzene, heat, 36 h (89%); ii, $LiAlH_4$, inverse addition, Et_2O, −50 °C, 25 min (73%); iii, MnO_2, CH_2Cl_2, 42 h (**8**, 75%); iv, **9**, BuLi, TMEDA, THF, −30 °C, 1.5 h; then **8**, −95 °C, 15 min (**10**, 93%); v, KH, benzene, 1 h, methyl 2-(bromomethyl)propenoate, 10 min (**11**, 65%); vi, 2% aq. acetone, PPTS, heat, 4 h (**12**, 91%); vii, propane-1,3-diol, PPTS, benzene, heat, 3 h (**13**, 83%); viii, TBDMSOTf, Et_3N, CH_2Cl_2, −20 °C, 30 min (**2**, 90%)



Scheme 3 *Reagents and conditions:* i, dimethyl (2-oxopropyl)-phosphonate, LiCl, $Pr^i{}_2EtN$, 39 h, DMF (**15**, 65%); ii, TBDMSOTf, Et_3N, CH_2Cl_2, −20 °C, 30 min (**3**, 86%)

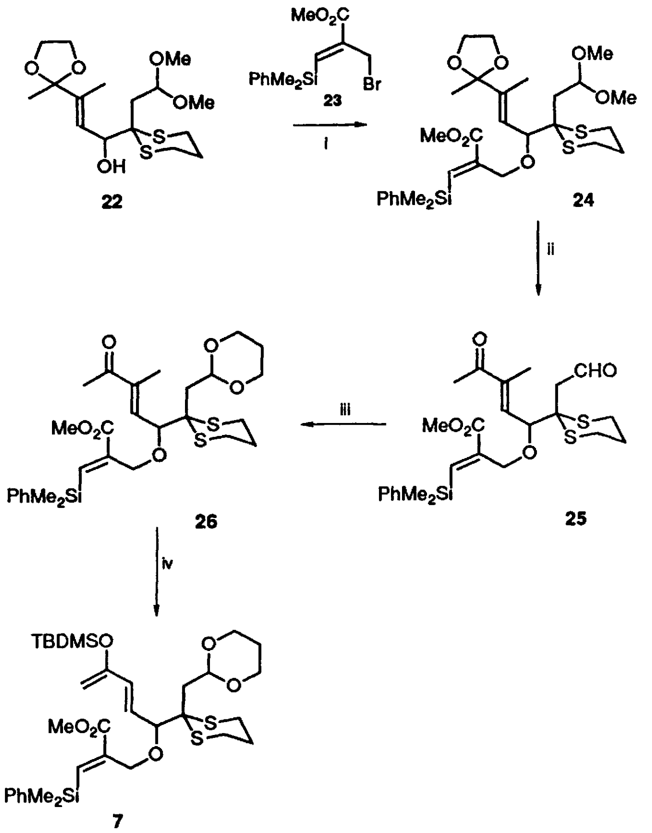
original work in this area.[8] All four routes employ standard reagents and are uneventful. The instability of trienes **4** and **5** is noteworthy and required their direct cyclisation following limited purification.



Scheme 4 *Reactions and conditions:* i, KH, THF, 17 min, methyl 2-(bromomethyl)propenoate, 30 min (**17**, 88%); ii, HF, pyridine, MeCN, 16 h (**18**, 77%); iii, DMSO, $(COCl)_2$, THF, −35 °C, 20 min; Et_3N, −78 °C to 21 °C (**19**, 70%); iv, α-diethoxyphosphonyl-γ-butyrolactone, LiCl, $Pr^i{}_2EtN$, MeCN, 24 h [(*Z*)-**20**, 13%; (*E*)-**21**, 42%]; v, Tebbe reagent

With the prerequisite trienes in hand the stage was set for examination of the comparative IMDA reactions (see Table 1). Before giving a detailed account of product distribution it is pertinent to make some general comments. First, we find that certain reactions, entries 3 and 4, proceed best in toluene solution containing acid scavengers, *e.g.* Hünig's base, and antioxidants, *e.g.* hydroquinone, and in silylated or base-washed glassware. If the diene component is constrained to planarity by annulation, as for entries 3 and 4, this allows the IMDA reaction to proceed at lower temperature, possibly by encouraging a more synchronous reaction co-ordinate (*vide infra*). The presence of a dimethyl(phenyl)silyl substituent on the diene terminus causes a small decrease in reaction rate. However, the large silyl group has a dramatic influence on the *endo*:*exo* ratio, with comparative examples showing higher *endo* selectivity in all cases. Moreover, incorporation of silicon has added utility in providing an additional stereogenic centre in the product which may be exploited as a remote stereocontrol element or a latent hydroxy group through stereospecific silyl Baeyer–Villiger reaction.[1,9]

It is also relevant at this stage to comment on the proof of structure of the various products as other stereoisomers are possible. While we have not exhaustively carried out complete product analysis the tabulated data indicate reaction composition as observed by 500 MHz ^1H NMR analysis of the crude reaction media. In addition, the subsequent transition-state analysis is in accord with the assigned products. Structure assignments follow from extensive spectroscopic and computational determinations or in certain cases through single-crystal X-ray analysis of later derivatives.



Scheme 5 *Reagents and conditions:* i, KH, benzene, 1 h, **23**, 16 h (**24**, 53%); ii, 2% aq. acetone, PPTS, heat, 24 h (**25**, 85%); iii, propane-1,3-diol, PPTS, benzene, heat, 16 h; 2% aq. acetone, PPTS, heat, 24 h (**26**, 78%) (2 steps); iv, TBDMSOTf, Et_3N, CH_2Cl_2, 30 min (**7**, 95%)

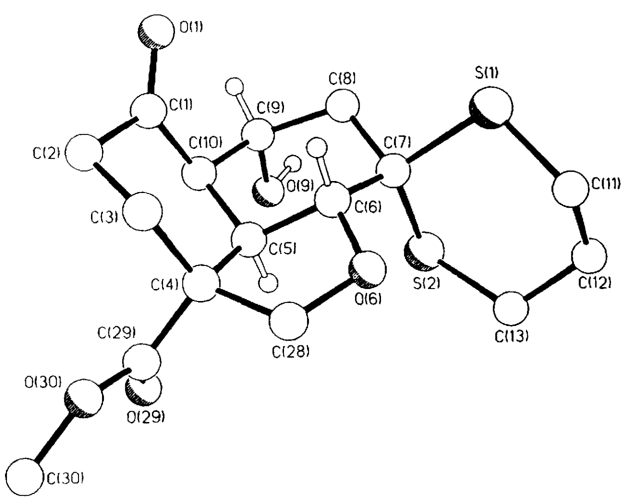
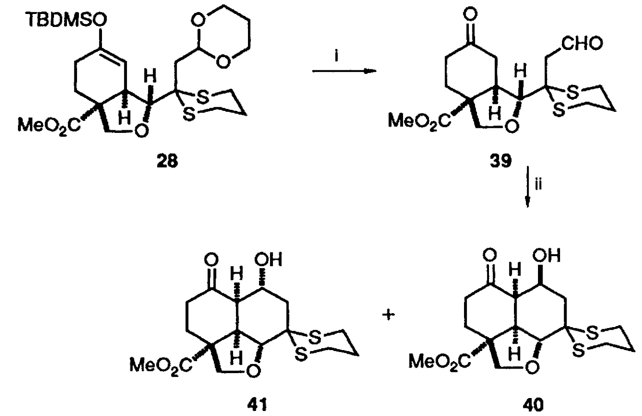


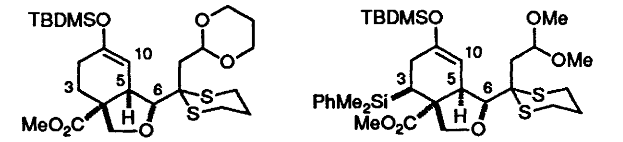
Fig. 1

For the cyclisation of triene **2** the relative stereochemistry of the major cycloadduct **28** was determined unequivocally through single-crystal X-ray analysis (Fig. 1) of a later derivative **41** obtained by the base-mediated intramolecular aldol condensation of the keto aldehyde **39** (Scheme 6). No attempt was made to isolate the minor component from the IMDA cyclisation of **2**; however, the structure assignment given is in accord with both transition-state analysis and product distribution for other related examples.

The outcome of IMDA reaction of triene **3** conforms with our appreciation of the stereodirecting role of the C(3) silicon substituent. The relative stereochemistry of the major



Scheme 6 *Reagents and conditions:* i, acetic acid–THF–water (3:1:1), 55 °C, 16 h (**39**, 85%); ii, KOH, MeOH, 1 h (**41**, 57%; **40**, 31%)



28	**30**
H(5) 3.52, br t, *J* 6.5 Hz	H(5) 3.25, br t, *J* 5.5 Hz
H(6) 3.76, d, *J* 7.0 Hz	H(6) 3.80, d, *J* 5.9 Hz
H(10) 5.09, d, *J* 4.3 Hz	H(10) 4.91, dd, *J* 1.9, 4.8 Hz

Fig. 2 Selected ^1H NMR data for compounds **28** and **30**

cycloadduct **30** in this system was assigned by 500 MHz, ^1H NMR homology to the *cis*-fused *exo*-product **28** from the cyclisation of triene **2**. In particular, the observed chemical shifts and coupling constants of H(5), H(6) and H(10) correlate well with the data for corresponding protons in the bicycle lacking silicon substitution at C(3) (Fig. 2).

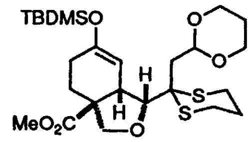
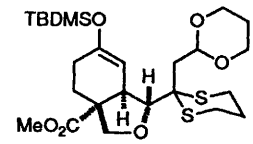
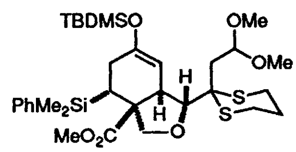
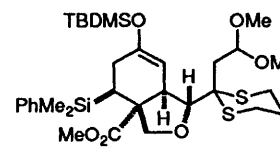
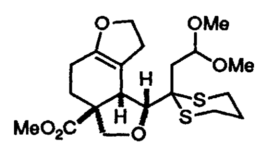
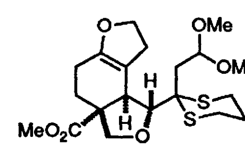
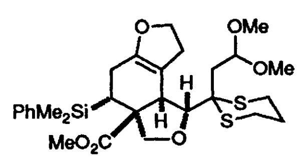
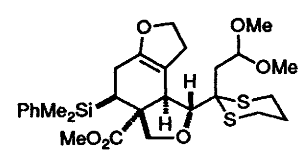
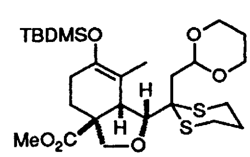
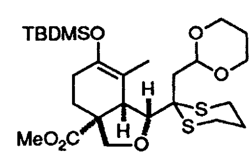
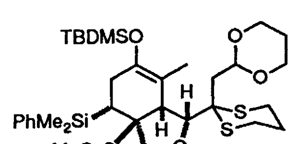
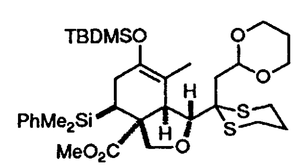
Further evidence was available from comparison of the H(5), H(10) coupling constants of the major diastereoisomer **30** ($J_{5,10}$ 4.8 Hz) and the minor one **29** {H(10), br s, $J_{5,10}$ <1 Hz}. Inspection of Drieding molecular models suggests the *trans*-fused *endo*-compound **29** to have a dihedral angle between H(5) and H(10) of near 90°, corresponding to a small vicinal coupling constant. In contrast, the reduced dihedral angle in the *cis*-fused *exo*-diastereoisomer **30** would suggest it to exhibit a larger coupling constant, as indeed is the case.

The minor cycloadduct **29** could not be obtained in pure form, thereby precluding its characterisation immediately after IMDA cyclisation. However, acid hydrolysis of the diastereoisomeric mixture of products in aqueous acetonitrile did afford the *trans*-fused bicyclic keto aldehyde **42**, derived from the minor cycloadduct in pure form, along with the corresponding *cis*-fused isomer **43** (Scheme 7). Full relative stereochemical assignment of compound **42** was based on NOE data as summarised in Fig. 3.

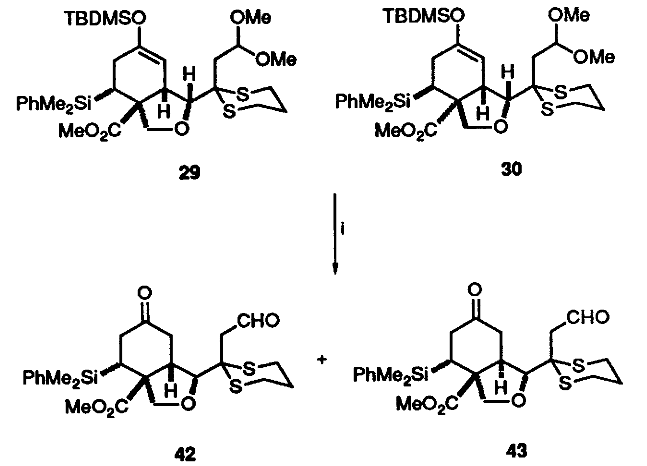
Cyclisation of the tetrahydrofuran constrained diene **4** was rapid and afforded the *cis*-fused *exo*-adduct **32** as the major product. Selected NOE experiments (Fig. 4) pointed to a *trans* arrangement of H(5) and H(6) but were inconclusive concerning the configuration of C(4).

Nevertheless, the small coupling constant of 5.7 Hz between H(5) and H(6) correlated well with the corresponding value in the structurally related *cis*-fused cycloadduct **36** ($J_{5,6}$ 4.5 Hz), whereas the *trans*-fused bicycle **35** exhibits a much larger coupling constant ($J_{5,6}$ 9.0 Hz).[8] Confirmation of this stereochemical assignment was obtained through single-crystal X-ray diffraction analysis (Fig. 5) of a subsequent compound, **46**, derived from the major cycloadduct **32** (Scheme 8). Once again no direct evidence was obtained for the configuration of

Table 1

Entry	Starting triene	Conditions	Yield (%)	Product ratio *endo*:*exo*		
1	**2**	7 h, 111 °C, toluene	84	 <1 **27**		 10 **28**
2	**3**	14 h, 111 °C, toluene	77	 1 **29**	:	 3.4 **30**
3	**4**	5 h, 60 °C, toluene	18[b]	 1 **31**	:	 8 **32**
4	**5**	4 h, 85 °C, toluene	29[b]	 2.4 **33**	:	 1 **34**
5	**6**	0.75 h, 135 °C, DMSO[a]	84	 2.1 **35**	:	 1 **36**
6	**7**	3 h, 111 °C, toluene	77	 >12 **37**	:	 1 **38**

[a] Dimethyl sulfoxide. [b] Yield for Tebbe methylenation and IMDA cyclisation.



Scheme 7 *Reagents and conditions:* i, PTSA, 3% aq. acetone, heat, 45 min (**42**, 40%; **43**, 41%)

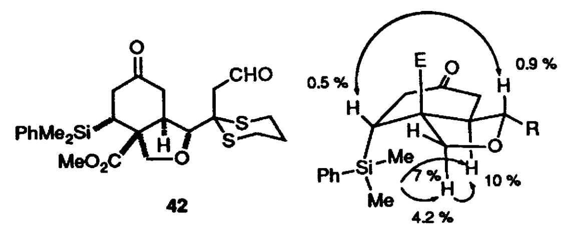


Fig. 3 Selected NOE data for compound **42**

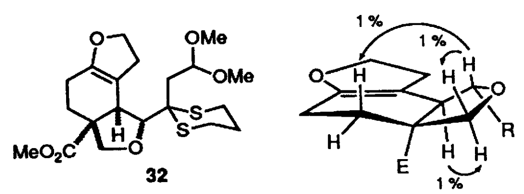
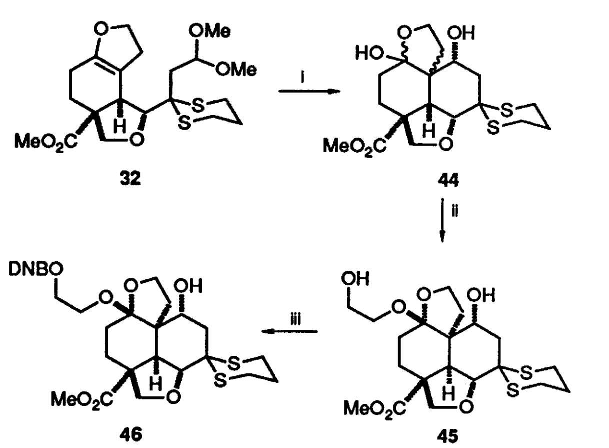


Fig. 4 Selected NOE data for compound **32**



DBN = 3, 5-dinitrobenzoyl

Scheme 8 *Reagents and conditions:* i, PTSA, 2% aq. acetone, heat, 4.5 h (**44**, 44%); ii, ethylene glycol, PTSA, benzene, heat, 2 h (**45**, 63%); iii, 3,5-dinitrobenzoyl chloride, pyridine, CH_2Cl_2, 30 min (**46**, 77%)

the minor cycloadduct **31** since it could not be separated and characterised. However, the assignment of the *trans*-fused structure follows from an analysis of reaction transition states (*vide infra*) and from evidence arising from the cyclisation of similar analogues.

