Pergamon

Tetrahedron, Vol. 52, No. 48, pp. 15289-15310, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00932-5

(Alkoxyallyl)sulfones as Enal and Enone β-Anion Equivalents. Synthesis of Mono-, Di- and Trisubstituted Furans

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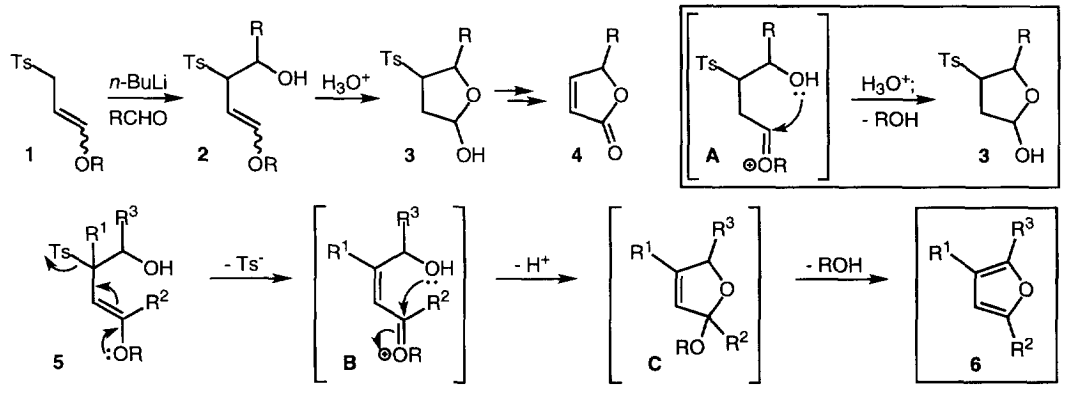
Abstract: Treatment of variously-substituted (alkoxyallyl)sulfones **1**, **7-9** with strong base followed by aldehydes gives alcohol adducts **5**. These may be converted into a wide range of substituted furans **6** by exposure to acid, or to silica gel in dichloromethane containing sulfuric acid in some cases.

INTRODUCTION

In the foregoing paper[1] we described the synthesis of 2(5*H*)-furanones **4** from the (benzyloxyallyl)sulfone **1** by sequential hydroxyalkylation, hydrolysis, oxidation and base-mediated elimination. Mechanistically, a likely first step in the conversion of initial adducts **2** to lactols **3** is protonation of the enol ether double bond, followed by intramolecular interception of the resultant oxonium ion **A** by the -OH group and hydrolysis of the presumed intermediate lactol ether *via* a cyclic oxonium species (Scheme 1). We reasoned that more substituted hydroxyalkylated intermediates **5** might react *via* an alternative pathway involving loss of tolylsulfinate ion, because of additional stabilisation of the resulting cation by hyperconjugatively electron-donating R^1 and R^2 groups. Intermediate **B** formed in this way would undergo cyclisation as before to give **C**, which would undergo aromatisation to furans **6** by loss of ROH. The anticipated ready availability of **5** bearing a range of substituents and substitution patterns encouraged us to pursue this idea, with the goal of developing a general synthesis of substituted furans.[2] Herein we report in full on the realisation of this objective.[3]

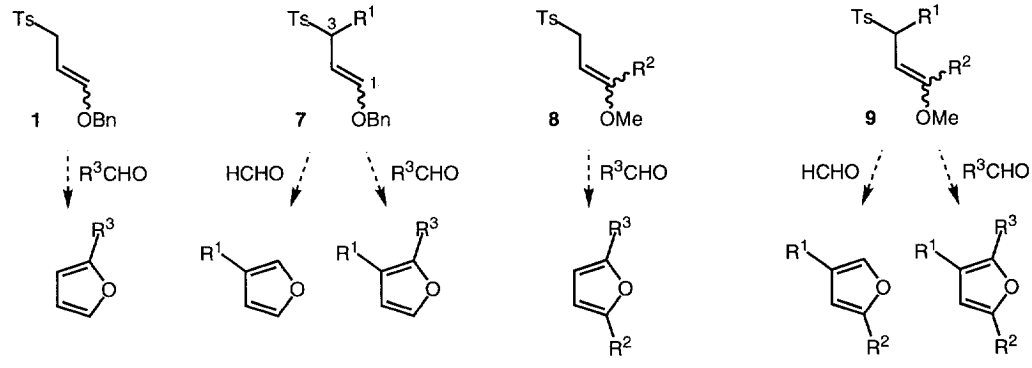


Scheme 1

RESULTS AND DISCUSSION

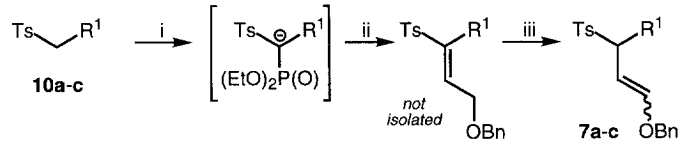
Synthesis of (alkoxyallyl)sulfones

Simple, versatile routes for the preparation of variously substituted (alkoxyallyl)sulfones were an essential prerequisite for the viability of the strategy. Scheme 2 shows the (alkoxyallyl)sulfones **1** and **7-9** which were targeted at the start of this study, and the furans which in principle would be available by combination of the derived anions either with formaldehyde or other aldehydes, followed by treatment with acid.



Scheme 2

Synthesis of 3-substituted (alkoxyallyl)sulfones 7. The synthesis of the parent, unsubstituted compound **1** was accomplished by sequential Wadsworth–Emmons olefination and base-mediated isomerisation as described in the foregoing article. The phosphonate species required for this approach could be generated either in a separate step or *in situ*[4] by phosphorylation of lithiated (4-tolylsulfonyl)methane. It occurred to us that it might be possible to effect phosphorylation, olefination *and* isomerisation in a single reaction vessel, thereby significantly shortening the sequence. The starting materials required for this approach to 3-substituted (alkoxyallyl)sulfones **7** were (4-tolylsulfonyl)alkanes **10**, which were straightforwardly prepared by S_N2 reaction of sodium 4-tolylsulfinate with the appropriate bromo- or iodoalkanes in DMSO. Sequential treatment of cold 4:1 THF–TMEDA solutions of **10a-c** with two equivalents of strong base, diethyl chlorophosphate and finally 2-benzyloxyethanal gave adducts which underwent olefination (as evidenced by tlc analysis) on warming the reaction mixtures to room temperature. Addition of excess potassium *tert*-butoxide to the mixtures gave **7a-c** in excellent yields for the one-pot procedure (Scheme 3, Table 1). The products so formed were identical to those prepared by carrying out the phosphorylation reactions of **10** in a separate step prior to olefination.



Reagents and conditions: (i) add **10** to 2 eq LDA, THF–TMEDA, add $(EtO)_2P(O)Cl$; (ii) add $BnOCH_2CHO$, -78°C→rt; (iii) 2 eq *t*-BuOK, rt; AcOH.

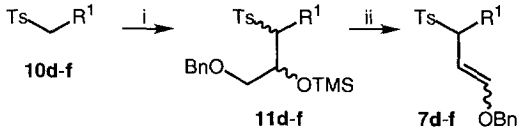
Scheme 3

entry	R^1	% yield of 7
a	*n*-C_7H_{15}	88
b	C_2H_5	87
c	CH_2Ph	93

Table 1. Synthesis of (Alkoxyallyl)sulfones **7a-c**.