The relative stereochemical assignment of the products arising from the IMDA cyclisation of trienes **5** and **6** may be found in preceding publications.[1,8] The stereochemistry of the major cycloadduct **37** arising from cyclisation of substrate **7** follows from ^1H NMR homology with compound **35**. In particular, a coupling constant of 8.9 Hz between (5)H and (6)H is in good agreement with that of 9.0 Hz observed for **35** (Fig. 6). Once more the minor cycloadduct was not isolated, its presence being inferred from 500 MHz ^1H NMR analysis of the crude reaction medium and its stereochemistry from transition-state analysis and product distribution for related examples.

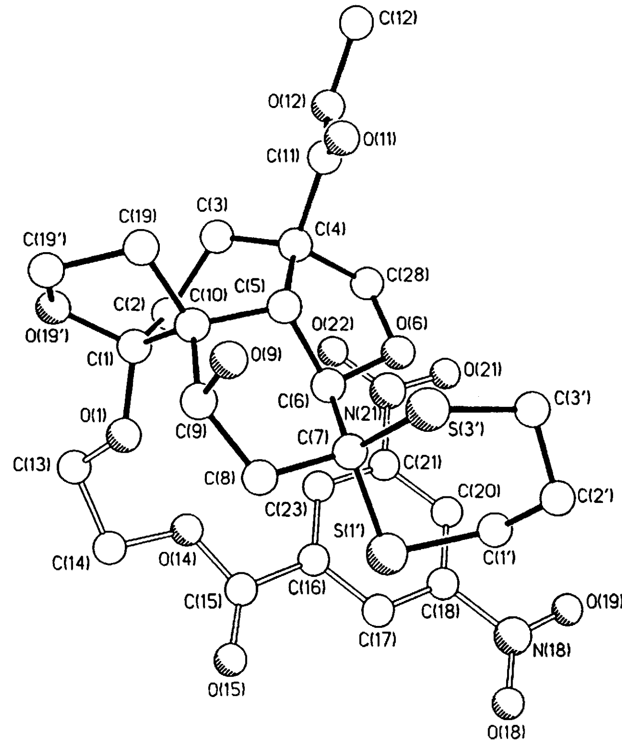
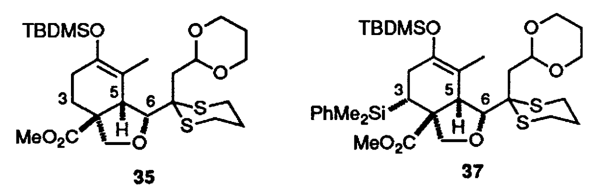


Fig. 5



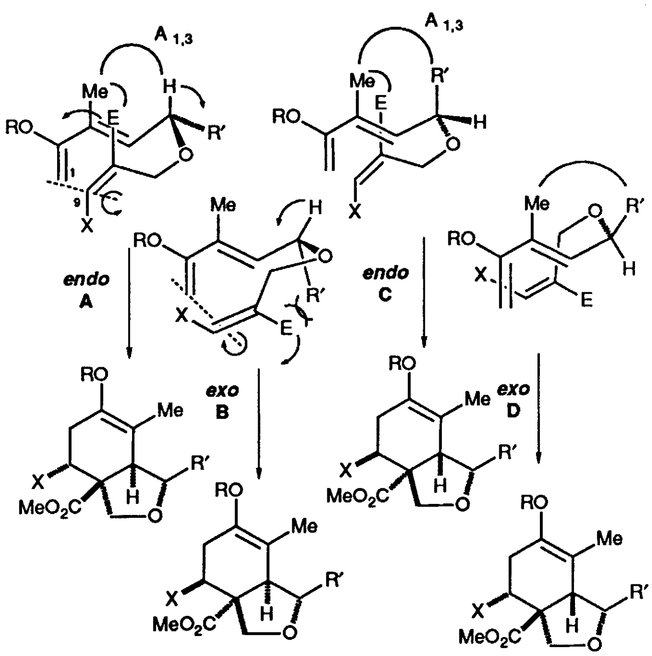
H(5) 3.29, br d, *J* 9.0 Hz
H(6) 4.83, d, *J* 9.0 Hz

H(5) 3.02, br d, *J* 8.9 Hz
H(6) 4.77, d, *J* 8.9 Hz

Fig. 6 Selected ^1H NMR data for compounds **35** and **37**

As regards the discussion of the transition-state geometries leading to the IMDA products, it is clear that our earlier picture[8] is insufficiently sophisticated to account for the current results, although the general guidelines originally delineated remain pertinent. First, Alder's *endo*-rule[5] is of limited predictive value for intramolecular reactions unless low temperatures and Lewis acid catalysis are employed.[10] Brown and Houk[7] have reported that the IMDA cyclisation of nona-1,3,8-trienes with electron-donating groups at C(2) and -withdrawing ones at C(8) proceeds with advanced peripheral-bond formation leading to preferred *cis*-fused *exo*-products. Such reactions are critically dependent upon frontier orbital considerations, which encourage advanced peripheral-bond formation, and upon the counteracting influence of the tethering chain, which encourages advanced internal-bond formation. The fact that intramolecular cyclisation of trienes **2** and **4** gives a similar *endo*:*exo* ratio, strongly favouring the *exo*-product, suggests comparable electronic properties and favoured transition states. In contrast, the triene **6** shows reversed selectivity indicating different transition-state properties. The origin of this disparity lies in the presence of a methyl group at C(3) in the conformationally flexible diene portion of compound **6**. Molecular mechanics calculations indicate that $A_{1,2}$ strain between this methyl substituent and the neighbouring C(2) siloxy group causes the diene to twist out of plane by as much as 20–30°.[11] Hence a more pronounced asynchronous reaction co-ordinate is possible, the extreme case of which would represent a double Michael addition. By comparison, the reduced $A_{1,2}$ strain in the diene portion of **2** and the constraints imposed by furan annulation in **4** encourage a more planar diene arrangement in these cases and hence a correspondingly more synchronous reaction profile. An inspection of the tabulated results reveals that the large dimethyl(phenyl)silyl group significantly alters the outcome of all examples in which it participates, in certain cases even overturning the inherent diastereoselection bias. For example, compare entry 1 with a 1:10 *endo*:*exo* ratio to entry **2** which has only a 1:3:4 ratio. For entry 3 the initial 1:8 *endo*:*exo* ratio is reversed with respect to its silicon-substituted analogue, entry 4, for which a 2.4:1 ratio is observed. Comparison of entries 5 and 6 shows a significant increase in *endo* selectivity for 2.1:1 to greater than 12:1; this highly pleasing result would have been of great importance to us during our earlier model studies had we recognised the power of the dimethyl(phenyl)silyl group as a stereocontrol element.

In order to account for the observed product distributions a careful transition-state analysis is needed. The presence of a stereogenic centre in the linking tether means that the diene π faces are diastereoisotropic and consequently a minimum of four transition states must be considered (Scheme 9).



Scheme 9 Intramolecular Diels–Alder reaction transition-state analysis

Transition states **C** and **D** both encounter highly unfavourable steric interactions involving the large dithiane-substituted side-chain and consequently are disfavoured in all cases. For more synchronous reaction co-ordinates the presence of $A_{1,3}$ strain and transannular interactions in transition state **A** means that this is less populated than **B** in which only developing pseudo 1,3-diaxial interactions are encountered. Hence, precursors having planar diene portions, *e.g.* **2**, **3** and **4**, give predominantly *cis*-fused *exo*-cycloadducts *via* transition state **B**. For less synchronous reaction co-ordinates advanced peripheral-bond exerts a torque about the newly forming bond as shown in Scheme 9. In the case of species **A** this reduces the C(1)–C(9) dihedral angle attenuating both $A_{1,3}$ strain and unfavourable transannular interactions. For **B** twist asynchronicity increases the C(1)–C(9) dihedral angle, introducing $A_{1,3}$ strain into the transition state. Hence, for non-planar dienes whose reaction co-ordinates display pronounced asynchronicity cyclisation mode A is predominant. In all cases the large C(9) dienophile substituent X = $PhMe_2Si$ favours *endo* over *exo* transition states.

In conclusion, we have shown that small changes in diene substitution patterns can have a drastic influence on the stereochemical outcome of IMDA reactions and that this effect can be overcome to a greater or lesser extent by employing a large silicon substituent suitably placed in the dienophile portion. To the best of our knowledge these results represent the first rational usage of twist asynchronicity to govern product stereochemistry and also of a large silicon dienophile substituent in the IMDA reaction. Studies are currently underway to explore the use of the latter control element in intermolecular Diels–Alder reactions.

Experimental

General.—^{1}H NMR spectra were recorded in $CDCl_3$ unless otherwise stated, at 90, 270 or 500 MHz on JEOL FX 90Q, JEOL GFX 270 or Bruker AM 500 spectrometers, respectively. Residual protic solvent, *i.e.*, $CHCl_3$ (δ_H 7.26) or C_6D_5H (δ_H 7.20), was used as internal reference. For clarity natural product (steroid) numbering is used and qualified diagramatically in the Results and Discussion section; however, IUPAC conventions are adopted throughout the Experimental section. Coupling constants (*J*) were measured in Hz. ^{13}C NMR spectra were recorded in $CDCl_3$ unless otherwise stated, at 125.8 MHz on a Bruker AM 500 spectrometer using the resonances of $CDCl_3$ (δ_C 77.0, t) or C_6D_6 (δ_C 128.0, t) as internal reference. IR spectra were recorded on a Perkin-Elmer 983G spectrometer. Mass spectra were recorded under EI conditions, unless otherwise stated, using VG-7070B, VG 12-253, Autospec O and VG ZAB-E instruments. Microanalyses were performed in the Imperial College Chemistry Department microanalytical laboratory and by MEDAC Ltd. at the Department of Chemistry, Brunel University. M.p.s were determined on a Reichert hot-stage apparatus and are uncorrected. Optical rotations (units: 10^{-1} deg cm^2 g^{-1}) were measured with an Optical Activity AA-1000 polarimeter using acid- and ethanol-free $CHCl_3$ as solvent unless otherwise stated. Molecular modelling was performed using the Tektronix CAChe system. Flash column chromatography was performed using Merck Kieselgel 60 (230–400 mesh) unless otherwise stated. Preparative HPLC was performed on a Dynamax Macro Si column. Florisil refers to 230–300 US mesh Florisil as supplied by BDH Ltd. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium–benzophenone ketyl; dichloromethane from phosphorus pentaoxide; toluene from sodium; acetonitrile from calcium hydride; and methanol from magnesium. Light petroleum refers to the fraction boiling in the range 40–60 °C, which was distilled prior to use as was ethyl acetate. Other solvents and reagents were purified by standard procedures as necessary. Analytical TLC was performed using pre-coated glass-backed plates (Merck Kieselgel 60 F_{254}) and compounds were visualised by acidic ammonium molybdate(IV) or iodine as appropriate.

Crystal Data for Methyl 6-*Hydroxy*-5-*oxoperhydronaphtho*-[1,8-bc]*furan*-8-*spiro*-2′-(1′,3′-*dithiane*)-2a-*carboxylate* **41**.—Single crystals suitable for analysis were grown from diethyl ether–light petroleum. $C_{16}H_{22}O_5S_2$, M = 358.5, monoclinic, a = 11.795(2), b = 11.167(2), c = 13.636(2) Å, β = 108.31(1)°,

Table 2 Atom co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound **41**

O(1)	2472(2)	6865(2)	316(1)
C(1)	2935(2)	5930(2)	685(2)
C(2)	2240(2)	4894(2)	890(2)
C(3)	2618(2)	4641(2)	2051(2)
C(4)	3964(2)	4373(2)	2490(2)
C(5)	4706(2)	5300(2)	2138(2)
C(6)	4742(2)	6314(2)	2887(2)
O(6)	4974(1)	5733(1)	3860(1)
C(7)	5628(2)	7285(2)	2845(2)
C(8)	5178(2)	7749(2)	1715(2)
C(9)	4996(2)	6799(2)	867(2)
O(9)	6101(2)	6330(2)	830(2)
C(10)	4256(2)	5726(2)	1016(2)
S(1)	5526(1)	8613(2)	3601(1)
C(11)	6283(3)	8184(2)	4917(2)
C(12)	7566(3)	7812(3)	5112(2)
C(13)	7678(2)	6678(3)	4547(2)
S(2)	7172(1)	6780(1)	3143(1)
C(28)	4423(2)	4579(2)	3678(2)
C(29)	4255(2)	3106(2)	2250(2)
O(29)	5054(2)	2827(2)	1941(2)
O(30)	3506(2)	2324(2)	2425(2)
C(30)	3697(4)	1079(2)	2240(3)

Table 3 Selected bond lengths (Å) and angles (°) for compound **41** with esds in parentheses

O(1)–C(1)	1.212(3)	C(1)–C(2)	1.493(4)
C(1)–C(10)	1.497(3)	C(2)–C(3)	1.530(3)
C(3)–C(4)	1.541(3)	C(4)–C(5)	1.528(3)
C(4)–C(28)	1.555(3)	C(4)–C(29)	1.515(3)
C(5)–C(6)	1.517(3)	C(5)–C(10)	1.528(3)
C(6)–O(6)	1.425(3)	C(6)–C(7)	1.519(3)
O(6)–C(28)	1.430(3)	C(7)–C(8)	1.552(3)
C(7)–S(1)	1.832(2)	C(7)–S(2)	1.826(2)
C(8)–C(9)	1.534(3)	C(9)–O(9)	1.420(4)
C(9)–C(10)	1.534(4)	S(1)–C(11)	1.800(2)
C(11)–C(12)	1.510(4)	C(12)–C(13)	1.509(4)
C(13)–S(2)	1.821(3)		
O(1)–C(1)–C(2)	122.9(2)	O(1)–C(1)–C(10)	123.1(2)
C(2)–C(1)–C(10)	114.0(2)	C(1)–C(2)–C(3)	109.8(2)
C(2)–C(3)–C(4)	111.6(2)	C(3)–C(4)–C(5)	111.6(2)
C(3)–C(4)–C(28)	110.8(2)	C(5)–C(4)–C(28)	100.4(2)
C(3)–C(4)–C(29)	111.9(2)	C(5)–C(4)–C(29)	112.0(2)
C(28)–C(4)–C(29)	109.6(2)	C(4)–C(5)–C(6)	101.1(2)
C(4)–C(5)–C(10)	118.2(2)	C(6)–C(5)–C(10)	111.7(2)
C(5)–C(6)–O(6	104.1(2)	C(5)–C(6)–C(7)	112.4(2)
O(6)–C(6)–C(7)	115.3(2)	C(6)–O(6)–C(28)	107.8(1)
C(6)–C(7)–C(8)	104.5(2)	C(6)–C(7)–S(1)	112.9(2)
C(8)–C(7)–S(1)	103.0(1)	C(6)–C(7)–S(2)	114.9(1)
C(8)–C(7)–S(2)	109.3(2)	S(1)–C(7)–S(2)	111.2(1)
C(7)–C(8)–C(9)	116.1(2)	C(8)–C(9)–O(9)	111.7(2)
C(8)–C(9)–C(10)	113.0(2)	O(9)–C(9)–C(10)	106.5(2)
C(1)–C(10)–C(5)	110.5(2)	C(1)–C(10)–C(9)	115.0(2)
C(5)–C(10)–C(9)	110.0(2)	C(7)–S(1)–C(11)	104.2(1)
S(1)–C(11)–C(12)	113.8(2)	C(11)–C(12)–C(13)	112.6(2)
C(12)–C(13)–S(2)	115.6(2)	C(7)–S(2)–C(13)	103.2(1)
C(4)–C(28)–O(6)	107.7(2)		

$V = 1704$ Å^3, space group $P2_1/a$, No. 14, $Z = 4$, $D_c = 1.40$ g cm^{-3}. Cu radiation, $\lambda = 1.541\ 78$ Å, μ(Cu-Kα) = 30 cm^{-1} $F(000) = 760$. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. 2304 Independent reflections ($2\theta \le 116°$) were measured, of which 2157 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The bridgehead and hydroxy protons on C-5, C-6, C-10 and O-9 were located from a ΔF map and refined isotropically. The positions of the remaining hydrogen atoms were idealised, C–H = 0.96 Å, assigned isotropic thermal parameters, U(H) = 1.2 U_{eq}(C), and allowed to ride on their parent carbon atoms. The methyl group was refined as a rigid body. Refinement was by block-cascade full-matrix least-squares to $R = 0.039$, $R_w = 0.045$ [$w^{-1} = \sigma^2(F) + 0.000\ 41F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.26 and -0.22 e Å^{-3}, respectively. The mean and maximum shift/error in the final refinement were 0.003 and 0.012, respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[12] Atomic co-ordinates and selected bond lengths and angles are given in Tables 2 and 3.*

Crystal Data for (2aR*,4aR*,7aR*,8R*,10aR*,10bR*)-*Methyl* 4a-[2-(3,5-*Dinitrobenzoyloxy*)*ethoxy*]-8-*hydroxyperhydronaphtho*[1,8-bc:5,4a-b′]*difuran*-10-*spiro*-2′-(1′,3′-*dithiane*)-2a-*carboxylate* **46**.—Single crystals suitable for analysis were grown from ethyl acetate. $C_{27}H_{32}N_2O_{12}S_2$, M = 640.7, monoclinic, $a = 10.102(2)$, $b = 8.934(2)$, $c = 31.196(6)$ Å, $\beta = 94.43(2)°$, $V = 2810$ Å^3, space group $P2_1/n$, No. 14, $Z = 4$, $D_c = 1.51$ g cm^{-3}, Cu radiation, $\lambda = 1.541\ 78$ Å, μ(Cu-Kα) = 23 cm^{-1}, $F(000) = 1344$. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. A crystal of dimensions 0.13 × 0.33 × 0.37 mm was used. 3792 Independent reflections [$2\theta \leqslant 116°$] were measured of which 3388 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The bridgehead protons on C-5 and C-6, and the hydroxy proton on O-9, were located from a ΔF map and refined isotropically. The positions of the remaining hydrogen atoms were idealised, C–H = 0.96 Å, assigned isotropic thermal parameters, U(H) = 1.2 U_{eq}(C), and allowed to ride on their parent carbon atoms. The methyl group was refined as a rigid body. Refinement was by block-cascade full-matrix least-squares to $R = 0.046$, $R_w = 0.052$ [$w^{-1} = \sigma^2(F) + 0.000\ 54F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.59 and -0.27 e Å^{-3}, respectively. The mean and maximum shift/error in the final refinement were 0.029 and 0.224, respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[12] Atomic co-ordinates and selected bond lengths and angles are given in Tables 4 and 5.*

(E)-*Methyl* 4,4-(*Ethylenedioxy*)*pentenoate*.—A mixture of (*E*)-methyl 4-oxopentenoate (11.7 g, 91.3 mmol), ethylene glycol (27 cm^3, 0.5 mol) and pyridinium toluene-*p*-sulfonate (PPTS) (2.43 g, 9.7 mmol) in anhydrous benzene (150 cm^3) was heated at reflux with azeotropic removal of water for 36 h. After cooling, the mixture was poured into saturated aq. sodium hydrogen carbonate (200 cm^3), then extracted with diethyl ether (4 × 200 cm^3), and the combined extracts were washed successively with saturated aq. sodium hydrogen carbonate (100 cm^3), water (200 cm^3) and brine (200 cm^3) and dried over anhydrous magnesium sulfate. Concentration gave an oil, which was purified by flash chromatography (gradient elution, 30–50% diethyl ether–light petroleum) to give the *title ketal* (13.99 g, 89%) as an oil (Found: C, 55.7; H, 7.2. $C_8H_{12}O_4$ requires C, 55.81; H, 7.02%); ν_{max}(film)/cm^{-1} 2989, 2953, 2890, 1723, 1660, 1434, 1374, 1306, 1203, 1168, 1040, 866 and 725; δ_H(500 MHz; $CDCl_3$) 1.48 (3 H, s, 5-H_3), 3.74 (3 H, s, CO_2Me), 3.85–3.87 (2 H, m, OCH_2CH_2O), 3.97–3.99 (2 H, m, OCH_2CH_2O), 6.07 (1 H, d,

* *Supplementary data* (see section 5.6.3 of Instructions to Authors, January issue). Other crystallographic material (hydrogen coordinates, thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre.

Table 4 Atom co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound **46**

O(1)	2912(2)	8087(2)	8760(1)
C(1)	3669(3)	7625(3)	8417(1)
C(2)	2782(3)	6837(4)	8064(1)
C(3)	3527(3)	5710(4)	7804(1)
C(4)	4128(3)	4433(3)	8082(1)
C(5)	4558(3)	4969(3)	8536(1)
C(6)	3448(3)	4402(3)	8810(1)
O(6)	3111(2)	2972(2)	8629(1)
C(7)	3890(3)	4381(3)	9286(1)
C(8)	4230(3)	6040(3)	9394(1)
C(9)	5156(3)	6848(3)	9100(1)
O(9)	6490(2)	6340(3)	9187(1)
C(10)	4834(3)	6637(3)	8605(1)
C(19)	6005(3)	7280(4)	8362(1)
C(19′)	5633(3)	8903(4)	8313(1)
O(19′)	4228(2)	8895(3)	8222(1)
S(1′)	2546(1)	3980(1)	9640(1)
C(1′)	2289(3)	1985(4)	9580(1)
C(2′)	3511(3)	1054(4)	9686(1)
C(3′)	4613(3)	1322(4)	9385(1)
S(3′)	5322(1)	3185(1)	9414(1)
C(11)	5313(3)	3723(4)	7862(1)
O(11)	6386(3)	3548(5)	8029(1)
O(12)	4995(2)	3356(3)	7468(1)
C(12)	6035(4)	2661(5)	7242(1)
C(13)	1802(3)	9029(3)	8670(1)
C(14)	804(3)	8656(3)	8994(1)
O(14)	306(2)	7177(3)	8888(1)
C(15)	−226(3)	6379(4)	9203(1)
O(15)	−363(3)	6843(3)	9556(1)
C(16)	−622(3)	4861(4)	9050(1)
C(17)	−1032(3)	3830(4)	9348(1)
C(18)	−1402(3)	2426(4)	9208(1)
N(18)	−1810(3)	1310(4)	9524(1)
O(18)	−1861(4)	1731(4)	9894(1)
O(19)	−2131(3)	53(3)	9389(1)
C(20)	−1402(3)	1988(4)	8786(1)
C(21)	−962(3)	3023(4)	8499(1)
N(21)	−923(3)	2582(3)	8045(1)
O(21)	−1223(3)	1307(3)	7945(1)
O(22)	−573(3)	3517(3)	7792(1)
C(23)	−586(3)	4444(4)	8621(1)
C(28)	3110(3)	3165(4)	8174(1)

Table 5 Selected bond lengths (Å) and angles (°) for compound **46** with esds in parentheses

O(1)–C(1)	1.416(3)	C(1)–C2)	1.544(4)
C(1)–C(10)	1.558(4)	C(1)–O(19′)	1.420(4)
C(2)–C(3)	1.521(5)	C(3)–C(4)	1.536(4)
C(4)–C(5)	1.533(4)	C(4)–C(11)	1.551(4)
C(4)–C(28)	1.576(4)	C(5)–C(6)	1.536(4)
C(5)–C(10)	1.529(4)	C(6)–O(6)	1.430(3)
C(6)–C(7)	1.523(4)	O(6)–C(28)	1.429(3)
C(7)–C(8)	1.554(4)	C(7)–S(1′)	1.836(3)
C(7)–S(3′)	1.823(3)	C(8)–C(9)	1.530(4)
C(9)–O(9)	1.432(3)	C(9)–C(10)	1.572(4)
C(10)–C(19)	1.554(4)	C(19)–C(19′)	1.503(5)
C(19′)–O(19′)	1.430(4)	S(1′)–C(1′)	1.809(3)
C(1′)–C(2′)	1.508(5)	C(2′)–C(3′)	1.518(5)
C(3′)–S(3′)	1.812(3)		
O(1)–C(1)–C(2)	110.8(2)	O(1)–C(1)–C(10)	108.0(2)
C(2)–C(1)–C(10)	113.8(2)	O(1)–C(1)–O(19′)	109.7(2)
C(2)–C(1)–O(19′)	106.8(2)	C(10)–C(1)–O(19′)	107.6(2)
C(1)–C(2)–C(3)	113.4(3)	C(2)–C(3)–C(4)	112.4(2)
C(3)–C(4)–C(5)	111.7(2)	C(3)–C(4)–C(11)	110.0(2)
C(5)–C(4)–C(11)	110.7(2)	C(3)–C(4)–C(28)	113.5(2)
C(5)–C(4)–C(28)	102.1(2)	C(11)–C(4)–C(28)	108.5(2)
C(4)–C(5)–C(6)	103.6(2)	C(4)–C(5)–C(10)	118.2(2)
C(6)–C(5)–C(10)	112.1(2)	C(5)–C(6)–O(6)	103.8(2)
C(5)–C(6)–C(7)	111.4(2)	O(6)–C(6)–C(7)	115.0(2)
C(6)–O(6)–C(28)	105.7(2)	C(6)–C(7)–C(8)	104.4(2)
C(6)–C(7)–S(1′)	113.8(2)	C(8)–C(7)–S(1′)	102.5(2)
C(6)–C(7)–S(3′)	113.8(2)	C(8)–C(7)–S(3′)	110.4(2)
S(1′)–C(7)–S(3′)	111.0(1)	C(7)–C(8)–C(9)	117.0(2)
C(8)–C(9)–O(9)	109.8(2)	C(8)–C(9)–C(10)	115.8(2)
O(9)–C(9)–C(10)	106.5(2)	C(1)–C(10)–C(5)	111.9(2)
C(1)–C(10)–C(9)	114.2(2)	C(5)–C(10)–C(9)	106.2(2)
C(1)–C(10)–C(19)	100.8(2)	C(5)–C(10)–C(19)	115.5(2)
C(7)–S(1′)–C(1′)	103.7(1)	S(1′)–C(1′)–C(2′)	114.2(2)
C(1′)–C(2′)–C(3′)	113.5(2)	C(2′)–C(3′)–S(3′)	114.6(2)
C(7)–S(3′)–C(3′)	102.8(1)		

J 15.6, 2-H) and 6.76 (1 H, d, *J* 15.6, 3-H); *m*/*z* (EI) 172 (M^+), 157 (M − CH_3), 141 (M − OMe), 113 (M − CO_2Me), 87 and 43.

(E)-4,4-(*Ethylenedioxy*)*pent-2-en-1-ol*.—Lithium aluminium hydride (0.986 g, 26.0 mmol) was added portionwise to a stirred solution of (*E*)-methyl 4,4-(ethylenedioxy)pentenoate (1.152 g, 6.69 mmol) in anhydrous diethyl ether (40 cm^3) at −52 °C during *ca.* 15 min. The mixture was stirred at −50 °C for 25 min and was then allowed to warm to 0 °C. The remaining reagent was quenched by *careful* dropwise addition of water (1 cm^3) followed by aq. sodium hydroxide (3 cm^3; 3 mol dm^{-3}) and then further water (1 cm^3). Further diethyl ether (40 cm^3) was also added. The mixture was stirred and allowed to warm to room temperature during 150 min. The solid was filtered off and the residue was washed with copious quantities of diethyl ether. Concentration and purification of the residue by flash chromatography with diethyl ether as eluant gave the *title alcohol* (0.708 g, 73%) as an oil (Found: C, 58.25; H, 8.5. $C_7H_{12}O_3$ requires C, 58.32; H, 8.39%); ν_{max}(film)/cm^{-1} 3414, 2984, 2886, 1672, 1374, 1210, 1082, 1039, 978, 910 and 861; δ_H(500 MHz; $CDCl_3$), 1.46 (3 H, s, 5-H_3), 1.63 (1 H, br s, OH), 3.92 (4 H, m, OCH_2CH_2O), 4.17 (2 H, br t, *J* 5.0, 1-H_2), 5.68 (1 H, dt, *J* 15.6, 1.7, 3-H) and 5.97 (1 H, dt, *J* 15.6, 5.1, 2-H); *m*/*z* (EI) 143 (M − H), 129, 113, 87, 85 and 43.

(E)-4,4-(*Ethylenedioxy*)*pent-2-enal* **8**.—Preactivated MnO_2 (3.26 g, 37.5 mmol) was added to a solution of (*E*)-4,4-(ethylenedioxy)pent-2-en-1-ol (0.676 g, 4.69 mmol) in anhydrous dichloromethane (40 cm^3). The resulting suspension was stirred for 18 h and further MnO_2 (1.6 g) was added. The mixture was stirred for 24 h. Filtration through a pad of Celite, washing of the filter with dichloromethane, and evaporation of the solvent and washings under reduced pressure gave the *aldehyde* **8** (0.498 g, 75%) as an oil which required no further purification (Found: C, 59.3; H, 7.3. $C_7H_{10}O_3$ requires C, 59.15; H, 7.09%); ν_{max}(film)/cm^{-1} 2989, 2890, 2823, 1691, 1474, 1443, 1374, 1216, 1168, 1127, 1086, 1037 and 981; δ_H(500 MHz; $CDCl_3$) 1.54 (3 H, s, 5-H_3), 3.87–3.92 (2 H, m, OCH_2CH_2O), 3.99–4.04 (2 H, m, OCH_2CH_2O), 6.31 (1 H, dd, *J* 15.7, 7.9, 2-H), 6.64 (1 H, d, *J* 15.7, 3-H) and 9.61 (1 H, d, *J* 7.8, 1-H); *m*/*z* (EI) 142 (M^+), 127 (M − CH_3), 113 (M − CHO) and 99 (M − C_2H_3O).

(E)-1-[2′-(2″,2″-*Dimethoxyethyl*)-1′,3′-*dithian*-2′-*yl*]-4,4-(*ethylenedioxy*)*pent-2-en-1-ol* **10**.—BuLi (2.4 cm^3 of a 2.5 mol dm^{-3} solution in hexanes, 6.0 mmol) was added dropwise to a stirred solution of the dithiane **9** (1.25 g, 6.0 mmol) and anhydrous *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.9, 6.0 mmol) in anhydrous THF (30 cm^3) at −30 °C. The yellow solution was stirred for 90 min at −30 °C and was then cooled to −95 °C. A solution of the enal **8** (0.426 g, 3.0 mmol) in THF (4 cm^3, +2 cm^3, rinse) was added *via* cannula. After 15 min, a solution of acetic acid in dry THF (3.4 cm^3; 10% w/v) was added dropwise and the mixture was allowed to warm to room temperature during 40 min. The flask contents were added to water (100 cm^3) and extracted with diethyl ether (4 × 100 cm^3). The combined organic layers were washed successively with water (100 cm^3) and brine (100 cm^3), then dried over anhydrous magnesium sulfate. Concentration and purification of the residue by flash chromatography (gradient elution, 20–60%

diethyl ether–light petroleum) gave the *alcohol* **10** (0.975 g, 93%) as an oil (Found: C, 51.2; H, 7.6. $C_{15}H_{26}O_5S_2$ requires C, 51.40; H, 7.48%); ν_{max}(film)/cm^{-1} 3453, 2983, 2932, 2894, 2829, 1439, 1422, 1373, 1278, 1208, 1071, 1041, 977, 949, 864 and 742; δ_H(500 MHz; $CDCl_3$) 1.49 (3 H, s, 5-H_3), 1.91–2.02 (2 H, m, 5′-H_2), 2.07 (1 H, dd, *J* 15.2, 3.6, 1″-H), 2.23 (1 H, dd, *J* 15.2, 5.8, 1″-H), 2.69–2.75 (2 H, m, CH_2S), 2.85–2.94 (2 H, m, CH_2S), 3.33 (3 H, s, OMe), 3.35 (3 H, s, OMe), 3.45 (1 H, d, *J* 4.1, OH), 3.88–3.98 (4 H, m, OCH_2CH_2O), 4.48 (1 H, br t, *J* 5.2, 2″-H), 4.78 (1 H, dd, *J* 5.7, 3.6, 1-H), 5.82 (1 H, d, *J* 15.5, 3-H) and 6.12 (1 H, dd, *J* 15.5, 5.1, 2-H); *m/z* (EI) 350 (M^+), 318 (M − MeOH), 303, 287, 259, 207, 176 and 75.