Attempted application of this procedure to the preparation of compounds **7d-f** possessing respectively isopropyl, vinyl and phenyl groups failed to provide acceptable yields of the (alkoxyallyl)sulfones. It was considered that this might be a consequence of insufficient reactivity of lithiated **10d-f** due to steric and/or electronic constraints, or more likely because of the intermediacy of even less reactive phosphonate-substituted anions. In order to counter this it was decided to form the key C–C bond by direct combination of lithiated **10** with 2-benzyloxyethanal, followed by dehydration and isomerisation. In the event the most effective sequence

involved *in situ* trapping of the intermediate lithium alkoxides by trimethylsilylation. Elimination and isomerisation were effected in a single step by treatment of the TMS ethers **11** with potassium *tert*-butoxide in THF (Scheme 4). 1-Benzyloxy-3-(4-tolylsulfonyl)-1,4-pentadiene was not isolated; instead the conjugated, isomeric compound 1-benzyloxy-3-(4-tolylsulfonyl)-1,3-pentadiene **7e** was formed in high yield. The yields for the preparation of (alkoxyallyl)sulfones **7d-f** using this route are collected in Table 2.



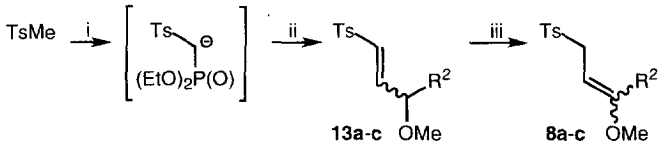
Reagents and conditions: (i) *n*-BuLi, THF–TMEDA, -78°C, add $BnOCH_2CHO$, add TMSCl, -78°C→rt; (ii) *t*-BuOK, *t*-BuOH, THF.

Scheme 4

entry	R^1	% yield of 11	% yield of 7
d	i-C_3H_7	56 (94)*	96
e	$CH{=}CH_2$	70 (94)	98 (R^1=:$CHCH_3$)
f	Ph	59 (90)	100[5]

Table 2. Synthesis of (Alkoxyallyl)sulfones **7d-f**. (*Yields in parentheses are based on recovered **10**).

Synthesis of 1-substituted (alkoxyallyl)sulfones **8**. The preparation of 1-substituted (alkoxyallyl)sulfones **8** was examined next. These were made using chemistry similar to that deployed in the synthesis of **7a-c**. *In situ* generation of lithiated diethyl (4-tolylsulfonyl)methylphosphonate was carried out as in the preparation of **1**; addition of aldehydes **12a-c** gave vinylic sulfones **13a-c**. Attempts to effect isomerisation *in situ* as for **7a-c** were unsuccessful. Therefore, **13a-c** were stored at this stage, and converted quantitatively into the somewhat labile isomeric (alkoxyallyl)sulfones **8a-c** when required by the action of potassium *tert*-butoxide as before. The formation of compound **13c** was accompanied by substantial isomerisation to give **8c**. Aldehydes **12** were made by ozonolysis of the corresponding allylic ethers, which were prepared by methylation of the products of coupling of vinylmagnesium bromide with the appropriate aldehydes.



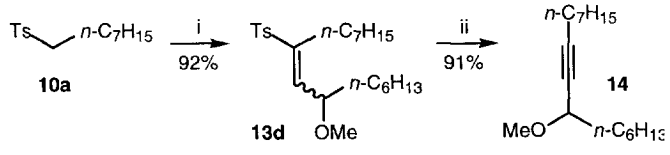
Reagents and conditions: (i) LDA, THF–TMEDA, add $(EtO)_2P(O)Cl$; (ii) add $MeOCHR^2CHO$ (**12a-c**), -78°C→rt; (iii) *t*-BuOK, *t*-BuOH, THF.

Scheme 5

entry	R^2	% yield of 8
a	c-C_6H_{11}	88
b	n-C_6H_{13}	87
c	Ph	93[5]

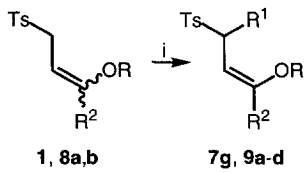
Table 3. Synthesis of (Alkoxyallyl)-sulfones **8a-c**.

Synthesis of 1,3-disubstituted (alkoxyallyl)sulfones **9**. The last class of substrates to be prepared was the 1,3-disubstituted (alkoxyallyl)sulfones **9**. On the basis of the methods used for the preparation of **8**, the most expedient route to these materials appeared to be *in situ* generation of a substituted phosphonate-stabilised anion as in Scheme 3 followed by olefination using aldehydes such as **12**. This plan was realised using sulfone **10a** and aldehyde **12b**, giving vinylic sulfone **13d** in excellent yield. However, **13d** was inert to *t*-BuOK, and attempted base-mediated isomerisation of **13d** instead cleanly gave the acetylene **14** (Scheme 6). In an alternative approach it was found that alkylation at the 3-position of freshly prepared, crude 1-substituted (alkoxyallyl)sulfones **8** could be achieved by lithiation followed by addition of 3-bromopropene, 1-iodooctane or benzyl bromide. The 3-monosubstituted substrate **7g** was similarly prepared by allylation of **1** (Scheme 7, Table 4). As with the analogous products of hydroxyalkylation of lithiated **1**,[1] compounds **9** made in this way were obtained with high selectivity for the *Z*-isomers.



Reagents and conditions: (i) 2 eq LDA, THF–TMEDA, add $(EtO)_2P(O)Cl$, add n-$C_6H_{13}CH(OMe)CHO$, -78°C→rt; (ii) *n*-BuLi, THF, -78°C→rt.

Scheme 6



1, 8a,b **7g, 9a-d**

Reagents and conditions: (i) *n*-BuLi, THF–TMEDA, R^1X, -78°C→rt.

Scheme 7

substrate	R	R^2	product	R	R^1	R^2	% yield
1	CH_2Ph	H	**7g**[6]	CH_2Ph	C_3H_5	H	96
8a	Me	*c*-C_6H_{11}	**9a**	Me	*n*-C_8H_{17}	*c*-C_6H_{11}	92
8a	Me	*c*-C_6H_{11}	**9b**	Me	CH_2Ph	*c*-C_6H_{11}	89
8b	Me	*n*-C_6H_{13}	**9c**	Me	*n*-C_8H_{17}	*n*-C_6H_{13}	97
8b	Me	*n*-C_6H_{13}	**9d**	Me	C_3H_5	*n*-C_6H_{13}	91

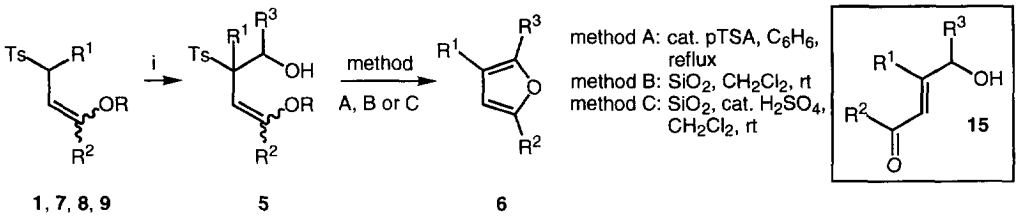
Table 4. Synthesis of (Alkoxyallyl)sulfones **7g** and **9a-d**.