(E)-*Methyl 2-{1′-[2″-(2‴,2‴-Dimethoxyethyl)-1″,3″-dithian-2″-yl]-4′,4′-(ethylenedioxy)pent-2′-enyloxymethyl}propenoate* **11**.—A solution of the alcohol **10** (0.958 g, 2.74 mmol) in benzene (5 cm^3, +2 cm^3 rinse) was added *via* cannula to a stirred suspension of KH (0.470 g, of a 35% dispersion in mineral oil, 4.11 mmol) in anhydrous benzene (25 cm^3). A yellow colour was produced and the mixture was stirred at room temperature for 1 h. Methyl 2-(bromomethyl)propenoate (1.25 cm^3, 11.0 mmol) was added *via* syringe. The colour discharged over a period of 2–3 min and a precipitate formed. After a further 10 min the reaction was quenched by careful addition of saturated aq. ammonium chloride (6 drops), followed 10 min later by saturated aq. sodium hydrogencarbonate (30 cm^3) and water (30 cm^3). Extraction with diethyl ether (4 × 50 cm^3) and washing of the combined organic layers successively with water (30 cm^3) and brine (50 cm^3), followed by drying over anhydrous magnesium sulfate and evaporation of the solvent, gave a yellow oil. Purification by flash chromatography (gradient elution, 30–60% diethyl ether–light petroleum) gave the *ether* **11** (0.800 g, 65%) as an oil (Found: C, 53.4; H, 7.1. $C_{20}H_{32}O_7S_2$ requires C, 53.55; H, 7.19%); ν_{max}(film)/cm^{-1} 2984, 2948, 2829, 1720, 1633, 1437, 1372, 1306, 1276, 1198, 1160, 1119, 1078, 1039, 978, 865 and 816; δ_H(500 MHz; $CDCl_3$) 1.49 (3 H, s, 5′-H_3), 1.94 (2 H, m, 5″-H_2), 2.12 (1 H, dd, *J* 15.0, 4.4, 1‴-H), 2.31 (1 H, dd, *J* 15.0, 4.6, 1‴-H), 2.72–2.79 and 2.89–2.97 (4 H, m, 4″- and 6″-H_2), 3.31 (3 H, s, OMe), 3.33 (3 H, s, OMe), 3.75 (3 H, s, CO_2Me), 3.84–3.99 (4 H, m, OCH_2CH_2O), 4.10 (1 H, dt, *J* 14.0, 1.5, allylic CH_2), 4.15 (1 H, d, *J* 8.0, 1′-H), 4.24 (1 H, dt, *J* 14.0, 1.6, allylic CH_2), 4.76 (1 H, t, *J* 4.5, 2‴-H), 5.67 (1 H, d, *J* 15.7, 3′-H), 5.96 (1 H, br s, 3-H), 5.97 (1 H, dd, *J* 15.6, 8.0, 2′-H) and 6.30 (1 H, br s, 3-H); *m/z* (EI) 448 (M^+), 417 (M − OMe), 241, 226, 207 and 75.

(E)-*Methyl 2-{1′-[2″-(1‴-Formylmethyl)-1″,3″-dithian-2″-yl]-4′-oxopent-2′-enyloxymethyl}propenoate* **12**.—A solution of the acetal **11** (0.785 g, 1.75 mmol) in 2% aq. acetone (25 cm^3) containing PPTS (0.135 g, 0.53 mmol) was heated at reflux for 4 h. The mixture was allowed to cool, poured into water (100 cm^3), and extracted with diethyl ether (4 × 50 cm^3). The combined organic layers were washed successively with saturated aq. sodium hydrogencarbonate (50 cm^3), water (50 cm^3), and brine (50 cm^3), then were dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure and purification of the residue by flash chromatography (80% diethyl ether–light petroleum) gave the *enone* **12** (0.572 g, 91%) as a pale yellow oil (Found: C, 53.45; H, 6.2. $C_{16}H_{22}O_5S_2$ requires C, 53.61; H, 6.19%); ν_{max}(film)/cm^{-1} 2907, 1714, 1675, 1627, 1435, 1359, 1309, 1275, 1254, 1199, 1163, 1068 and 983; δ_H(500 MHz; $CDCl_3$) 1.96–2.06 (2 H, m, 5″-H_2), 2.32 (3 H, s, 5′-H_3), 2.69 (1 H, dd, *J* 16.5, 2.7, 1‴-H), 2.76–2.80 (1 H, m, 4″- or 6″-H), 2.83 (1 H, dd, *J* 16.6, 2.6, 1‴-H), 2.83–2.85 (1 H, m, 6″- or 4″-H), 2.94–2.99 (2 H, m, 4″-H and/or 6″-H), 3.76 (3 H, s, CO_2Me), 4.16 (1 H, dt, *J* 13.2, 1.2, allylic CH_2), 4.30 (1 H, dt, *J* 13.2, 1.2, allylic CH_2), 4.32 (1 H, dd, *J* 6.7, 1.1, 1′-H), 5.90 (1 H, dt, *J* 1.4, 1.4, 3-H), 6.28 (1 H, dd, *J* 16.0, 1.0, 3′-H), 6.33 (1 H, d, *J* 1.2, 3-H), 6.85 (1 H, dd, *J* 13.0, 6.6, 2′-H), 9.84 (1 H, t, *J* 2.7, CHO); *m/z* (EI) 358 (M^+), 340, 327, 294, 161 and 133.

(E)-*Methyl 2-{1′-[2″-(1,3-Dioxan-2-ylmethyl)-1″,3″-dithian-2″-yl]-4′-oxopent-2′-enyloxymethyl}propenoate* **13**.—A mixture of the aldehyde **12** (4.36 g, 12.2 mmol), PPTS (0.307 g, 1.22 mmol), and propane-1,3-diol (0.88 cm^3, 12.2 mmol) in anhydrous benzene (150 cm^3) was heated at reflux with azeotropic removal of water for 3 h. After cooling, the flask contents were poured into saturated aq. sodium hydrogen carbonate (300 cm^3) and extracted with diethyl ether (4 × 200 cm^3). The combined organic extracts were washed successively with saturated aq. sodium hydrogencarbonate (100 cm^3) and brine (100 cm^3), then were dried over anhydrous sodium sulfate and concentrated. Purification by flash chromatography (90% diethyl ether–light petroleum) gave the *dioxane* **13** (4.20 g, 83%) as a pale yellow oil (Found: C, 54.6; H, 6.6. $C_{19}H_{28}O_6S_2$ requires C, 54.79; H, 6.78%); ν_{max}(film) 2952, 2854, 1719, 1675, 1627, 1433, 1359, 1307, 1275, 1253, 1198, 1160, 1132, 1086, 991 and 816; δ_H(500 MHz; $CDCl_3$) 1.30–1.34 (1 H, m, CH_2CH_2O), 1.94–2.02 (2 H, m, 5″-H), 2.03–2.10 (1 H, m, CH_2CH_2O), 2.14 (1 H, dd, *J* 15.3, 4.2, 1‴-H), 2.31 (3 H, s, 5′-H_3), 2.34 (1 H, dd, *J* 15.4, 4.3, 1‴-H), 2.75–2.81 (2 H, m, 4″- or 6″-H_2), 2.90–2.97 (2 H, m, 6″- or 4″-H_2), 3.76 (3 H, s, CO_2Me), 3.76–3.82 (2 H, m, CH_2CH_2O), 4.06–4.10 (2 H, m, CH_2CH_2O), 4.16 (1 H, dt, *J* 13.7, 1.4, allylic CH_2), 4.25 (1 H, dt, *J* 13.7, 1.5, allylic CH_2), 4.36 (1 H, dd, *J* 7.0, 1.1, 1′-H), 4.90 (1 H, t, *J* 4.2, 2‴-H), 5.97 (1 H, dd, *J* 3.3, 1.7, 3-H), 6.24 (1 H, dd, *J* 16.2, 1.0, 3′-H), 6.32 (1 H, dd, *J* 2.8, 1.4, 3-H) and 6.89 (1 H, dd, *J* 16.1, 6.8, 2′-H); *m/z* (EI) 416 (M^+), 385 (M − OMe), 354, 315, 309, 302, 255, 219 and 87.

(E)-*Methyl 2-{4′-(*tert*-Butyldimethylsiloxy)-1′-[2″-(1,3-dioxan-2-ylmethyl)-1″,3″-dithian-2″-yl]penta-2′,4′-dienyloxymethyl}propenoate* **2**.—Triethylamine (331 mm^3, 2.38 mmol) was added to a stirred solution of the enone **13** (330 mg, 0.792 mmol) in anhydrous dichloromethane at −20 °C followed by *tert*-butyldimethylsilyl triflate (TBDMSOTf) (219 mm^3, 0.95 mmol). After being stirred at −20 °C for 30 min the mixture was poured into saturated aq. sodium hydrogencarbonate (50 cm^3) and the aqueous layer was extracted with dichloromethane (2 × 50 cm^3). The combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated off under reduced pressure to give a pale yellow oil. Purification by flash chromatography (gradient elution, 30–50% diethyl ether–light petroleum) gave the *silyl dienol ether* **2** (0.376 g, 90%) as an oil (Found: C, 56.7; H, 8.05. $C_{25}H_{42}O_6S_2Si$ requires C, 56.57; H, 7.98%); ν_{max}(film)/cm^{-1} 2953, 2929, 2855, 1719, 1634, 1593, 1460, 1430, 1307, 1277, 1254, 1157, 1133, 1088, 1027, 1004, 839 and 782; δ_H(500 MHz; $CDCl_3$) 0.18 (3 H, s, MeSi), 0.19 (3 H, s, MeSi), 0.97 (9 H, s, Bu^{t}Si), 1.28–1.32 (1 H, m, CH_2CH_2O), 1.90–1.96 (2 H, m, 5″-H_2), 1.99–2.09 (1 H, m, CH_2CH_2O), 2.19 (1 H, dd, *J* 15.3, 4.0, 1‴-H), 2.35 (1 H, dd, *J* 15.3, 4.1, 1‴-H), 2.74–2.81 (2 H, m, 6″-H_2), 2.86–2.82 (2 H, m, 4″-H_2), 3.75 (3 H, s, CO_2Me), 3.74–3.93 (2 H, m, CH_2CH_2O), 4.03–4.08 (2 H, m, CH_2CH_2O), 4.10 (1 H, dt, *J* 14.1, 1.6, allylic CH_2), 4.19 (1 H, d, *J* 7.2, 1′-H), 4.25 (1 H, dt, *J* 14.1, 1.6, allylic CH_2), 4.36 (2 H, d, *J* 6.8, 5′-H_2), 4.90 (1 H, t, *J* 4.0, 2‴-H), 5.98 (1 H, dd, *J* 3.6, 2.8, 3-H), 6.09 (1 H, d, *J* 15.4, 3′-H), 6.14 (1 H, dd, *J* 15.4, 7.2, 2′-H) and 6.30 (1 H, dd, *J* 3.0, 1.5, 3-H); *m/z* (EI) 530 (M^+), 499 (M − OMe), 475, 423, 275, 252 and 219.

(2E)-*Methyl 2-{(E)-1′-[2-(2‴,2‴-Dimethoxyethyl)-1,3-dithian-2-yl]-4′-oxopent-2-enyloxymethyl}-3-[dimethyl(phenyl)silyl]propenoate* **15**.—Flame-dried lithium chloride (50 mg, 1.18 mmol) was added to a stirred solution of dimethyl (2-oxopropyl)phosphonate (156 cm^3, 1.13 mmol) and the aldehyde **14**[1] (200 mg, 0.40 mmol) in dimethylformamide (DMF) (1.5 cm^3). Diisopropylethylamine (150 cm^3, 0.86 mmol) was introduced during 18 h, using a syringe pump. The solution was stirred for a further 6 h and then further lithium chloride (50 mg, 1.18 mmol) and dimethyl (2-oxopropyl)phosphonate (156 cm^3, 1.13 mmol) were added, followed by slow addition (15 h) of diisopropylethylamine (130 cm^3, 0.75 mmol). After addition was complete, the brown reaction mixture was stirred for a further 9 h, then poured into saturated aq. ammonium chloride (15 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic layers were washed with brine (50 cm^3), dried over anhydrous magnesium sulfate, and concentrated. Purification of the residue by flash chromatography (35% diethyl ether–light petroleum) gave, in order of elution, the starting aldehyde **14** (37 g, 19% recovery) and the (E,E)-*diene* **15** (140 mg, 65%) as a pale yellow oil {Found [M − $(C_3H_6S_2)CCH_2CH(OMe)_2$] 331.1358. $C_{18}H_{23}O_4Si$ requires *m/z* 331.1366; Found: C, 58.0; H, 7.1. $C_{26}H_{38}O_6S_2Si$ requires C, 57.96; H, 7.11%}; ν_{max}(film)/cm^{-1} 3066, 3043, 2948, 2828, 1716, 1675, 1624, 1426, 1359, 1250, 1225, 1116, 1073, 837, 736 and 702; δ_H(500 MHz; $CDCl_3$) 0.47 (3 H, s, Me), 0.48 (3 H, s, Me), 1.90–1.81 (1 H, m, 5″-H), 1.91 (1 H, dd, *J* 4.9, 15.1, 1‴-H), 2.02–1.94 (1 H, m, 5″-H), 2.12 (1 H, dd, *J* 4.1, 15.1, 1‴-H), 2.26 (3 H, s, 5′-H_3), 2.66–2.57 (2 H, m, 4″- and 6″H), 3.30 (3 H, s, OMe), 3.76 (3 H, s, CO_2Me), 4.08 (1 H, d, *J* 10.6, allylic CH_2O), 4.19 (1 H, d, *J* 10.7, allylic CH_2O), 4.24 (1 H, dd, *J* 0.8, 7.1, 1′-H), 4.73 (1 H, t, *J* 4.5, 2‴-H), 6.14 (1 H, dd, *J* 0.8, 16.2, 3′-H), 6.77 (1 H, dd, *J* 7.1, 16.2, 2′-H), 7.16 (1 H, s, 3-H), 7.41–7.32 (3 H, m, Ph) and 7.53–7.48 (2 H, m, Ph); *m/z* (EI) 431 [M − $CH(OMe)_2$ − MeOH, 0.3%], 381 (0.3), 331 [M − $(C_3H_6S_2)CCH_2CH(OMe)_2$, 0.5], 319 (M − $C_{12}H_{15}O_2Si$, 0.5), 279 (1.9), 233 ($C_{13}H_{17}O_2Si$, 3.2), 207 [$(C_3H_6S_2)CCH_2$-$CH(OMe)_2$, 22] and 75 [$CH(OMe)_2$, 75].

(2E)-*Methyl* 2-{(E)-4′-tert-*Butyldimethylsiloxy*-1′-[2″-(2‴,2‴-*dimethoxyethyl*)-1″,3″-*dithian*-2″-*yl*]*penta*-2′,4′-*dienyloxymethyl*}-3-[*dimethyl*(*phenyl*)*silyl*]*propenoate* **3**.—*tert*-Butyldimethylsilyl triflate (30 mm^3, 0.13 mmol) was added dropwise *via* syringe to a stirred solution of the enone **15** (50 mg, 0.093 mmol) and triethylamine (45 mm^3, 0.32 mmol) in dichloromethane (1.5 cm^3) under argon at −20 °C. After 30 min, the mixture was poured into saturated aq. sodium hydrogencarbonate (10 cm^3) and the aqueous layer was extracted with dichloromethane (3 × 15 cm^3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated. Purification of the residue by flash chromatography on Florisil (20% diethyl ether–light petroleum) afforded the silyl enol ether **3** (52 mg, 86%) as an oil; ν_{max}(film)/cm^{-1} 3068, 3045, 2951, 2929, 2855, 1717, 1592, 1459, 1426, 1308, 1251, 1223, 1116, 1072, 1025, 839, 782, 734 and 700; δ_H(500 MHz; C_6D_6) 0.25 (3 H, s, Me), 0.27 (3 H, s, Me), 0.44 (3 H, s, Me), 0.46 (3 H, s, Me), 1.11 (9 H, s, Bu^t), 1.64–1.57 (2 H, m, 5″-H_2), 2.37 (1 H, dd, *J* 4.60, 14.9, 1‴-H), 2.45–2.37 (2 H, m, 4″- and 6″-H), 2.59 (1 H, dd, *J* 4.1, 14.9, 1‴-H), 2.91–2.81 (2 H, m, 4″- and 6″-H), 3.30 (3 H, s, OMe), 3.33 (3 H, s, OMe), 3.58 (3 H, s, CO_2Me), 4.28 (1 H, d, *J* 10.4, allylic CH_2O), 4.39 (1 H, s, 5′-H), 4.41 (1 H, br d, *J* 8.4, 1′-H), 4.47 (1 H, s, 5′-H), 4.47 (1 H, d, *J* 10.4, allylic CH_2O), 5.14 (1 H, t, *J* 4.4, 2-H), 6.20 (1 H, dd, *J* 0.5, 15.4, 3′-H), 6.59 (1 H, dd, *J* 8.1, 15.4, 2′-H), 7.29–7.22 (3 H, m, Ph), 7.41 (1 H, s, 3-H), and 7.56–7.51 (2 H, m, Ph); *m/z* (EI) 233 ($C_{13}H_{17}O_2Si$, 6.5%), 207 [$(C_3H_6S_2)CCH_2CH(OMe)_2$, 2.7], 135 ($PhMe_2Si$, 17), 89 [$CH_2CH(OMe)_2$, 20] and 75 [$CH(OMe)_2$, 75].

Methyl 2-{2′-tert-*Butyldimethylsiloxy*-1′-[2″-(2‴,2‴-*dimethoxyethyl*)-1″,3″-*dithian*-2″-*yl*]*ethoxymethyl*}*propenoate* **17**.—A solution of the alcohol **16** [1] (2.08 g, 5.44 mmol) in THF (15 cm^3, +2 × 2 cm^3 rinse) was added *via* cannula to a stirred suspension of potassium hydride (1.4 g of a 35% suspension in mineral oil, 12.2 mmol) in anhydrous THF (35 cm^3). The mixture was stirred at room temperature until gas evolution had ceased (17 min), causing a yellow colour to develop. Methyl 2-(bromomethyl)propenoate (1.25 cm^3, 10.84 mmol) was added. The colour discharged over 2–3 min and a precipitate formed. After 30 min, the reaction was quenched by slow addition of saturated aq. ammonium chloride (20 cm^3). The mixture was extracted with diethyl ether (3 × 50 cm^3) and the combined organic layers were washed with brine (50 cm^3), dried over anhydrous magnesium sulfate, and concentrated. Purification of the residue by flash chromatography (20% diethyl ether–light petroleum) gave the *ether* **17** (2.3 g, 88%) as an oil (Found: C, 52.5; H, 8.6. $C_{21}H_{40}O_6S_2Si$ requires C, 52.47; H, 8.39%); ν_{max}(film)/cm^{-1} 2950, 2929, 2855, 1719, 1634, 1437, 1276, 1256, 1120, 1081, 838 and 777; δ_H(500 MHz; $CDCl_3$) 0.05 (3 H, s, MeSi), 0.06 (3 H, s, MeSi), 0.89 (9 H, s, Bu^t), 2.02–1.88 (2 H, m, 5″-H_2), 2.10 (1 H, dd, *J* 4.3, 15.2, 1‴-H), 2.34 (1 H, dd, *J* 4.5, 15.1, 1‴-H), 2.75 (2 H, ddd, *J* 3.7, 7.1, 14.2, 4″- and 6″-H), 2.97–2.88 (2 H, m, 4″- and 6″-H), 3.33 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.74 (3 H, s, CO_2Me), 3.89–3.82 (2 H, m, 2′-or 1′-H and 2′-H), 4.21 (1 H, dd, *J* 0.5, 9.0, 1′- or 2′-H), 4.46 (1 H, dt, *J* 14.4, 1.9, allylic CH_2O), 4.63 (1 H, dt, *J* 14.4, 1.8, allylic CH_2O), 4.76 (1 H, t, *J* 4.4, 2‴-H), 5.99 (1 H, q, *J* 2.0, 3-H) and 6.29 (1 H, q, *J* 1.7, 3-H); *m/z* (EI) 480 (M^+, 0.3%), 449 (M − OMe, 1.1), 4.33 (M − CH_2SH, 0.2), 423 (M − Bu^t, 0.2), 405 [M − $CH(OMe)_2$, 0.2], 391 [M − $CH_2CH(OMe)_2$, 0.2], 335 (M − $CH_2OTBDMS$, 0.3), 273 [M −$(C_3H_6S_2)CCH_2CH(OMe)_2$, 0.7], 207 [$(C_3H_6S_2)CCH_2CH(OMe)_2$ 38], 89 [$CH_2CH(OMe)_2$, 5.5] and 75 [Me_2SiOH and $CH(OMe)_2$, 100].

Methyl 2-{1′-[2″-(2‴,2‴-*Dimethoxyethyl*)-1″,3″-*dithian*-2″-*yl*]-2′-*hydroxyethoxymethyl*}*propenoate* **18**.—Hydrogen fluoride (3.1 cm^3 of a 40% aq. solution, 71.2 mmol) was added *via* syringe to a stirred solution of the silyl ether **17** (9 g, 18.7 mmol) and pyridine (6 cm^3, 74.2 mmol) in acetonitrile (80 cm^3). After 16 h, the reaction was quenched by careful addition of saturated aq. sodium hydrogencarbonate (60 cm^3) and the mixture was stirred vigorously until effervescence ceased. The mixture was extracted with diethyl ether (3 × 80 cm^3) and the combined organic layers were washed with brine (75 cm^3), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. Flash chromatography of the residue (70% diethyl ether–light petroleum) afforded the *alcohol* **18** (5.3 g, 77%) as a pale yellow oil (Found: C, 48.9; H, 7.3. $C_{15}H_{26}O_6S_2$ requires C, 49.16; H, 7.15%); ν_{max}(film)/cm^{-1} 3473, 2932, 2829, 1713, 1633, 1439, 1343, 1277, 1197, 1118, 1077 and 960; δ_H(500 MHz; $CDCl_3$) 1.97–1.85 (1 H, m, 5″-H), 2.07–1.99 (1 H, m, 5″-H), 2.05 (1 H, dd, *J* 4.4, 15.2, 1‴-H), 2.29 (1 H, dd, *J* 4.4, 15.1, 1‴-H), 2.78–2.69 (2 H, m, 4″- and 6″-H), 3.02–2.93 (2 H, m, 4″-and 6″-H), 3.33 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.47 (1 H, dd, *J* 3.8, 9.8, OH), 3.84–3.73 [1 H, m (obscured by CO_2Me), 3.79 (3 H, s, CO_2Me), 3.97 (1 H, dd, *J* 3.5, 7.6, 1′-H), 4.04 (1 H, ddd, *J* 3.6, 9.8, 11.9, 2′-H), 4.50 (1 H, dd, *J* 1.1, 11.4, allylic CH_2O), 4.57 (1 H, br d, *J* 11.4, allylic CH_2O), 4.77 (1 H, t, *J* 4.4, 2‴-H), 5.93 (1 H, q, *J* 1.1, 3-H) and 6.31 (1 H, br d, *J* 1.2, 3-H); *m/z* (EI) 366 (M^+, 0.4%), 335 (M − OMe, 0.3), 334 (M − MeOH, 0.6), 303 (1.8), 245 (1.6), 207 [$(C_3H_6S_2)CCH_2CH(OMe)_2$, 32], 159 [M − $(C_3H_6S_2)CCH_2CH(OMe)_2$, 2.5], 99 ($C_5H_7O_2$ 1.5) and 75 [$CH(OMe)_2$, 100].

Methyl 2-{[2″-(2‴,2‴-*Dimethoxyethyl*)-1″,3″-*dithian*-2″-*yl*]-*formylmethoxymethyl*}*propenoate* **19**.—Anhydrous dimethyl sulfoxide (DMSO) (2.8 cm^3, 39.5 mmol) was added *via* syringe to a solution of oxalyl dichloride (1.75 cm^3, 20.1 mmol) in THF (50 cm^3) at −78 °C under argon. The mixture was warmed to −35 °C for 3 min, then was recooled to −78 °C, and a solution of the alcohol **18** (5.2 g, 14.28 mmol) in THF (10 cm^3) was added *via* cannula. After warming to −35 °C for 20 min, the reaction mixture was recooled to −78 °C and triethylamine (7 cm^3, 50.2 mmol) was added. The opaque solution was allowed to warm to room temperature, causing the formation of a thick precipitate.

The reaction mixture was poured directly onto a silica column (200 g) and the crude product was eluted with 60% diethyl ether–light petroleum. Subsequent purification by flash chromatography (55% diethyl ether–light petroleum) gave the *aldehyde* **19** (3.64 g, 70%) as a pale yellow oil [Found: (M − OMe), 333.0836. $C_{14}H_{21}O_5S_2$ requires *m/z*, 333.0830]; ν_{max}(film)/cm^{-1} 2948, 2830, 1723, 1634, 1437, 1278, 1197, 1120, 1079 and 962; δ_H(270 MHz; $CDCl_3$) 1.84–2.15 (2 H, m, 5″-H_2), 2.20 (1 H, dd, *J* 4.4, 15.1, 1‴-H), 2.41 (1 H, dd, *J* 5.0, 15.0, 1‴-H), 2.81–2.64 (2 H, m, 4″- and 6″-H), 2.91–3.10 (2 H, m, 4″- and 6″-H), 3.33 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.76 (3 H, s, CO_2Me), 4.09 (1 H, d, *J* 2.9, 1′-H), 4.28 (1 H, dt, *J* 13.4, 1.4, allylic CH_2O), 4.43 (1 H, dt, *J* 13.4, 1.4, allylic CH_2O), 4.77 (1 H, t, *J* 4.6, 2‴-H), 5.99 (1 H, q, *J* 1.6, 3-H), 6.35 (1 H, br d, *J* 1.2, 3-H) and 9.75 (1 H, d, *J* 3.2, 2′-H), *m/z* (EI) 364 (M^+, 0.1%), 335 (M − CHO, 1.1), 333 (M − OMe, 0.9), 289 [M − CH$(OMe)_2$, 0.1], 275 [M − CH_2CH$(OMe)_2$, 1.1], 207 [($C_3H_6S_2$)CCH_2CH$(OMe)_2$, 19], 99 ($C_5H_7O_2$ 2.3) and 75 [CH$(OMe)_2$, 100].

(E)-*Methyl* 2-{1′-[2″-(2‴,2‴-*Dimethoxyethyl*)-1″,3″-*dithian*-2″-*yl*]-2′-(2⁗-*oxotetrahydrofuran*-3⁗-*ylidene*)*ethoxymethyl*}-*propenoate* **21** *and its* (Z) *Isomer* **20**.—Anhydrous lithium chloride (125 mg, 2.95 mmol) was added to a solution of α-diethoxyphosphoryl-γ-butyrolactone (512 mg, 2.3 mmol) in acetonitrile (7.5 cm^3). Following addition of a solution of the aldehyde **19** (425 mg, 1.17 mmol) in acetonitrile (3 cm^3, + 2 × 0.3 cm^3 rinse) a solution of diisopropylethylamine (188 mg, 1.45 mmol) in acetonitrile (1.7 cm^3) was introduced over a period of 1.5 h *via* syringe pump. The mixture was stirred for 22 h, then was poured into water (30 cm^3) and extracted with diethyl ether (3 × 30 cm^3). The combined organic layers were washed with brine (25 cm^3), dried over anhydrous magnesium sulfate, and concentrated. Purification of the residue by flash chromatography (80% diethyl ether–light petroleum) gave, in order of elution, the (Z) *compound* **20** (68 mg, 13%) as an oil (Found: C, 52.8; H, 6.7. $C_{19}H_{28}O_7S_2$ requires C, 52.76; H, 6.52); ν_{max}(film)/cm^{-1} 2928, 2829, 1748, 1723, 1670, 1634, 1437, 1376, 1277, 1190, 1119, 1075, 1027, 960, 915 and 732; δ_H(500 MHz; $CDCl_3$) 1.82–1.92 (1 H, m, 5″-H), 1.95–2.04 (1 H, m, 5″-H), 2.08 (1 H, dd, *J* 3.8, 15.1, 1‴-H), 2.32 (1 H, dd, *J* 4.8, 15.1, 1‴-H), 2.64 (1 H, ddd, *J* 3.4, 6.7, 14.2, 6″- or 4″H), 2.69 (1 H, ddd, *J* 3.1, 6.8, 14.3, 4″-or 6″-H), 3.14–2.96 (4 H, m, 4″-H and 6″-H), 3.37 (3 H, s, OMe), 3.35 (3 H, s, OMe), 3.74 (3 H, s, CO_2Me), 4.22 (1 H, dt, *J* 13.9, 1.4, allylic CH_2O), 4.28 (1 H, dt, *J* 13.9, 1.4, allylic CH_2O), 4.39 (2 H, t, *J* 7.4, 5⁗-H), 4.79 (1 H, dd, *J* 3.8, 4.7, 2‴-H), 5.82 (1 H, d, *J* 10.1, 1′-H), 5.96 (1 H, q, *J* 1.7, 3-H), 6.29 (1 H, dt, *J* 1.4, 1.1, 3-H) and 6.32 (1 H, dt, *J* 10.1, 2.4, 2′-H); δ_C(125.8 MHz; $CDCl_3$) 169.9 (CO_2R), 166.1 (CO_2R′), 137.5, 137.1, 128.0, 126.5, 102.6 [CH$(OMe)_2$], 74.8, 67.9, 65.5, 53.9, 53.5, 53.1, 51.7, 39.3, 29.1, 26.4, 26.2 and 24.54; *m/z* (EI, 18 eV) 432 (M^+, 0.1%), 402 (M −CH_2O, 0.2), 400 (M − MeOH, 0.3), 369 (0.4), 285 (0.6), 254 (0.6), 240 (1), 207 [($C_3H_6S_2$)CCH_2CH$(OMe)_2$, 100] and 75 [CH$(OMe)_2$, 64]; and the (E)-*compound* **21** (211 mg, 42%) as a viscous oil (Found: C, 52.5; H, 6.7%); ν_{max}(film)/cm^{-1} 2922, 2830, 1754, 1720, 1679, 1635, 1437, 1379, 1279, 1196, 1118, 1075, 1031, 963 and 730; δ_H(500 MHz; $CDCl_3$) 1.91–2.01 (2 H, m, 5″-H_2), 2.17 (1 H, dd, *J* 4.3, 15.0, 1‴-H), 2.39 (1 H, dd, *J* 5.0, 15.0, 1‴-H), 2.72–2.84 (2 H, m, 4″- and 6″-H), 2.85–2.97 (2 H, m, 4″-and 6″-H), 2.99–3.08 (2 H, m, 4⁗-H_2), 3.32 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.75 (3 H, s, CO_2Me), 4.14 (1 H, dt, *J* 13.7, 1.5, allylic CH_2O), 4.21 (1 H, dt, *J* 13.7, 1.5, allylic CH_2O), 4.43–4.34 (2 H, m, 5⁗-H_2), 4.45 (1 H, d, *J* 8.6, 1′-H), 4.75 (1 H, t, *J* 4.6, 2‴-H), 5.96 (1 H, q, *J* 1.6, 3-H), 6.31 (1 H, q, *J* 1.3, 3-H) and 6.92 (1 H, dt, *J* 8.6, 2.9, 2′-H), *m/z* (EI) 432 (M^+, <0.1%), 402 (M −CH_2O, <0.1), 400 (M − MeOH, <0.1), 357 [M − CH$(OMe)_2$, 0.1], 343 [M − CH_2CH$(OMe)_2$, 0.1], 341 (0.1), 244 (0.3), 225 [M − ($C_3H_6S_2$)C-CH_2CH$(OMe)_2$, 0.1], 207 [($C_3H_6S_2$)CCH_2CH$(OMe)_2$, 12], 99 ($C_5H_7O_2$, 1.9) and 75 [CH$(OMe)_2$, 100].