Synthesis of substituted furans **6**

With a range of some fifteen (**1**, **7a-g**, **8a-c** and **9a-d**) differently substituted (alkoxyallyl)sulfones in hand, we were in a position to assess their utility as intermediates for furan synthesis. Deprotonation could readily be effected using *n*-butyllithium, or LDA in the case of **7e**, and gave intensely red-coloured THF solutions of the lithiated species which reacted with a range of aldehydes, *including paraformaldehyde* to give alcohols **5**; these were isolated by simple extractive work-up. In the case of the adduct of the parent (alkoxyallyl)sulfone **1** and undecanal, furan formation was carried out by exposure to catalytic 4-tolylsulfonic acid in boiling benzene (method A). Treatment of the other crude adducts **5** with silica gel in dichloromethane (method B) cleanly gave the substituted furans in excellent yields. Adducts **5** derived from **7d** and **7f** (R^1=*i*-Pr, Ph), and from the combination of **9** with aldehydes other than paraformaldehyde required the addition of a small

starting material	R	R^1	R^2	product	R^1	R^2	R^{3*}	method	% yield
1	CH_2Ph	H	H	**6a**	H	H	*n*-$C_{11}H_{23}$	**A**	88
7a	CH_2Ph	*n*-C_7H_{15}	H	**6b**	*n*-C_7H_{15}	H	H	**B**	95
7a	CH_2Ph	*n*-C_7H_{15}	H	**6c**	*n*-C_7H_{15}	H	*n*-C_6H_{13}	**B**	98
7a	CH_2Ph	*n*-C_7H_{15}	H	**6d**	*n*-C_7H_{15}	H	C_6H_5	**B**	85
7a	CH_2Ph	*n*-C_7H_{15}	H	**6e**	*n*-C_7H_{15}	H	*c*-C_6H_{11}	**B**	86
7a	CH_2Ph	*n*-C_7H_{15}	H	**6f**	*n*-C_7H_{15}	H	$(CH_2)_5OP$	**B**	97
7b	CH_2Ph	C_2H_5	H	**6g**	C_2H_5	H	C_6H_5	**B**	95
7b	CH_2Ph	C_2H_5	H	**6h**	C_2H_5	H	$(CH_2)_5OP$	**B**	97
7c	CH_2Ph	CH_2Ph	H	**6i**	CH_2Ph	H	H	**B**	98
7c	CH_2Ph	CH_2Ph	H	**6j**	CH_2Ph	H	*n*-C_6H_{13}	**B**	95
7c	CH_2Ph	CH_2Ph	H	**6k**	CH_2Ph	H	*c*-C_6H_{11}	**B**	93
7d	CH_2Ph	*i*-C_3H_7	H	**6l**	*i*-C_3H_7	H	*n*-C_6H_{13}	**C**	93
7e	CH_2Ph	:$CHCH_3$	H	**6m**	CH:CH_2	H	CH:CHPh	**B**	63
7f	CH_2Ph	C_6H_5	H	**6n**	C_6H_5	H	*n*-C_6H_{13}	**C**	88
7f	CH_2Ph	C_6H_5	H	**6o**	C_6H_5	H	C_6H_5	**C**	90
7g	CH_2Ph	C_3H_5	H	**6p**	C_3H_5	H	*n*-C_6H_{13}	**B**	95
7g	CH_2Ph	C_3H_5	H	**6q**	C_3H_5	H	C_6H_5	**B**	96
7g	CH_2Ph	C_3H_5	H	**6r**	C_3H_5	H	*c*-C_6H_{11}	**B**	91
7g	CH_2Ph	C_3H_5	H	**6s**	C_3H_5	H	$(CH_2)_5OP$	**B**	97
8b	Me	H	*n*-C_6H_{13}	**6t**	H	*n*-C_6H_{13}	*i*-C_4H_9	**B**	94
8b	Me	H	*n*-C_6H_{13}	**6u**	H	*n*-C_6H_{13}	C_6H_5	**B**	81
8c	Me	H	C_6H_5	**6u**	H	C_6H_5	*n*-C_6H_{13}	**B**	87
9a	Me	*n*-C_8H_{17}	*c*-C_6H_{11}	**6v**	*n*-C_8H_{17}	*c*-C_6H_{11}	*i*-C_4H_9	**C**	93
9b	Me	CH_2Ph	*c*-C_6H_{11}	**6w**	CH_2Ph	*c*-C_6H_{11}	H	**B**	94
9c	Me	*n*-C_8H_{17}	*n*-C_6H_{13}	**6x**	*n*-C_8H_{17}	*n*-C_6H_{13}	*i*-C_4H_9	**C**	97
9d	Me	C_3H_5	*n*-C_6H_{13}	**6y**	C_3H_5	*n*-C_6H_{13}	*c*-C_6H_{11}	**C**	95

Table 5. Synthesis of Substituted Furans **6** from (Alkoxyallyl)sulfones **1**, **7**, **8** and **9**. *P = TBDPS.



1, 7, 8, 9 **5** **6**

Reagents and conditions: (i) *n*-BuLi (LDA for **7e**), THF, -78°C, add R^3CHO, -78°C; AcOH, sat. aq. $NaHCO_3$, -78°C→rt.

Scheme 8

amount of concentrated sulfuric acid to the two-phase silica gel–dichloromethane mixture (method C). The furan-forming sequences summarised in Table 5 are depicted in Scheme 8.

Some observations relating to the furan-forming reactions are worthy of comment. Firstly, intermediate alcohols **5** could be isolated, but not purified. The lability of the crude products was minimised by the addition of saturated aqueous sodium hydrogencarbonate after the acetic acid quench but before warming to room temperature. Chromatography of crude **5** on silica gel invariably led to decomposition, as did exposure to the atmosphere for prolonged periods, which was accompanied by the formation of intensely green-coloured material. Treatment with a range of Brønsted acids (TFA, CSA, pTSA and AcOH) in dichloromethane gave the same highly-coloured mixtures, as did the use of Lewis acidic reagents such as magnesium bromide etherate, magnesium sulfate, zinc chloride, and 4Å molecular sieves. For disubstituted furans **6l**, **n**, **o**, and trisubstituted analogues **6v**, **x**, **y** the addition of a small amount of concentrated sulfuric acid to the silica gel–dichloromethane reagent mixture was essential to minimise the formation of enals/enones **15**.

A final, brief study was undertaken to determine whether alkylation reactions of 1-substituted (alkoxyallyl)sulfones **8** and hydroxyalkylation reactions of the derived 1,3-disubstituted substrates **9** could be carried out in a one-pot process. In this context it was discovered that low-temperature lithiation of **8a** in THF–TMEDA, followed by benzylation with benzyl bromide, relithiation, addition of paraformaldehyde and warming to room temperature gave the expected primary alcohol. This was converted into 4-benzyl-2-cyclohexylfuran (**6w**) in high yield by silica gel treatment as before. Trisubstituted furan **6v** was prepared from **8a** using a similar sequence involving 1-iodooctane and 3-methylbutanal. Full details of these one-pot procedures are provided in the Experimental section

CONCLUSIONS

The results presented herein demonstrate that (alkoxyallyl)sulfones **1**, **7**-**9** are readily available enal and enone β-anion equivalents which may be deployed in the high-yielding synthesis of a large variety of substituted furans. Importantly, the present method provides a simple, direct route to difficultly accessible 3-substituted analogues. We are currently looking at the application of (alkoxyallyl)sulfones and related compounds to the synthesis of six-membered heterocycles such as dihydropyrans and piperidines. The results of these studies will be reported in due course.

ACKNOWLEDGEMENTS

We thank the SERC/EPSRC (Quota Studentship to C. J. E.) and ICI plc (Strategic Research Initiative) for financial support of this research. We acknowledge support from the Wolfson Foundation for establishing the Wolfson Centre for Organic Chemistry in Medical Science. We thank Ms Hilary O'Callaghan (Imperial College) for carrying out elemental combustion analyses. We gratefully acknowledge the SERC Mass Spectrometry Service Centre, University College of Swansea for providing high-resolution mass spectra.