(2E)-*Methyl* 2-{(E)-1′-[2″-(2‴,2‴-*Dimethoxyethyl*)-1″,3″-*dithian*-2″-*yl*]-4′,4′-(*ethylenedioxy*)-3′-*methylpent*-2′-*enyloxymethyl*}-3-[*dimethyl*(*phenyl*)*silyl*]*propenoate* **24**.—A solution of the allyl alcohol **22**[8] (0.232 g, 0.64 mmol) in dry benzene (5 cm^3) was added *via* cannula to a stirred suspension of potassium hydride (0.108 g, 35% dispersion in mineral oil; 0.96 mmol) in dry benzene (4 cm^3) under argon. After being stirred at ambient temperature for 1 h a yellow solution remained. A solution of the bromo ester **23**[1] (0.200 g, 0.64 mmol) in dry benzene (8 cm^3) was then added *via* cannula and the mixture was stirred for 16 h. The flask contents were then poured into saturated aq. sodium hydrogencarbonate (10 cm^3) and extracted with diethyl ether (3 × 20 cm^3). The combined organic extracts were dried over anhydrous sodium sulfate and concentrated. Flash chromatography (50% diethyl ether–light petroleum) gave the *ether* **24** (0.200 g, 53%) as an oil (Found: C, 58.5; H, 7.4. $C_{29}H_{44}O_7S_2Si_2$ requires C, 58.4; H, 7.4%); ν_{max}(film)/cm^{-1} 2947, 1716, 1426, 1371, 1316, 1222, 1199, 1068, 866 and 734; δ_H(500 MHz; $CDCl_3$) 0.48 (6 H, s, PhMe_2Si), 1.44 (3 H, s, 5′-H_3), 1.67 (3 H, d, *J* 1.4, 3′-Me), 1.89 (2 H, m, 5″-H_2), 2.02 (1 H, dd, *J* 15.0 and 4.2, 1‴-H), 2.16 (1 H, dd, *J* 14.8 and 4.4 1‴-H), 2.69 (2 H, m, 4″- and 6″-H), 2.96 (2 H, m, 4″- and 6″-H), 3.31 (6 H, s, OMe), 3.65–3.9 (4 H, m, OCH_2CH_2O), 3.77 (3 H, s, CO_2Me), 3.94 (1 H, d, *J* 10.0, allylic CH_2), 4.09 (1 H, d, *J* 10.0, allyl CH_2), 4.37 (1 H, d, *J* 10.1, 1′-H), 4.73 (1 H, t, *J* 4.3, 2‴-H), 5.84 (1 H, dd, *J* 10.1 and 1.4, 2′-H), 7.13 (1 H, s, 3-H), 7.36 (3 H, m, *p*- and *m*-Ph) and 7.50 (2 H, m, *o*-Ph); *m/z* (EI) 596 (M^+, 0.2%), 581 (M − CH_3, 0.1), 564 (M − CH_3OH, 0.2), 532 (M − 2CH_3OH, 0.1) and 519 (M −Ph, 0.3).

(2E)-*Methyl* 3-[*Dimethyl*(*phenyl*)*silyl*]-2-{(E)-1′-[2″-*formylmethyl*)-1″,3″-*dithian*-2″-*yl*]-3′-*methyl*-4′-*oxopent*-2′-*enyloxymethyl*}*propenoate* **25**.—A solution of the ether **24** (0.200 g, 0.34 mmol) and PPTS (0.025 g, 0.10 mmol) in aq. acetone (20 cm^3; 2% v/v) was heated at reflux for 6 h. The flask contents were then cooled, concentrated (~3 cm^3) under reduced pressure, and partitioned between saturated aq. sodium hydrogencarbonate (10 cm^3) and diethyl ether (3 × 20 cm^3). The combined organic fractions were dried over anhydrous sodium sulfate and concentrated to give the *keto aldehyde* **25** (0.148 g, 85%) as an oil (Found: M^+, 506.1619. $C_{25}H_{34}O_5SiS_2$ requires M, 506.1617); ν_{max}(film)/cm^{-1} 2949, 1712, 1426, 1369, 1225, 1114, 1093, 1059, 836, 790 and 735; δ_H(500 MHz; $CDCl_3$) 0.46 (6 H, s, PhMe_2Si), 1.79 (3 H, d, *J* 1.4, 3′-Me), 1.86 (2 H, m, 5″-H_2), 2.31 (3 H, s, 5′-Me), 2.68 (1 H, dd, *J* 16.6 and 2.6, 1‴-H), 2.7 (3 H, m, 1‴-, 4″-and 6″-H), 2.95 (2 H, m, 4″-and 6″-H), 3.77 (3 H, s, CO_2Me), 3.98 (1 H, d, *J* 10.1, allyl CH_2), 4.07 (1 H, d, *J* 10.0, allyl CH_2), 4.46 (1 H, d, *J* 9.6, 1′-H), 6.49 (1 H, dd, *J* 9.6 and 1.4, 2′-H), 7.19 (1 H, s, 3-H), 7.38 (3 H, m, *p*- and *m*-Ph), 7.50 (2 H, m, *o*-Ph) and 9.78 (1 H, t, *J* 2.6, 2‴-H); *m/z* (EI) 506 (M^+, <0.1%), 491 (M − CH_3, 0.1), 446 (M − CH_3O − CHO, 0.1), 429 (0.1) and 389 (0.3)

(2E)-*Methyl* 3-[*Dimethyl*(*phenyl*)*silyl*]-2-{(E)-1′-[2″-(1,3-*dioxan*-2-*ylmethyl*)-1″,3″-*dithian*-2″-*yl*]-3′-*methyl*-4′-*oxopent*-2′-*enyloxymethyl*}*propenoate* **26**.—A solution of keto aldehyde **25** (0.140 g, 0.277 mmol), propane-1,3-diol (0.020 cm^3, 0.021 g, 0.30 mmol), and PPTS (5 mg) in dry benzene was heated at reflux with azeotropic removal of water for 4 h. The flask contents were then cooled, poured into saturated aq. sodium hydrogen carbonate (10 cm^3), and extracted with diethyl ether (3 × 20 cm^3). The combined extracts were dried over anhydrous sodium sulfate and concentrated. The resulting oil was dissolved in aq. acetone (20 cm^3; 2% v/v), PPTS (5 mg) was added, and the solution was heated at reflux for 16 h. After cooling the flask's contents were poured into saturated aq. sodium hydrogencarbonate (10 cm^3) and extracted with diethyl ether (3 × 20 cm^3). The combined extracts were dried over anhydrous sodium sulfate and concentrated. Flash chromatography (50% diethyl ether–light petroleum) gave the 1,3-*dioxane* **26** (0.200 g, 78%) as an oil (Found: M^+, 564.2040. $C_{28}H_{40}O_6SiS_2$ requires M, 546.2036); ν_{max}(film)/cm^{-1} 2951, 2922, 2853, 2249, 1715, 1426, 1371, 1347, 1303, 1275, 1133, 1091, 1058, 992, 911 and 837; δ_H(500 MHz; $CDCl_3$) 0.46 (6 H, s, PhMe_2Si), 1.32 (1 H, m, OCH_2CH_2), 1.75 (3 H, d, *J* 1.4, 3′-Me), 1.93 (3 H, m, OCH_2CHH and 5″-H_2), 2.04 (1 H, dd, *J* 15.4 and 3.6, 1‴-H), 2.17 (1 H, dd, *J* 15.4 and 3.5, 1‴-H), 2.31 (3 H, s, 5′-H_3), 2.7 (2 H, m, 4″- and 6″-H), 3.0 (2 H, m, 4″- and 6″-H), 3.77 (3 H, s, CO_2Me), 3.78 (2 H, m, OCH_2CH_2), 4.00 (1 H, d, *J* 9.9, allyl CH_2), 4.03 (2 H, m, OCH_2CH_2), 4.05 (1 H, d, *J* 10.0, allyl CH_2), 4.52 (1 H, d, *J* 9.6, 1′-H), 4.90 (1 H, t, *J* 3.9, 2‴-H), 6.65 (1 H, dd, *J* 9.7 and 1.3, 2′-H), 7.16 (1 H, s, 3-H), 7.37 (3 H, m, *p*- and *m*-Ph) and 7.50 (2 H, m, *o*-Ph); *m/z* (EI) 564 (M^+, 0.4%), 549 (M − CH_3, <0.1), 490 (0.1), 410 (0.1) and 346 (1.2).

(2E)-*Methyl* 2-{(E)-4′-(tert-*Butyldimethylsilyl*)-1′-[2″-(1,3-*dioxan-2-ylmethyl*)-1″,3″-*dithian-2″-yl*]-3′-*methylpenta*-2′,4′-*dienyloxymethyl*}-3-[*dimethyl(phenyl)silyl*]*propenoate* **7**.—*tert*-Butyldimethylsilyl triflate (0.010 cm^3, 44 μmol) was added dropwise to a stirred solution of enone **26** (0.010 g, 17.3 μmol) and triethylamine (0.012 cm^3, 88 μmol) in dry dichloromethane (2 cm^3) under argon at −20 °C. After the reaction mixture had been stirred at −20 °C for 0.5 h, saturated aq. sodium hydrogen carbonate (0.010 cm^3) was added and the flask was allowed to warm to ambient temperature. Anhydrous sodium sulfate was added and the mixture was stirred vigorously for 15 min, filtered, and concentrated under reduced pressure. Flash chromatography (40% diethyl ether–light petroleum doped with 1% triethylamine) gave the *silyl enol ether* **7** (0.0112 g, 95%) (Found: M^+, 678.2900. $C_{34}H_{54}O_6Si_2S_2$ requires M, 678.2900); ν_{max}(film)/cm^{-1} 3046, 2952, 2927, 2891, 2854, 2731, 1719, 1595, 1459, 1426, 1375, 1316, 1250, 1222, 1134, 1115, 1094, 1059, 1040, 1019, 1004, 939 and 893; δ_H(500 MHz; $CDCl_3$) 0.18 (3 H, s, Bu^tMe_2Si), 0.20 (3 H, s, Bu^tMe_2Si), 0.45 (3 H, s, PhMe_2Si), 0.46 (3 H, s, PhMe_2Si), 0.89 (9 H, s, Bu^{t}Me$_2$Si), 1.28 (1 H, m, OCH_2CH_2), 1.74 (3 H, d, *J* 1.1, 3′-Me), 1.87 (2 H, m, 5″-H_2), 1.98 (1 H, dd, *J* 15.1 and 3.9, 1‴-H), 2.03 (1 H, m, OCH_2CH_2), 2.11 (1 H, dd, *J* 15.2 and 3.8, 1‴-H), 2.58 (1 H, m, 4″- or 6″-H), 2.66 (1 H, m, 6″- or 4″-H), 3.04 (2 H, m, 4″- and 6″-H), 3.77 (3 H, s, CO_2Me), 3.78 (2 H, m, OCH_2CH_2), 3.89 (1 H, d, *J* 9.9, allyl CH_2), 4.04 (2 H, m, OCH_2CH_2), 4.08 (1 H, d, *J* 10.1, allyl CH_2), 4.34 (1 H, d, *J* 0.9, 5′-H), 4.43 (1 H, d, *J* 10.2, 1′-H), 4.49 (1 H, d, *J* 1.1, 5′-H), 4.90 (1 H, t, *J* 3.8, 2‴-H), 6.23 (1 H, dd, *J* 10.2 and 1.0, 2′-H), 7.11 (1 H, s, 3-H), 7.34 (3 H, m, *p*- and *m*-Ph) and 7.50 (2 H, m, *o*-Ph); *m/z* (EI) 678 (M^+, 0.1%), 603 (0.1), 490 (0.1) and 459 (2.1).

(1R*,3aR*,7aR*)-*Methyl* 6-(tert-*Butyldimethylsiloxy*)-1-[2-(1,3-*dioxan-2-ylmethyl*)-1,3-*dithian*-2-*yl*]-1,4,5,7a-*tetrahydro*-3H-*isobenzofuran*-3a-*carboxylate* **28**.—A solution of the triene **2** (4.58 g, 8.63 mmol) in anhydrous toluene (350 cm^3) was heated at reflux for 7 h. After cooling, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (gradient elution, 40–70% diethyl ether–light petroleum) to give the *cyclised product* **28** (3.85 g, 84%) as a pale yellow oil (Found: C, 56.3; H, 8.1. $C_{25}H_{42}O_6S_2Si$ requires C, 56.57; H, 7.98%); ν_{max}(film)/cm^{-1} 2951, 2929, 2855, 1729, 1664, 1459, 1258, 1230, 1197, 1133, 1050, 878, 840 and 780; δ_H(500 MHz; $CDCl_3$) 0.12 (3 H, s, MeSi), 0.14 (3 H, s, MeSi), 0.91 (9 H, s, Bu^{t}Si), 1.31–1.34 (1 H, m, $CHHCH_2O$), 1.94–2.16 (7 H, m, 4- and 5-H_2, CH_2CH_2S and $CHHCH_2O$), 2.26 (1 H, dd, *J* 15.2, 3.5, 1″-H), 2.33 (1 H, dd, *J* 15.2, 4.2, 1″-H), 2.74–2.82 (2 H, m, CH_2S), 2.88–2.93 (2 H, m, CH_2S), 3.52 (1 H, br t, *J* 6.5, 7a-H), 3.69 (3 H, s, CO_2Me), 3.76 (1 H, d, *J* 7.0, 1-H), 3.79 (1 H, dd, *J* 12.5, 2.1, CH_2CH_2O), 2.84 (1 H, dd, *J* 12.0, 2.1, CH_2CH_2O), 4.07 (1 H, d, *J* 8.5, 3-H), 4.06–4.11 (2 H, m, CH_2CH_2O), 4.24 (1 H, d, *J* 7.9, 3-H), 4.93 (1 H, t, *J* 3.9, 2″-H) and 5.09 (1 H, d, *J* 4.3, 7-H); *m/z* (EI) 530 (M^+), 423, 251, 219, 87 and 73.