EXPERIMENTAL

General procedures

General procedures were as described in the preceding paper. ^{13}C Nmr spectra were recorded on a Jeol GX-270Q spectrometer at 68 MHz using residual isotopic solvent ($CDCl_3$, δ_C= 77 ppm) as an internal reference. Elemental combustion analysis were performed in the Imperial College Chemistry Department microanalytical laboratory. 2-Benzyloxyethanal was prepared as described in the preceding paper.

Preparation of 2-cyclohexyl-2-methoxyethanal (12a).

This was carried out analogously to the preparation of 2-benzyloxyethanal[1] on a 49.4 mmol scale starting from 1-cyclohexyl-1-methoxy-2-propene to give, after chromatography (10% ether–petrol), 2-cyclohexyl-2-methoxyethanal (**12a**) (5.59 g, 72%) as a colourless liquid; R_f 0.33, 10% ether–petrol; ν_{max} (film) 2929, 2855, 2826, 1733, 1451, 1273, 1181, 1120, 1111, 1093, 1079, 994 and 931 cm^{-1}; δ_H (270 MHz) 9.61 (1H, d, J 2.5 Hz, CHO), 3.37 (3H, s, OMe), 3.24 (1H, dd, J 5.5 and 2.5 Hz, H-2) and 1.83-1.60 and 1.39-1.11 (11H, m, *c*-C_6H_{11}); *m/z* (CI) 174 $[M+NH_4]^+$, 156 $[M]^+$, 139, 127 $[M-CHO]^+$, 112, 95, 81, 58 (Found $[M+NH_4]^+$, 174.1495. $C_9H_{16}O_2$ requires $[M+NH_4]^+$, 174.1494).

Preparation of 2-methoxyoctanal (12b).

This was carried out analogously to the preparation of 2-benzyloxyethanal[1] on a 50.7 mmol scale starting from 3-methoxynonene to give, after chromatography (10% ether–petrol), 2-methoxyoctanal (**12b**) (7.21 g, 90%) as a colourless liquid; R_f 0.40, 10% ether–petrol; ν_{max} (film) 2930, 2877, 2850, 2830, 1735, 1451, 1273, 1180, 1120, 1111, 1096, 1079, 990, 920, 889 and 739 cm^{-1}; δ_H (270 MHz) 9.62 (1H, t, J 2.5 Hz, CHO), 3.53 (1H, td, J 7.5 and 2.5 Hz, H-2), 3.42 (3H, s, OMe), 1.69-1.56 (2H, m, H-3), 1.40-1.22 (8H, m, H-4 to H-7) and 0.87 (3H, t, J 7.5 Hz, H-8); *m/z* (CI) 176 $[M+NH_4]^+$, 158 $[M]^+$, 141 , 135, 129 $[M-CHO]^+$, 127 $[M-OMe]^+$, 95, 81, 58 (Found $[M]^+$, 158.1306. $C_{10}H_{11}O_2$ requires $[M]^+$, 158.1307).

Preparation of 2-methoxy-2-phenylethanal (12c).

This was carried out analogously to the preparation of 2-benzyloxyethanal[1] on a 15.4 mmol scale starting from 1-methoxy-1-phenyl-2-propene to give, after chromatography (10% ether–petrol), 2-methoxy-2-phenylethanal (**12c**) (2.09 g, 90%) as a colourless liquid; R_f 0.45, 10% ether–petrol; ν_{max} (film) 3031, 2825, 1737, 1202, 1101, 1074, 1027 and 701 cm^{-1}; δ_H (270 MHz) 9.60 (1H, s, CHO), 7.47-7.31 (5H, m, Ph), 4.67 (1H, s, H-2) and 3.46 (3H, s, OMe); *m/z* (CI) 168 $[M+NH_4]^+$, 151 $[MH]^+$, 135 $[M-Me]^+$, 121 $[M-CHO]^+$, 105, 94, 58, 22 (Found $[M+NH_4]^+$, 150.0681. $C_9H_{10}O_2$ requires $[M+NH_4]^+$, 150.0681).

Preparation of 1-benzyloxy-3-(4-tolylsulfonyl)decene (7a).

A solution of 1-(4-tolylsulfonyl)octane (**10a**) (3.58 g, 13.3 mmol) in THF (10 ml plus 5 ml rinse) was added *via* cannula to a solution of LDA (prepared from *i*-Pr_2NH (1.92 ml, 29.3 mmol, 2.2 eq) and *n*-BuLi (11.74 ml of a 2.5M solution in hexanes, 29.3 mmol, 2.2 eq)) in THF (21.3 ml) and TMEDA (5.32 ml) at -78°C under a nitrogen atmosphere. The resultant golden-yellow solution was allowed to stir for 30 min at -78°C after which time diethyl chlorophosphate (1.93 ml, 13.3 mmol) was added dropwise *via* syringe, causing the reaction mixture to gradually become bright lemon-yellow in colour. After stirring for 2 h at -78°C, a solution of 2-benzyloxyethanal (2.00 g, 13.3 mmol) in THF (10 ml plus 2 ml rinse) was added *via* cannula causing the solution to become paler in colour. The resulting solution was allowed to warm to rt and after 15 h *t*-BuOK (26.7 ml of a 1M solution in THF, 26.7 mmol, 2 eq) was added causing the colour to deepen to a dark orange-red. After stirring for a further 10 min the reaction mixture was quenched with AcOH solution (29.3 ml

of a 1M solution in THF, 29.3 mmol, 2.2 eq) causing the colour to fade to pale yellow. The reaction mixture was further treated with saturated aqueous $NaHCO_3$ (10 ml) and diluted with water (20 ml). The organic layer was separated and the aqueous layer extracted with ether (3 x 50 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (50 ml), water (50 ml), brine (50 ml), dried over K_2CO_3 and the solvents removed under reduced pressure to give a yellow oil. Chromatography (10% ether–petrol), gave a 7:1 mixture of *E:Z* isomers of 1-benzyloxy-3-(4-tolylsulfonyl)decene (**7a**) (4.73 g, 88%); mp 57-58°C, R_f 0.55, 50% ether–petrol; ν_{max} (CH_2Cl_2) 3032, 2924, 2858, 1646, 1597, 1496, 1455, 1380, 1300, 1213, 1146, 1085, 1019, 938, 816, 740, 698 and 664 cm^{-1}; δ_H (270 MHz) 7.75 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.65 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *E*-isomer), 7.42-7.24 and 7.11-7.03 (14H, m, H-3 and H-5 of Ts and Ph, both isomers), 6.21 (1H, d, J 13.0 Hz, H-1, *E*-isomer), 6.16 (1H, d, 6.0 Hz, H-1, *Z*-isomer), 4.73 (2H, s, CH_2Ph, *E*-isomer), 4.57 (1H, dd, J 13.0 and 10.5 Hz, H-2, *E*-isomer), 4.56 (1H, d, J 13.5 Hz, CH_2Ph, *Z*-isomer) 4.48 (1H, d, J 13.5 Hz, CH_2Ph, *Z*-isomer), 4.28 (1H, dd, J 10.5 and 6.0 Hz, H-2, *Z*-isomer), 4.18 (1H, td, J 10.5 and 3.0 Hz, H-3, *Z*-isomer), 3.32 (1H, td, J 10.5 and 3.0 Hz, *E*-isomer), 2.42 (6H, s, Me of Ts), 2.11-2.03 (2H, m, H-4, both isomers), 1.58-1.49 (2H, m, H-4, both isomers), 1.43-1.14 (20H, m, H-5 to H-9, both isomers) and 0.87 (6H, t, J 6.5 Hz, H-10, both isomers); *m/z* (EI) 245, 214, 199, 181, 167, 159, 153, 139, 124, 107, 91, 77, 65, 55, 41 (Found: C, 72.09; H, 8.32. $C_{24}H_{32}O_3S$ requires C, 71.96; H, 8.32%).

Preparation of 1-benzyloxy-3-(4-tolylsulfonyl)pentene (7b).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)decene (**7a**) on a 8.68 mmol scale starting from 1-(4-tolylsulfonyl)propane (**10b**) to give, after chromatography (30% ether–petrol), a 5:1 *E:Z* mixture of isomers of 1-benzyloxy-3-(4-tolylsulfonyl)pentene (**7b**) (2.51 g, 87%) as a colourless, crystalline solid; mp 64-65°C, R_f 0.42, 50% ether–petrol; ν_{max} (CH_2Cl_2) 2971, 2934, 2877, 2349, 1646, 1598, 1495, 1456, 1383, 1308, 1235, 1143, 1084, 940, 818, 740, 699 and 663 cm^{-1}; δ_H (270 MHz) 7.74 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *Z*-isomers), 7.64 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *E*-isomers), 7.42-7.23 (14H, m, H-3 and H-5 of Ts and Ph, both isomers), 6.23 (1H, d, J 11.5 Hz, H-1, *E*-isomer), 6.20 (1H, d, J 6.0 Hz, H-1, *Z*-isomer), 4.74 (2H, s, CH_2Ph, *E*-isomer), 4.68 (2H, s, CH_2Ph, *Z*-isomer), 4.56 (1H, dd, J 11.5 and 9.5 Hz, H-2, *E*-isomer), 4.28 (1H, dd, J 9.5 and 6.0 Hz, H-2, *Z*-isomer), 4.13 (1H, td, 9.5 and 3.5 Hz, H-3, *Z*-isomer), 3.25 (1H, td, 9.5 and 2.5 Hz, H-3, *E*-isomer), 2.43 (3H, s, Me of Ts, *Z*-isomer), 2.40 (3H, s, Me of Ts, *E*-isomer), 2.21-2.06 (1H, m, H-4, *E*-isomer), 1.91-1.81 (1H, m, H-4, *Z*-isomer), 1.76-1.47 (1H, m, H-4, both isomers) and 1.02-0.97 (6H, m, H-5, both isomers); *m/z* (EI) 246, 214, 184, 175 $[M\text{-}Ts]^+$, 157, 91 $[C_7H_7]^+$, 65, 43, 39, 29 (Found: C, 69.25; H, 6.84. $C_{19}H_{22}O_3S$ requires C, 69.06; H, 6.71%).

Preparation of 1-benzyloxy-4-phenyl-3-(4-tolylsulfonyl)butene (7c).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)decene (**7a**) on a 4.60 mmol scale starting from 2-phenyl-1-(4-tolylsulfonyl)ethane (**10c**) to give, after chromatography (30% ether–petrol), a 5:1 *E:Z* mixture of isomers of 1-benzyloxy-4-phenyl-3-(4-tolylsulfonyl)butene (**7c**) (1.69 g, 93%) as a solid, mp 74-75°C, R_f 0.46, 50% ether–petrol; ν_{max} (CH_2Cl_2) 3030, 1645, 1599, 1495, 1452, 1305, 1143, 1084, 815, 738, 699 and 664 cm^{-1}; δ_H (270 MHz) 7.82 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.80 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *E*-isomer), 7.37-7.02 (14H, m, H-3 and H-5 of Ts and Ph, both isomers), 6.00 (1H, d, J 6.0 Hz, H-1, *Z*-isomer), 5.93 (1H, d, J 13.5 Hz, H-1, *E*-isomer), 4.70 (2H, s, CH_2Ph, *E*-isomer), 4.66-4.58 (3H, m, CH_2Ph, *Z*-isomer and H-2, *E*-isomer), 4.34 (1H, m, H-2, *Z*-isomer), 3.58-3.44 (2H, m, H-4, both isomers), 3.37-3.31 (2H, m, H-4, both isomers), 2.85 (1H, dd, J 11.5 and 6.0 Hz, H-3, *Z*-isomer), 2.76 (1H, dd, J 13.5 and 11.3 Hz, H-3, *E*-isomer), 2.46 (3H, s, Me of Ts, *Z*-isomer) and 2.44 (3H, s, Me of Ts, *E*-isomer); *m/z* (EI) 236 $[M\text{-}TsH]^+$, 207, 149, 145, 139, 124, 117, 104, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 65 (Found: C, 73.29; H, 6.11. $C_{24}H_{24}O_3S$ requires C, 73.44; H, 6.16%).

Preparation of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)-2-(trimethylsilyloxy)pentane (11d).

To a solution of 2-methyl-1-(4-tolylsulfonyl)propane (**10d**) (5.65 g, 26.6 mmol) in THF (106.5 ml) and TMEDA (26.6 ml) at -78°C under a nitrogen atmosphere was added *n*-BuLi (11.71 ml of a 2.5M solution in hexanes, 29.3 mmol, 1.1 eq) causing the reaction mixture to become yellow-orange in colour. After 30 min a solution of 2-benzyloxyethanal (4.00 g, 26.6 mmol) in THF (10 ml plus 5 ml rinse) was added *via* cannula causing the colour to become yellow. After another 30 min chlorotrimethylsilane (3.72 ml, 29.3 mmol, 1.1 eq) was added and the pale yellow solution allowed to warm to rt. The reaction was diluted with water (50ml), the organic layer separated, the aqueous layer extracted with ether (3 x 60 ml) and the combined layers washed with water (60 ml), brine (60 ml) and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure followed by chromatography (20% ether–petrol), gave a 1:1 mixture of diastereomers (A:B) of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)-2-(trimethylsilyloxy)pentane (**11d**) (6.53 g, 56 %; 94% based on recovered 2-methyl-1-(4-tolylsulfonyl)propane) as a colourless oil; R_f 0.51, 50% ether–petrol; ν_{max} (film) 3031, 2959, 2902, 2879, 1454, 1300, 1251, 1143, 1119, 1084, 845, 815, 749, 699 and 669 cm^{-1}; δ_H (270 MHz) 7.86 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, diast A), 7.82 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, diast B), 7.46-7.23 (14H, m, H-3 and H-5 of Ts and Ph, both diast), 4.61 (2H, d, J 1.0 Hz, CH_2Ph, diast B), 4.50 (1H, td, J 6.0 and 2.5 Hz, H-2, diast A), 4.40 (2H, d, J 1.0 Hz, CH_2Ph, diast A), 4.29 (1H, td, J 4.5 and 2.5 Hz, H-2, diast B), 3.93 (1H, dd, J 10.0 and 4.5 Hz, H-3, diast B) and 3.75 (1H, dd, J 9.5 and 6.0 Hz, H-3, diast A), 3.58-3.46 (2H, m, H-4, both diast), 3.36 (1H, t, J 2.5 Hz, H-1, diast A), 3.25 (1H, t, J 2.5 Hz, H-1, diast B), 2.50 (3H, s, Me of Ts, diast B), 2.49 (3H, s, Me of Ts, diast A), 2.57-2.45 (2H, m, H-1, both diast), 1.34 (3H, d, J 7.0 Hz, H-5, diast A), 1.29 (3H, d, J 7.0 Hz, H-5, diast A), 1.19 (3H, d, J 7.0 Hz, H-5, diast B), 1.11 (3H, d, J 7.0 Hz, H-5, diast B), 0.18 (9H, s, MeSi, diast A) and 0.07 (9H, s, MeSi, diast B); *m/z* (CI) 452 $[M+NH_4]^+$, 435 $[MH]^+$, 302, 150, 108 $[BnOH]^+$, 91 $[C_7H_7]^+$, 73 (Found: $[MH]^+$, 435.2025. $C_{23}H_{34}O_4SSi$ requires $[MH]^+$, 435.2025).