(1R*,3aS*,4S*,7aR*)-*Methyl* 6-(tert-*Butyldimethylsiloxy*)-1-[2′-(2″,2″-*dimethoxyethyl*)-1′,3′-*dithian*-2′-*yl*]-4-[*dimethyl*-(*phenyl*)*silyl*]-1,4,5,7a-*tetrahydro*-3H-*isobenzofuran*-3a-*carboxylate* **30** *and its* (1R*,3aR*,4R*,7aR*)-*Isomer* **29**.—A solution of the triene **3** (42 mg, 64 μmol) in anhydrous toluene (2 cm^3) was heated to reflux under argon for 14 h. After cooling, the solvent was removed under reduced pressure to obtain the crude cycloadducts as a yellow oil (as a 3.4:1 mixture of stereoisomers **30** and **29**). Purification of the residue by flash chromatography (25% diethyl ether–light petroleum) gave, in order of elution, the pure *bicycle* **30** (13.4 mg, 32%) as an oil [Found: (M − MeOH), 620.2492. $C_{31}H_{48}O_5S_2Si_2$ requires *m/z*, 620.2482]; ν_{max}(film)/cm^{-1} 2951, 2927, 2854, 1726, 1674, 1426, 1359, 1250, 1193, 1115, 1068, 836, 776 and 701; δ_H(500 MHz; $CDCl_3$) 0.09 (6 H, s, Me), 0.285 (3 H, s, Me), 0.29 (3 H, s, Me), 0.89 (9 H, s, Bu^t), 1.80–2.01 (6 H, m, 4- and 1″-H, and 5- and 5′-H_2), 2.10 (1 H, dd, *J* 4.5, 15.0, 1″-H), 2.58 (1 H, ddd, *J* 2.8, 6.6, 13.9, 6′- or 4′-H), 2.66 (1 H, ddd, *J* 3.0, 6.9, 13.7, 4′- or 6′-H), 3.03 (1 H, ddd, *J* 2.9, 10.2, 14.1, 6′- or 4′-H), 3.07 (1 H, ddd, *J* 2.7, 9.8, 13.8, 4′- or 6′-H), 3.25 (1 H, v br t, *J* 5.5, 7a-H), 3.28 (1 H, d, *J* 9.2, 3-H), 3.30 (3 H, s, OMe), 3.32 (3 H, s, OMe), 3.42 (3 H, s, CO_2Me), 3.80 (1 H, d, *J* 5.9 1-H), 4.38 (1 H, d, *J* 9.1, 3-H), 4.75 (1 H, t, *J* 4.2, 2″-H), 4.91 (1 H, dd, *J* 1.9, 4.8, 7-H), 7.38–7.31 (3 H, m, Ph) and 7.50–7.44 (2 H, m, Ph); *m/z* (EI) 621 (M − OMe, 0.1%), 620 (M − MeOH, 0.1), 445 [M − ($C_3H_6S_2$)$CCH_2CH(OMe)_2$, 0.4], 223 (0.8), 207 [($C_3H_6S_2$)$CCH_2CH(OMe)_2$, 0.3], 149 (6.4), 101 (2.4), 75 [$CH(OMe)_2$, 2.3], 72 (24) and 59 ($C_2H_3O_2$, 81); and a mixture of bicycles **30** and **29** (18.7 mg, 45%, as a ~1.5:1 mixture). The ^{1}H NMR spectrum of isomer **29** was obscured by signals from the major isomer. Characterisation of the minor stereoisomer was carried out after hydrolysis and diastereoisomeric separation by flash chromatography (*vide infra*).

(1R*,3aR*,8bR*)-*Methyl* 1-[2-(2″,2″-*Dimethoxyethyl*)-1,3-*dithian*-2-*yl*]-1,4,5,7,8,8b-*hexahydro*-3H-*benzo*[1,2-b:3,4-c′]-*difuran*-3a-*carboxylate* **32**.—Tebbe reagent (720 mm^3 of a freshly prepared 0.5 mol dm^{-3} solution in toluene, 0.36 mmol) was added dropwise during 20 min to a stirred solution of the lactone **21** (144 mg, 0.33 mmol) and pyridine (10 mm^3, 0.12 mmol) in a mixture of toluene (0.56 cm^3) and THF (0.28 cm^3) at −40 °C under argon. The dark red solution was stirred at −40 °C for 15 min, then was allowed to warm slowly to −15 °C during 2 h. The reaction was quenched by addition of 15% aq. sodium hydroxide (0.1 cm^3) to the vigorously stirred mixture and consequent warming of the mixture to room temperature. After effervescence had ceased (5 min), diethyl ether (8 cm^3) was added, and the orange mixture was dried over anhydrous sodium sulfate and filtered. The solvent was removed under reduced pressure and the orange residue was filtered through basic alumina (activity grade III; 4.2 g; 60% diethyl ether–light petroleum) to obtain the crude triene **4** as a yellow oil. The very unstable triene was used directly without further purification. An analytical sample was purified by flash chromatography (basic alumina; 60% diethyl ether–light petroleum), ν_{max}(film)/cm^{-1} 3052, 2927, 1720, 1675, 1638, 1438, 1378, 1270, 1196, 1118, 1075, 962 and 736; δ_H(500 MHz; C_6D_6) 1.47–1.64 (2 H, m, 5″-H_2), 2.32–2.69 (6 H, m, 4″-, 6″- and 4‴-H_2) 2.49 (1 H, dd, *J* 3.8, 14.8, 1‴-H), 2.74 (1 H, dd, *J* 5.1, 14.8, 1‴-H), 3.26 (3 H, s, OMe), 3.28 (3 H, s, OMe), 3.38 (3 H, s, CO_2Me), 3.71 (1 H, br q, *J* 7.8, 5⁗-H), 3.78 (1 H, dt, *J* 5.6, 8.4, 5⁗-H), 4.27 (1 H, dt, *J* 13.9, 1.5, allylic CH_2O), 4.40 (1 H, dt, *J* 13.9, 1.7, allylic CH_2O), 4.53 (1 H, d, *J* 9.6, 1′-H), 4.60 (1 H, d, *J* 2.0, enol ether CH_2), 4.63 (1 H, d, *J* 2.0, enol ether CH_2), 5.09 (1 H, dd, *J* 3.8, 5.1 2‴-H), 6.00 (1 H, q, *J* 1.8, 3-H), 6.35 (1 H, q, *J* 1.5, 3-H) and 6.51 (1 H, dt, *J* 9.6, 2.6, 2′-H).

A solution of the crude triene **4** in anhydrous toluene (1.5 cm^3) was heated to 60 °C under argon for 5 h. After cooling, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (basic alumina, activity grade III; 4 g; 60% diethyl ether–light petroleum) to give the *tricycle* **32** (25.5 mg, 18% from **21**, contaminated with ~11% of an impurity, probably the C-3a epimer) as an oil [Found: (M − MeOH), 398.1211. $C_{19}H_{26}O_5S_2$ requires *m/z*, 398.1222]; ν_{max}(film)/cm^{-1} 2946, 1728, 1619, 1433, 1329, 1226, 1199, 1119, 1050 and 813; δ_H(500 MHz; C_6D_6; major isomer only) 1.47–1.55 (1 H, m, 5′-H), 1.56–1.66 (1 H, m, 5′-H), 1.82 (1 H, ddd, *J* 5.7, 7.8, 13.3, 4-H$_\beta$), 1.90–1.99 (1 H, m, 5-H), 2.05 (1 H, dt, *J* 13.3, 5.9, 4-H$_\alpha$), 2.12–2.22 (1 H, m, 5-H), 2.41 (1 H, dd, *J* 3.5, 14.8, 1″-H), 2.44–2.55 (3 H, m, 4′- and 6′-H and 8-H$_\alpha$) 2.72 (1 H, dd, *J* 4.9, 14.8, 1″-H), 2.63–2.77 (2 H, m, 8-H$_\beta$ and 6′- or 4′-H), 2.81 (1 H, ddd, *J* 3.9, 8.0, 10.0, 4′-or 6′-H), 3.34 (6 H, s, 2 × OMe), 3.37 (3 H, s, CO_2Me), 3.62 (1 H, d, *J* 8.5, 3-H$_\beta$), 4.03 (1 H, br d, *J* 5.7, 8b-H), 4.07 (2 H, br t, *J* 9.3, 7-H$_2$), 4.34 (1 H, d, *J* 5.7, 1-H), 4.58 (1 H, d, *J* 8.5, 3-H$_\alpha$) and 5.14 (1 H, dd, *J* 3.6, 5.0, 2″-H); δ_C(125.8 MHz; C_6D_6; major isomer only) 174.4 (1 C, s, CO_2Me), 152.1 (1 C, s, C-5a), 105.0 (1 C, s, C-8a), 103.3 (1 C, d, C-2″), 93.4 (1 C, d, C-1), 73.9 and 69.1 (2 C, t, C-3, -7), 55.2 and 55.0 (2 C, s, C-3a, -2′), 53.2 (1 C, q, OMe), 52.3 (1 C, q, OMe), 51.8 (1 C, q, OMe), 44.3 (1 C, d, C-8b), 41.0 (1 C, t), 34.2 (1 C, t), 28.3 (1 C, t), 26.9 (1 C, t), 26.7 (1 C, t), 24.9 (1 C, t) and 20.6 (1 C, t); *m/z* (EI) 430 (M$^+$, 0.3%), 398 (M − MeOH, 2), 367 (0.2), 355 [M − CH(OMe)$_2$, 0.1], 341 [M − CH$_2$CH(OMe)$_2$, 1.9], 223 [M − ($C_3H_6S_2$)-CCH$_2$CH(OMe)$_2$, 2.5], 207 [($C_3H_6S_2$)CCH$_2$CH(OMe)$_2$, 21], 175 (4), 135 (7.9) and 75 [CH(OMe)$_2$, 100].

(1R*,3aR*,4R*,7aR*)-*Methyl* 6-tert-*Butyldimethylsiloxy*-4-*dimethyl(phenyl)silyl*-1-[2′-(1,3-*dioxan*-2-*ylmethyl*)-1′,3′-*dithian*-2′-*yl*]-7-*methyl*-1,4,5,7a-*tetrahydro*-3H-*isobenzofuran*-3a-*carboxylate* **37**.—A solution of the triene **7** (0.0112 g, 16.5 μmol) in anhydrous toluene (2 cm^3) was heated at reflux under argon for 3 h. After cooling, the solvent was removed under reduced pressure to obtain the crude cycloadducts as an oil. Purification of the residue by flash chromatography (40% diethyl ether–light petroleum doped with 1% triethylamine) gave *title compound* **37** (0.0086 g, 77%) (Found: M$^+$, 678.2900. $C_{34}H_{54}O_6Si_2S_2$ requires M, 678.2900); ν_{max}(film)/cm^{-1} 2925, 2853, 2040, 1717, 1652, 1459, 1425, 1375, 1317, 1251, 1202, 1132, 1038, 930 and 837; δ_H(500 MHz; CDCl$_3$) 0.10 (3 H, s, Bu^t*Me*$_2$Si), 0.10 (3 H, s, Bu^t*Me*$_2$Si), 0.39 (3 H, s, Ph*Me*$_2$Si), 0.48 (3 H, s, Ph*Me*$_2$Si), 0.89 (9 H, s, *Bu^t*Me$_2$Si), 1.30 (1 H, m, OCH$_2$C*H*$_2$), 1.80 (3 H, d, *J* 1.1, 7-Me), 1.87 (1 H, m, 5′-H), 1.99 (1 H, m, 5′-H), 2.02 (1 H, dd, *J* 15.6 and 8.1, 5-H), 2.07 (1 H, m, OCH$_2$C*H*$_2$), 2.2–2.35 (4 H, m, 4- and 5-H and 1″-H$_2$), 2.64 (1 H, m, 4′- or 6′-H), 2.75 (1 H, m, 5′-H or 4′-H), 2.84 (1 H, m, 4′- and 6′-H), 3.02 (1 H, br d, *J* 8.9, 7a-H), 3.63 (3 H, s, CO_2Me), 3.64 (1 H, d, *J* 8.9, 3-H), 3.80 (1 H, m, OC*H*$_2$CH$_2$), 3.87 (1 H, d, *J* 8.9, 3-H), 4.10 (1 H, m, OC*H*$_2$CH$_2$), 4.77 (1 H, d, *J* 8.9, 1-H), 4.91 (1 H, dd, *J* 15.0 and 3.0, 2″-H), 7.33 (3 H, m, *p*- and *m*-Ph) and 7.56 (2 H, m, *o*-Ph); *m/z* (EI) 678 (M$^+$, 1.1%), 663 (M − CH$_3$, 0.1), 647 (M − CH$_3$O, 0.1), 619 (0.1), 603 (0.7), 589 (0.4) and 572 (0.8).

(1R*,3aR*,7aR*)-*Methyl* 1-[2-(*Formylmethyl*)-1,3-*dithian*-2-*yl*]-6-*oxoperhydroisobenzofuran*-3a-*carboxylate* **39**.—A solution of the silyl enol ether **28** (87.3 mg, 0.164 mmol) in acetic acid–THF–water (3:1:1; 20 cm^3) was heated to 55 °C for 16 h. After cooling, the flask contents were concentrated and the residue was partitioned between dichloromethane (20 cm^3) and water (20 cm^3) and solid sodium hydrogen carbonate was added until effervescence ceased. The aqueous layer was extracted with dichloromethane (3 × 20 cm^3) and the combined organic layers were dried over anhydrous sodium sulfate and concentrated. Purification of the residue by flash chromatography (gradient elution, 80–100% diethyl ether–light petroleum) gave the *keto aldehyde* **39** (50.0 mg, 85%) as an oil (Found: M$^+$, 358.0917. $C_{16}H_{22}O_5S_2$ requires M, 358.0909); ν_{max}(film)/cm^{-1} 2949, 1712, 1425, 1278, 1229, 1120, 1048 and 909; δ_H(500 MHz; CDCl$_3$) 1.95–2.08 (3 H, m, 4-H$_2$ and 5-H), 2.31–2.39 (3 H, m, 7-H and C*H*$_2$CH$_2$S), 2.62 (1 H, dd, *J* 15.6, 7.0, 7-H), 2.71 (1 H, dd, *J* 16.4, 2.4, 1″-H), 2.76–2.84 (4 H, m, CH$_2$S, 5-H, and including dd, *J* 16.4, 1.1, 1″-H), 2.92–2.98 (2 H, m, CH$_2$S), 3.28 (1 H, dd, *J* 14.0, 7.0, 7a-H), 3.67 (1 H, d, *J* 9.3, 3-H), 3.79 (3 H, s, CO_2Me), 4.05 (1 H, d, *J* 7.7, 1-H), 4.33 (1 H, d, *J* 9.3, 3-H) and 9.83 (1 H, t, *J* 2.9, 2″-H); *m/z* (EI) 358 (M$^+$), 340 (M − H$_2$O), 327, 233, 197 and 161.

(2aR*,5aR*,6S*,8aR*,8bR*)-*Methyl* 6-*Hydroxy*-5-*oxoperhydronaphtho*[1,8-bc]*furan*-8-*spiro*-2′-(1′,3′-*dithiane*)-2a-*carboxylate* **40** *and its* (2aR*,5aR*,6R*,8bR*)-*Isomer* **41**.—A solution of potassium hydroxide in methanol (555 mm^3; 0.244 mol dm^{-3}) was added to a stirred solution of the keto aldehyde **39** (32.4 mg, 90.4 μmol) in anhydrous methanol (2 cm^3) at room temperature. After being stirred for 1 h the reaction mixture was quenched with aq. hydrochloric acid (2 cm^3; 1 mol dm^{-3}) and water (10 cm^3). The mixture was extracted with dichloromethane (4 × 10 cm^3), and the combined extracts were washed with saturated aq. sodium hydrogencarbonate (10 cm^3), dried over anhydrous sodium sulfate, and then concentrated. Purification of the residue by flash chromatography (gradient elution, 60–100% diethyl ether–light petroleum) gave, in order of elution, the β-*alcohol* **40** (10.2 mg, 31%) as microcrystals, m.p. 185–195 °C (Found: C, 53.8; H, 6.2. $C_{16}H_{22}O_5S_2$ requires C, 53.61; H, 6.19%); ν_{max}(film)/cm^{-1} 3502, 2921, 1725, 1700, 1426, 1344, 1274, 1248, 1151 and 1074; δ_H(500 MHz; CDCl$_3$) 1.85–1.90 (1 H, dd, *J* 13.8, 12.0, 7-H$_\beta$), 1.96 (1 H, m, C*H*$_2$CH$_2$S), 2.06–2.12 (1 H, m, C*H*$_2$CH$_2$S), 2.19–2.26 (1 H, m, 3-H), 2.30–2.35 (1 H, m, 3-H), 2.39 (1 H, ddd, *J* 13.8, 4.8, 1.1 7-H$_\alpha$), 2.53–2.63 (3 H, m, 4-H$_2$ and CH$_2$S), 2.71 (1 H, ddd, *J* 13.8, 6.2, 3.3, CH$_2$S), 3.24–3.31 (3 H, m, 8b- and 5a-H and CH$_2$S), 3.39 (1 H, ddd, *J* 13.8, 11.0, 2.7, CH$_2$S), 3.84 (3 H, s, CO_2Me), 3.88 (1 H, d, *J* 11.6, OH), 3.89 (1 H, d, *J* 8.8, 2-H), 3.92 (1 H, d, *J* 11.1, 8a-H), 3.97–4.03 (1 H, m, 6-H) and 4.27 (1 H, d, *J* 8.8, 2-H); *m/z* (EI) 358 (M$^+$), 340 (M − H$_2$O), 266, 251, 233, 161, 147, 132, 119 and 106; and the α-*alcohol* **41** (18.6 mg, 57%) as rods, m.p. 131–135 °C (Found: C, 53.5; H, 6.1. $C_{16}H_{22}O_5S_2$ requires C, 53.61; H, 6.19%); ν_{max}(film)/cm^{-1} 3446, 2919, 1709, 1429, 1326, 1242, 1196, 1136, 1075, 1036 and 734; δ_H(CDCl$_3$) 1.87 (1 H, dd, *J* 15.4, 3.8, 7-H), 2.01–2.05 (2 H, m, C*H*$_2$CH$_2$S), 2.15–2.22 (1 H, m, 3-H$_\beta$), 2.29–2.33 (1 H, m, 4-H$_\beta$), 2.54–2.65 (3 H, m, 3- and 4-H$_\alpha$ and 7-H), 2.82–2.92 (2 H, m, CH$_2$S), 3.15–3.22 (4 H, m, 5a-H, OH and CH$_2$S), 3.46 (1 H, ddd, *J* 13.0, 6.1, 1.3, 8b-H), 3.76 (1 H, d, *J* 11.8, 8a-H), 3.84 (3 H, s, CO_2Me), 3.90 (1 H, d, *J* 8.8, 2-H), 4.27 (1 H, d, *J* 8.8, 2-H) and 4.46–4.49 (1 H, m, 6-H); *m/z* (EI) 358 (M$^+$), 340 (M − H$_2$O), 266, 251, 233, 161, 119, 106 and 82.