Preparation of 5-benzyloxy-3-(4-tolylsulfonyl)-4-(trimethylsilyloxy)pentene (11e).

This was carried out analogously to the preparation of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)-2-(trimethylsilyloxy)pentane (**11d**) on a 14.2 mmol scale starting from 1-(4-tolylsulfonyl)-2-propene (**10e**) to give, after chromatography (30% ether–petrol), a 1:1 mixture of diastereomers (A:B) of 1-benzyloxy-3-(4-tolylsulfonyl)-4-(trimethylsilyloxy)pentene (**11e**) (4.16 g, 70%; 94% based on recovered 1-(4-tolylsulfonyl)-2-propene) as a colourless oil; R_f 0.51, 50% ether–petrol; ν_{max} (film) 3062, 3033, 2956, 2919, 2865, 1598, 1452, 1316, 1297, 1253, 1153, 1120, 1087 and 848 cm^{-1}; δ_H (270 MHz) 7.78 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, diast A), 7.77 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, diast B), 7.44-7.33 (14H, m, H-3 and H-5 of Ts and Ph, both diast), 6.06 (1H, dt J 19.5 and 7.0 Hz, H-4, diast B), 5.77 (1H, dt J 17.0 and 7.0 Hz, H-4, diast A), 5.38-5.31 (2H, m, H-5H_E, both diast), 5.15 (2H, d, J 17.0 Hz, H-5$_Z$, diast A), 4.96-4.89 (2H, m, H-5$_Z$, diast B and H-2, diast A), 4.66-4.47 (5H, m, CH_2Ph, both diast and H-2, diast B), 3.93-3.85 (2H, m, H-1, both diast), 3.77 (1H, dd, J 10.0 and 2.0 Hz, H-1, diast B), 3.62 (1H, dd, J 10.0 and 6.5 Hz, H-1, diast A), 3.46 (1H, dd, J 10.0 and 5.5 Hz, H-1, diast B), 3.35 (1H, dd, J 10.0 and 8.0 Hz, H-1, diast A), 2.49 (6H, s, Me of Ts), 0.24 (9H, s, SiMe, diast B) and 0.16 (9H, MeSi, diast A); *m/z* (EI) 526, 491, 436 $[M+NH_4]^+$, 419 $[MH]^+$, 403 $[M-Me]^+$, 286, 229, 173 $[M-TMSO-TsH]^+$, 139, 108 $[BnOH]^+$, 91 $[C_7H_7]^+$ (Found: $[M+NH_4]^+$, 436.1978. $C_{22}H_{30}O_4SSi$ requires $[M+NH_4]^+$, 436.1978).

Preparation of 3-benzyloxy-1-phenyl-1-(4-tolylsulfonyl)-2-(trimethylsilyloxy)pentane (11f).

This was carried out analogously to the preparation of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)-2-(trimethylsilyloxy)pentane (**11d**) on a 3.19 mmol scale starting from phenyl(4-tolylsulfonyl)methane (**10f**) to give, after chromatography (20% ether–petrol), a 1:1 mixture of diastereomers of 3-benzyloxy-1-phenyl-1-(4-tolylsulfonyl)-2-(trimethylsilyloxy)pentane (**11f**) (0.887 g, 59%; 90% based on recovered phenyl(4-tolylsulfonyl)methane) as a colourless oil; R_f 0.60 and 0.50, 30% ether–petrol; ν_{max} (film) 2955, 2923, 2865,

1454, 1318, 1303, 1291, 1251, 1150, 1123, 1087, 1029, 968, 844, 815, 749, 699 and 649 cm^{-1}; δ_H (270 MHz) 7.55-7.10 (28H, m, Ts, Ph), 5.24-5.22 (1H, m, H-2), 4.99-4.93 (1H, m, H-2), 4.70-4.35 (6H, m, CH_2Ph and H-3, both diast), 3.61-3.45 (2H, m, H-1), 3.32 (1H, dd, J 10.0 and 4.5 Hz, H-1), 3.22 (1H, t, J 8.5 Hz, H-1), 2.37 (3H, s, Me of Ts), 2.34 (3H, s, Me of Ts), 0.32 (9H, s, MeSi) and 0,31 (9H, s, MeSi); *m/z* (EI) 486 $[M+NH_4]^+$, 469 $[MH]^+$, 319, 264, 229, 108 $[BnOH]^+$, 91 $[C_7H_7]^+$, 73 (Found: $[MH]^+$, 469.1869. $C_{26}H_{32}O_4SSi$ requires $[MH]^+$, 469.1869).

Preparation of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)pentene (7d).

To a solution of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)-2-(trimethylsilyloxy)pentane (**11d**) (2.14 g, 4.93 mmol) in THF (24.6 ml) and *t*-BuOH (4.65 ml, 49.3 mmol, 10 eq) was added *t*-BuOK (5.42ml of a 1M solution in THF, 5.42 mmol, 1.1 eq) causing the formation of an initial pale yellow cloudy colour which gradually became orange-red. After 10 min the mixture was quenched with AcOH (5.42 ml of a 1M solution in THF, 5.42 mmol, 1.1 eq), followed by saturated aqueous $NaHCO_3$ (10 ml) and water (20 ml), causing the colour to disappear. The organic layer was separated, the aqueous layer extracted with ether (3 x 40 ml), the combined organic layers washed with water (40 ml), brine (40 ml), dried (K_2CO_3) and the solvents removed under reduced pressure. The resulting pale yellow oil was purified by chromatography (30% ether–petrol), to give a >20:<1 *Z:E* mixture of isomers of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)pentene (**7d**) (1.63 g, 96%) as an oily white solid; R_f 0.38, 30% ether–petrol; ν_{max} (film) 2963, 2930, 2874, 1645, 1598, 1495, 1455, 1311, 1302, 1287, 1140, 1084, 742 and 668 cm^{-1}; δ_H (270 MHz) 7.57 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts), 7.32-7.16 (7H, m, H-3 and H-5 of Ts and Ph), 5.96 (1H, d, J 12.5 Hz, H-1), 4.77 (1H, dd, J 12.5 and 11.0 Hz, H-2), 4.66 (2H, d, J 2.0 Hz, CH_2Ph), 3.13 (1H, dd, J 11.0 and 3.0 Hz, H-3), 2.56 (1H, septuple d, J 7.0 and 3.0 Hz, H-4), 2.32 (3H, s, Me of Ts), 0.99 (3H, d, J 7.0 Hz, H-5) and 0.85 (3H, d, J 7.0 Hz, H-5); *m/z* (CI) 362 $[M+NH_4]^+$, 264, 230, 189 $[M-Ts]^+$, 174, 139, 108 $[BnOH]^+$, 91 $[C_7H_7]^+$ (Found: 362.1787, $[M+NH_4]^+$. $C_{20}H_{24}O_3S$ requires $[M+NH_4]^+$, 362.1790).

Preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1,3-pentadiene (7e).

This was carried out analogously to the preparation of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)pentene (**7d**) on a 4.27 mmol scale starting from 5-benzyloxy-3-(4-tolylsulfonyl)-4-(trimethylsilyloxy)pentene (**11e**) to give a 6:1 3*E*:3*Z* mixture of isomers of 1-benzyloxy-3-(4-tolylsulfonyl)-1,3-pentadiene (1.38 g, 98%) as a colourless oil, which was not purified further; R_f 0.40, 30% ether–petrol; ν_{max} (film) 3033, 2922, 1647, 1598, 1496, 1454, 1378, 1300, 1149, 1135, 1086, 1041, 1029, 1018 and 987 cm^{-1}; δ_H (270 MHz) 7.79 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.53-7.29 (14H, m, H-3 and H-5 of Ts and Ph, both isomers), 7.12-7.06 (2H, m, H-2 and H-4, *Z*-isomer), 6.98 (1H, q, J 7.0 Hz, H-4, *E*-isomer), 6.86 (1H, d, J 13.0 Hz, H-2, *E*-isomer), 6.28 (1H, d, J 6.5 Hz, H-1, *Z*-isomer), 5.44 (1H, d, J 13.0 Hz, H-1, *E*-isomer), 4.89 (2H, s, CH_2Ph, *E*-isomer), 4.77 (2H, s, CH_2Ph, *Z*-isomer), 2.48 (3H, s, Me of Ts, *E*-isomer), 2.45 (3H, s, Me of Ts, *Z*-isomer), 1.93 (3H, d, J 7.0 Hz, H-5, *E*-isomer) and 1.93 (3H, dd, J 7.0 and 1.0 Hz, H-5, *Z*-isomer); *m/z* (EI) 346 $[M+NH_4]^+$, 329 $[MH]^+$, 256, 237 $[M-Bn]^+$, 173 $[M-Ts]^+$, 155 $[Ts]^+$, 139, 108 $[BnOH]^+$, 91 $[C_7H_7]^+$, 65 (Found: $[M+NH_4]^+$, 346.1473. $C_{19}H_{20}O_3S$ requires $[M+NH_4]^+$, 346.1477).

Preparation of 1-benzyloxy-3-phenyl-3-(4-tolylsulfonyl)propene (7f).

This was carried out analogously to the preparation of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)pentene (**7d**) on a 1.29 mmol scale starting from 1-benzyloxy-3-phenyl-1-(4-tolylsulfonyl)-2-(trimethylsilyloxy)pentane (**11f**) to give 1-benzyloxy-3-phenyl-3-(4-tolylsulfonyl)propene (**7f**) (0.488 g crude yield, ca. 100%) which was used in subsequent reactions without further purification; R_f 0.33, 50% ether–petrol; ν_{max} (film) 3035, 2903, 1644, 1599, 1497, 1452, 1300, 1150, 1070, 815, 738, 699 and 664 cm^{-1}; δ_H (270 MHz) 7.62 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.46 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *E*-isomer), 7.43-7.06 (14H, m,

H-3 and H-5 of Ts and Ph, both diast), 6.56 (1H, d, J 12.0 Hz, H-1, *E*-isomer), 6.27 (1H, d, J 6.0 Hz, H-1, *Z*-isomer), 5.39 (1H, d, J 10.0 Hz, H-3, *Z*-isomer), 5.31 (1H, d, J 10.0 Hz, H-3, *E*-isomer), 5.03 (1H, dd, J 10.5 and 6.0 Hz, H-2, *E*-isomer), 4.83 (2H, s, CH_2Ph, *E*-isomer), 4.64 (2H, d, J 6.5 Hz, CH_2Ph, *Z*-isomer), 4.57 (1H, dd, J 12.0 and 10.0 Hz, H-2, *Z*-isomer), 2.42 (3H, s, Me of Ts, *Z*-isomer) and 2.40 (3H, s, Me of Ts, *E*-isomer).

Preparation of 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)propene (13a).

A solution of (4-tolylsulfonyl)methane (5.63 g, 33.1 mmol) in THF (15 ml plus 5 ml rinse) was added *via* cannula to a solution of LDA (prepared from *i*-Pr_2NH (10.2 ml, 72.7 mmol, 2.2 eq) and *n*-BuLi (29.1 ml of a 2.5M solution in hexanes, 72.7 mmol, 2.2 eq)) in THF (52.9 ml) and TMEDA (13.2 ml) at -78°C under a nitrogen atmosphere. The resultant orange-yellow solution was allowed to stir for 30 min at -78°C after which time diethyl chlorophosphate (4.78 ml, 33.1 mmol) was added dropwise *via* syringe, causing the reaction mixture gradually to become bright lemon-yellow in colour. After stirring for 1 h at -78°C, a solution of 2-cyclohexyl-2-methoxyethanal (**12a**) (5.17 g, 33.1 mmol) in THF (10 ml plus 5 ml rinse) was added *via* cannula and the dark yellow reaction mixture allowed to warm to rt. After 1 h the yellow solution was quenched with AcOH (6.61 ml of a 1M solution in THF, 6.61 mmol, 0.2 eq), causing the colour to fade. Water (50 ml) was added to the reaction mixture, the organic phase separated and the aqueous layer extracted with ether (3 x 100 ml). The organic layers were washed with water (3x 100 ml), brine (100 ml), dried ($MgSO_4$) and the solvents evaporated under reduced pressure. The resulting yellow oil was purified by chromatography (30% ether–petrol) to give a 9:1 *E:Z* mixture of isomers of 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)propene (**13a**) (8.92 g, 87%) as a colourless oil; R_f 0.46, 50% ether–petrol; ν_{max} (film) 2928, 2853, 2828, 1597, 1450, 1318, 1303, 1289, 1147, 1887 and 910 cm^{-1}; δ_H (270 MHz) 7.85 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.83 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *E*-isomer), 7.42 (2H, d, J 8.0 Hz, H-3 and H-5 of Ts, *Z*-isomer), 7.40 (2H, d, J 8.0 Hz, H-3 and H-5 of Ts, *E*-isomer), 6.91 (1H, dd, J 15.0 and 5.5 Hz, H-2, *E*-isomer), 6.54 (1H, dd, J 15.0 and H-1, *E*-isomer), 6.51 (1H, dd, J 11.5 and 1.0 Hz, H-1, *Z*-isomer), 6.09 (1H, dd, J 11.5 and 9.0 Hz, H-2, *Z*-isomer), 4.79-4.74 (1H, m, H-3, *Z*-isomer), 3.63-3.58 (1H, m, H-3, *E*-isomer), 3.32 (3H, s, OMe, *Z*-isomer), 3.31 (3H, s, OMe, *E*-isomer), 2.51 (3H, s, Me of Ts, *Z*-isomer), 2.50 (3H, s, Me of Ts, *E*-isomer) and 1.81-1.49 and 1.36-0.91 (22H, m, *c*-C_6H_{11}, both isomers); *m/z* (EI) 326 $[M+NH_4]^+$, 309 $[MH]^+$, 282, 277 $[M-OMe]^+$, 243, 226, 153 $[M-Ts]^+$, 139, 71 $[C_6H_5]^+$ (Found: $[M+NH_4]^+$, 326.1760. $C_{17}H_{24}O_3S$ requires $[M+NH_4]^+$, 326.1790).

Preparation of 3-methoxy-1-(4-tolylsulfonyl)nonene (13b).