(1R*,3aR*,4R*,7aR*)-*Methyl* 4-*Dimethyl(phenyl)silyl*-1-[2′-(*formylmethyl*)-1′,3′-*dithian*-2′-*yl*]-6-*oxoperhydroisobenzofuran*-3a-*carboxylate* **42** *and its* -1R*,3aS*,4S*,7aR*)-*Isomer* **43**.—Toluene-*p*-sulfonic acid monohydrate (PTSA) (2 mg, 10 μmol) was added to a solution of the mixture of silyl enol ethers **29** and **30** (18.6 mg, 28.5 μmol) in 3% water–acetone (1 cm^3). The solution was heated to 50 °C for 45 min and was then poured into saturated aq. sodium hydrogencarbonate (5 cm^3). Extraction of the mixture with diethyl ether (3 × 10 cm^3), drying over anhydrous magnesium sulfate, and evaporation of the solvent under reduced pressure gave a mixture of the diastereoisomeric ketoaldehydes. The diastereoisomers were separated by column chromatography (60% diethyl–light petroleum) to obtain the *less polar, major* (1R*,3aS*,4S*,7aR*) isomer **43** (5.7 mg, 41%) as an oil and the *more polar, minor isomer* **42** (5.6 mg, 40%, contaminated with 13% of the C-3a,C-4 epimer) as an oil (Found: M$^+$, 492.1460. $C_{24}H_{32}O_5S_2Si$ requires M, 492.1461); ν_{max}(film)/cm^{-1} 2949, 2913, 1709, 1425, 1255, 1202, 1114, 1016, 816, 735 and 703; δ_H(500 MHz; CDCl$_3$) 0.42 (3 H, s, Me), 0.46 (3 H, s, Me), 1.93–2.03 (2 H, m, 5′-H_2), 2.18 (1 H, dd, *J* 3.7, 8.8, 4-H), 2.35 (1 H, dd, *J* 9.0, 16.0, 5-H_β), 2.46 (1 H, dd, *J* 2.1, 16.2, C*H*$_2$CHO), 2.56 [1 H, ddd, *J* 1.0 (long-range coupling to 7-H_α), 3.7, 16.1, 5-H_α], 2.61 (1 H, ddd, *J* 5.8, 9.6, 13.2, 7-H_α), 2.63 (1 H, dd, *J* 3.5, 16.3, C*H*$_2$CHO), 2.73 (1 H, ddd, *J* 4.1, 7.1, 14.3, 6′- or 4′-H), 2.78–2.93 (4 H, m, 7-H_α, 4′- and 6′-H and 4′- or 6′-H), 3.17 (1 H, dd, *J* 13.3, 16.2, 7-H_β), 3.54 (1 H, d, *J* 8.6, 3-H_α), 3.75 (3 H, s, CO_2Me), 3.91 (1 H, d, *J* 8.6, 3-H_β), 4.40 (1 H, d, *J* 9.6, 1-H), 7.35–7.42 (3 H, m, Ph), 7.55–7.49 (2 H, m, Ph) and 9.75 (1 H, dd, *J* 2.2, 3.4, CHO); *m/z* (EI) 492 (M^+, 1.6%), 477 (M − Me, 0.2), 474 (M − H_2O, 0.3), 463 (M − CHO, 0.2), 461 (M − OMe, 0.2), 449 (M − CH_2CHO, 0.1), 433 (M − OMe − CO, 0.1), 415 (M − Ph, 0.2), 331 [M − ($C_3H_6S_2$)CCH_2CHO, 26], 253 (49), 193 (32), 161 [($C_3H_6S_2$)C-CH_2CHO, 74] and 135 ($PhMe_2Si$, 100).

(1R*,3aS*,4S*,7aR*)-*Methyl* 4-*Dimethyl(phenyl)silyl*-1-[2′-*(formylmethyl)*-1′,3′-*dithian*-2′-*yl*]-6-*oxoperhydroisobenzofuran*-3a-*carboxylate* **43**.—PTSA (1.7 mg, 8.9 μmol) was added to a solution of the silyl enol ether **30** (13.4 mg, 20.5 μmol) in 3% water–acetone (1 cm^3) and the solution was heated at 50 °C for 4.5 h. After cooling, the solution was poured into saturated aq. sodium hydrogencarbonate (5 cm^3) and the mixture was extracted with diethyl ether (3 × 15 cm^3). The combined organic layers were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. Purification of the residue by flash chromatography (60% diethyl ether–light petroleum) afforded the *keto aldehyde* **43** (9.2 mg, 91%) as an oil (Found: M^+, 492.1458. $C_{24}H_{32}O_5S_2Si$ requires M, 492,1461); ν_{max}(film)/cm^{-1} 3072, 3045, 2950, 2915, 2849, 1711, 1426, 1251, 1230, 1113, 1069, 819, 735 and 703; δ_H(500 MHz; $CDCl_3$) 0.29 (3 H, s, Me), 0.31 (3 H, s, Me), 1.85–1.95 (1 H, m, 5′-H), 1.97–2.05 (1 H, m, 5′-H), 2.24 (1 H, dd, *J* 14.3, 17.7, 5-H_{ax}), 2.31 (1 H, dd, *J* 3.3, 14.2, 4-H), 2.41 (1 H, dd, *J* 3.3, 17.7, 5-H_{eq}), 2.52 (1 H, dd, *J* 2.6, 16.6, C*H*$_2$CHO), 2.56–2.62 (1 H, m, 7-H), 2.67 (1 H, dd, *J* 2.6, 16.6, C*H*$_2$CHO), 2.67–2.75 (2 H, m, 4′- and 6′-H), 2.94–3.03 (4 H, m, 7-, 7a-, 4′- and 6′-H), 3.37 (1 H, d, *J* 10.0, 3-H), 3.56 (3 H, s, OMe), 3.73 (1 H, d, *J* 7.2, 1-H), 4.47 (1 H, d, *J* 9.9, 3-H), 7.34–7.41 (3 H, m, Ph), 7.43–7.49 (2 H, m, Ph) and 9.80 (1 H, t, *J* 2.6, CHO); *m/z* (EI) 492 (M^+, 2.8%), 474 (M − H_2O, 6.7), 460 (M − MeOH, 0.2), 459 (M − H_2O − Me, 0.3), 442 (M − MeOH − H_2O, 0.4), 415 (M − Ph, 0.9), 397 (0.9), 367 (4.9), 331 [M − ($C_3H_6S_2$)CCH_2CHO, 4.6], 253 (5.9), 229 (6.9), 161 [($C_3H_6S_2$)CCH_2CHO, 61] and 135 ($PhMe_2Si$, 100).

(2aR*,4aR*S*,7aR*S*,8R*,10aR*,10bR*)-*Methyl* 4a,8-*Dihydroxyperhydronaphtho*[1,8-bc:5.4a-b′]*difuran*-10-*spiro*-2′-(1′,-3′-*dithiane*)-2a-*carboxylate* **44**.—A solution of the tricycle **32** (28 mg, 65 μmol) and PTSA (10 mg, 52.6 μmol) in 2% water–acetone (1 cm^3) was heated at reflux for 4.5 h. After cooling, the solution was poured into saturated aq. sodium hydrogencarbonate (2 cm^3) and extracted with diethyl ether (3 × 5 cm^3). The combined organic layers were washed with brine (2 cm^3), dried over anhydrous magnesium sulfate, and concentrated. Purification of the residue by flash chromatography (Et_2O) afforded the diastereoisomeric *tetracycles* **44** (11.5 mg, 44%, as an inseparable 1:1 mixture) as a foam (Found: M^+, 402.1162. $C_{18}H_{26}O_6S_2$ requires M, 402.1171); ν_{max}(film)/cm^{-1} 3414, 2949, 2889, 1724, 1432, 1280, 1226, 1033, 911 and 732; *m/z* (EI) 402 (M^+, 38%), 384 (M − H_2O, 13), 370 (M − MeOH, 23), 342 (M − OMe − CO, 0.8), 241 (15.9), 223 (39), 161 (100) and 106 (76).

(2aR*,4aR*,7aR*,8R*,10aR*,10bR*)-*Methyl* 8-*Hydroxy*-4a-(2-*hydroxyethoxy)perhydronaphtho*[1,8-bc:5,4a-b′]*difuran*-10-*spiro*-2′-(1′,3′-*dithiane*)-2a-*carboxylate* **45**.—A mixture of the hemiketals **44** (70 mg, 0.174 mmol), ethylene glycol (150 mm^3, 2.69 mmol) and PTSA (4 mg, 0.02 mmol) in benzene (10 cm^3) was heated at reflux with azeotropic removal of water for 2 h. After cooling, the mixture was poured into saturated aq. sodium hydrogencarbonate (10 cm^3) and extracted with diethyl ether (4 × 15 cm^3). The combined extracts were washed with brine (10 cm^3), dried over anhydrous magnesium sulfate, and concentrated. Flash chromatography of the residue (Et_2O) gave the *ketal* **45** (49 mg, 63%) as a foam (Found: C, 53.7; H, 7.0. $C_{20}H_{30}O_7S_2$ requires C, 53.79; H, 6.77%); ν_{max}(film)/cm^{-1} 3432, 2949, 2885, 1724, 1433, 1285, 1228, 1085, 1035, 909 and 731; δ_H(500 MHz; $CDCl_3$) 1.74 (1 H, dt, *J* 14.7, 6.4, 4- or 3-H), 1.86 (1 H, br dt, *J* 12.8, 9.8, 7-H), 1.91 (2 H, br t, *J* 6.3, 4- or 3-H_2), 2.04 (2 H, br quint, *J* 5.7, 5′-H_2), 2.25 (1 H, dt, *J* 14.5, 6.0, 3- or 4-H), 2.33 (1 H, dd, *J* 3.6, 14.8, 9-H), 2.36 (1 H, br s, OH), 2.53 (1 H, br dd, *J* 6.2, 14.1, 9-H), 2.66 (1 H, ddd, *J* 1.9, 6.7, 12.8, 7-H), 2.84 (1 H, br dt, *J* 13.4, 5.8, 4′-or 6′-H), 2.94 (1 H, br dt, *J* 14.0, 5.8, 6′- or 4′-H), 3.05 (1 H, d, *J* 11.7, 10b-H), 3.09 (1 H, br dt, *J* 13.5, 5.6, 6′- or 4′-H), 3.18 (1 H, br dt, *J* 13.4, 5.7, 4′- or 6′-H), 3.42 (1 H, br d, *J* 7.7, OH), 3.61–3.65 (1 H, m, $HOCH_2CH_2O$), 3.67–3.72 (2 H, m, $HOCH_2CH_2O$), 3.70 (1 H, d, *J* 8.9, 2-H), 3.73–3.77 (1 H, m, $HCOH_2CH_2O$), 3.76 (3 H, s, CO_2Me), 3.77–3.89 (2 H, m, 6-H_2), 4.21 (1 H, br dt, *J* 3.3, 7.0, 8-H), 4.23 (1 H, d, *J* 11.7, 10a-H) and 4.27 (1 H, d, *J* 8.9, 2-H); *m/z* (EI) 446 (M^+, 30%), 428 (M − H_2O, 0.6), 415 (M − OMe, 0.8), 384 [M − $C_2H_4(OH)_2$, 45], 366 [M − $C_2H_4(OH)_2$ − H_2O, 0.5], 353 [M − $C_2H_4(OH)_2$ − OMe, 2.1], 278 (28), 223 (88), 161 (55) and 120 (100).

(2aR*,4aR*,7aR*,8R*,10aR*10bR*)-*Methyl* 4a-[2-(3,5-*Dinitrobenzoyloxy)ethoxy*]-8-*hydroxyperhydronaphtho*-[1,8-bc:5,4a-b′]*difuran*-10-*spiro*-2′-(1′,3′-*dithiane*)-2a-*carboxylate* **46**.—3,5-Dinitrobenzoyl chloride (23 mg, 100 μmol) was added to a stirred solution of the alcohol **45** (30 mg, 67 μmol) and pyridine (16 mm^3, 200 μmol) in dichloromethane (0.25 cm^3). After 30 min, the mixture was poured into saturated aq. ammonium chloride (5 cm^3) and extracted with diethyl ether (3 × 10 cm^3). The combined organic layers were washed with brine (10 cm^3), dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. Purification of the residue by flash chromatography (85% diethyl ether–light petroleum) and recrystallisation from ethyl acetate gave the *dinitrobenzoate* **46** (33 mg, 77%) as yellow squares, m.p. 153 °C (Found: C, 50.8; H, 5.1; N, 4.3. $C_{27}H_{32}N_2O_{12}S_2$ requires C, 50.62; H, 5.03; N, 4.37%); ν_{max}(film)/cm^{-1} 3522, 3101, 2950, 2884, 1726, 1627, 1597, 1543, 1459, 1344, 1280, 1228, 1168, 1090, 1036 and 729; δ_H(500 MHz; $CDCl_3$) 1.72–1.80 (1 H, m, 4- or 3-H), 1.84 (1 H, dt, *J* 12.8, 9.9, 7-H) 1.94 (2 H, br t, *J* 6.1, 3- or 4-H_2), 1.95–2.04 (2 H, m, 5′-H_2), 2.25–2.34 (1 H, m, 3- or 4-H, obscured by 9-H), 2.29 (1 H, dd, *J* 3.9, 14.7, 9-H), 2.51 (1 H, br dd, *J* 5.5, 14.2 9-H), 2.67 (1 H, ddd, *J* 3.4, 5.1, 12.8, 7-H), 2.77–2.87 (2 H, m, 4′- and 6′-H), 2.92–3.00 (1 H, m, 6′- or 4′-H), 3.05 (1 H, d, *J* 11.7, 10b-H), 3.09–3.18 (1 H, m, 4′- or 6′-H), 3.28 (1 H, br d, *J* 8.0, OH), 3.69 (1 H, d, *J* 8.9, 2-H), 3.76 (3 H, s, CO_2Me), 3.77–3.86 (2 H, m, 6-H_2), 3.90 (1 H, ddd, *J* 2.7, 6.8, 11.3, DNBOCH$_2$C*H*$_2$O), 3.98 (1 H, ddd, *J* 2.9, 5.6, 11.2, DNBOCH$_2$C*H*$_2$O), 4.09–4.15 (1 H, m, 8-H), 4.14 (1 H, d, *J* 11.7, 10a-H), 4.25 (1 H, d, *J* 8.9, 2-H), 4.56 (1 H, ddd, *J* 2.7, 5.6, 11.7, DNBOC*H*$_2$CH$_2$O), 4.63 (1 H, ddd, *J* 2.9, 6.8, 11.6, DNBOC*H*$_2$CH$_2$O), 9.17 (2 H, m, *o*-Ph) and 9.23 (1 H, t, *J* 2.0, *p*-Ph); *m/z* (EI) 640 (M^+, 0.2%), 609 (M − OMe, <0.1), 428 (M − $C_7H_4N_2O_6$, 0.8), 384 (M − $C_9H_8N_2O_7$, 55), 223 (90), 195 ($C_7H_3N_2O_5$, 49), 161 (100) and 135 (67).

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