This was carried out analogously to the preparation of 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)propene (**13a**) on a 5.78 mmol scale starting from 2-methoxyoctanal (**12b**) and (4-tolylsulfonyl)methane to give, after chromatography (30% ether–petrol), 3-methoxy-1-(4-tolylsulfonyl)nonene (**13b**) (1.69 g, 94%); R_f 0.48 and 0.42, 50% ether–petrol; ν_{max} (film) 3047, 2930, 2859, 2828, 1598, 1461, 1319, 1303, 1146, 1087, 830, 813 and 705 cm^{-1}; δ_H (270 MHz), 7.82 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.80 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *E*-isomer), 7.38 (2H, d, J 8.5 Hz, H-3 and H-5 of Ts, *E*-isomer), 7.30 (2H, d, J 8.5 Hz, H-3 and H-5 of Ts, *Z*-isomer), 6.88 (1H, dd, J 15.0 and 5.0 Hz, H-2, *E*-isomer), 6.55 (1H, dd, J 15.0 and 1.0 Hz, H-1, *E*-isomer), 6.45 (1H, dd, J 11.5 and 1.0 Hz, H-1, *Z*-isomer), 6.10 (1H, dd, J 11.5 and 9.0 Hz, H-2, *Z*-isomer), 4.93 (1H, m, H-3, *Z*-isomer), 3.83 (1H, m, H-3, *E*-isomer), 3.32 (3H, s, OMe, *Z*-isomer), 3.31 (3H, s, OMe, *E*-isomer), 2.49 (3H, s, Me of Ts, *E*-isomer), 2.48 (3H, s, Me of Ts, *Z*-isomer), 1.64-1.56 (4H, m, H-4, both isomers), 1.47-1.14 (16H, m, H-5 to H-8, both isomers) and 0.90 (3H, t, J 6.5 Hz, H-9); *m/z* (EI) 328 $[M+NH_4]^+$, 311 $[MH]^+$, 296 $[MH-Me]^+$, 284, 279 $[M-OMe]^+$, 225, 155 $[M-Ts]^+$, 139, 123, 97, 86, 71 $[C_6H_5]^+$ (Found: $[M+NH_4]^+$, 328.1964. $C_{17}H_{26}O_3S$ requires $[M+NH_4]^+$, 328.1947).

Preparation of (*E*)- and (*Z*)-3-methoxy-3-phenyl-1-(4-tolylsulfonyl)propene ((*E*)- and (*Z*)-13c) and (*Z*)-1-methoxy-1-phenyl-3-(4-tolylsulfonyl)propene (8c).

This was carried out analogously to the preparation of 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)propene (**13a**) on a 11.3 mmol scale starting from 2-methoxy-2-phenylethanal (**12c**) to give, after chromatography (50% ether–petrol), an 8:5:11 inseparable mixture of (*E*)- and (*Z*)-3-methoxy-3-phenyl-1-(4-tolylsulfonyl)propene ((*E*)- and (*Z*)-**13c**) and (*Z*)-1-methoxy-1-phenyl-3-(4-tolylsulfonyl)propene (**8c**) (combined yield 3.23 g, 95%); R_f 0.30, 50% ether–petrol; ν_{max} (film) 3030, 2970, 2930, 1597, 1493, 1454, 1315, 1302, 1149, 1138, 1087, 770 and 701 cm^{-1}; δ_H (270 MHz) 7.99 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, **8c**), 7.82 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, (*E*)-**13c**), 7.81 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, (*Z*)-**13c**), 7.54-7.26 (21H, m, H-3 and H-5 of Ts and Ph, all isomers), 7.01 (1H, dd, J 14.5 and 4.0 Hz, H-2, (*E*)-**13c**), 6.72 (1H, dd, J 14.5 and 1.0 Hz, H-1, (*E*)-**13c**), 6.40 (2H, m, H-1 and H-2, (*Z*)-**13c**), 6.17 (1H, d, J 7.5 Hz, H-3, (*Z*)-**13c**), 5.15 (1H, t, J 8.0 Hz, H-2, **8c**), 4.80 (1H, m, H-3, (*E*)-**13c**), 4.13 (2H, d, J 8.0 Hz, H-3, **8c**), 3.40 (3H, s, OMe, (*Z*)-**13c**), 3.37 (3H, s, OMe, **8c**), 3.19 (3H, s, OMe, (*E*)-**13c**) and 2.43 (6H, s, Me of Ts, (*E*)- and (*Z*)-**13c**) and 2.42 (3H, s, Me of Ts, **8c**);*m/z* (EI) 320 $[M+NH_4]^+$, 303 $[MH]^+$, 290 $[M+NH_3\text{-}MeO]^+$, 271 $[M\text{-}OMe]^+$, 214, 200, 147 $[M\text{-}Ts]^+$, 132, 115 $[M\text{-}Ts\text{-}MeOH]^+$, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$ (Found: $[MH]^+$, 303.1055. $C_{17}H_{18}O_3S$ requires $[MH]^+$, 303.1055).

Preparation of 10-methoxy-8-(4-tolylsulfonyl)-8-hexadecene (13d).

This was carried out analogously to the preparation of 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)propene (**13a**) on a 6.31 mmol scale starting from 1-(4-tolylsulfonyl)octane (**10a**) and 2-methoxyoctanal (**12b**) to give, after chromatography (10% ether–petrol) an isomeric mixture of 10-methoxy-8-(4-tolylsulfonyl)-8-hexadecene (**13d**) (2.37 g, 92%) as a colourless oil; R_f 0.66 and 0.59, 50% ether–petrol; ν_{max} (film) 2927, 2857, 1597, 1463, 1301, 1150, 1086, 814, 714, 694 and 654 cm^{-1}; δ_H (270 MHz) 7.76-7.71 (4H, m, H-2 and H-6 of Ts, both isomers), 7.33-7.29 (4H, m, H-3 and H-5 of Ts, both isomers), 6.63 (1H, d, J 9.0 Hz, H-9, *E*-isomer), 5.81 (1H, d, J 9.0 Hz, H-9, *Z*-isomer), 4.90 (1H, td, J 9.0 and 1.0 Hz, H-10, *E*-isomer), 3.92-3.80 (1H, m, H-10, *E*-isomer), 3.23 (3H, s, OMe, *Z*-isomer), 3.21 (3H, s, OMe, *E*-isomer), 2.42 (6H, s, Me of Ts, both isomers), 2.27-2.21 (4H, m, H-11, both isomers), 1.56-1.14 (40H, m, H-2 to H-7 and H-12 to H-15, both isomers) and 0.93-0.82 (12H, m, H-1 and H-16, both isomers); *m/z* (EI) 408 $[M]^+$, 393 $[M\text{-}Me]^+$, 323 $[C_6H_{13}]^+$, 253 $[M\text{-}Ts]^+$, 195, 167, 153, 139, 97, 91 $[C_7H_7]^+$, 83, 67, 55 (Found: $[M]^+$, 408.2699. $C_{24}H_{40}O_3S$ requires $[M]^+$, 408.2670).

Preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-hexadiene (7g).

To a stirred solution of 1-benzyloxy-3-(4-tolylsulfonyl)propene (**1**) (1.37 g, 4.53 mmol) in THF (45.3 ml) under argon at -78°C was added *n*-BuLi (2.00 ml of a 2.5M solution in hexanes, 4.99 mmol, 1.1 eq) causing the solution to become dark red in colour. After 30 min a solution of 3-bromopropene (0.59 ml, 6.81 mmol, 1.5 eq) in THF (10 ml) was added *via* cannula and the cloudy yellow solution allowed to warm to rt. After the addition of water (50 ml), the organic phase was separated and the aqueous layer extracted with ether (3 x 50 ml). The combined organic layers were washed with water (50 ml), brine (50 ml), dried (K_2CO_3) and concentrated under reduced pressure to give a pale yellow oil. Chromatography (20% ether–petrol), yielded a 10:1 *Z:E* mixture of isomers of 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-hexadiene (**7g**) (1.50 g, 96%) as a colourless, crystalline solid; mp 73-74°C, R_f 0.32, 50% ether–petrol; ν_{max} (CH_2Cl_2) 3065, 3028, 2977, 2927, 2877, 1655, 1599, 1447, 1370, 1300, 1290, 1212, 1141, 1104, 1080, 922, 813, 742, 701 and 658 cm^{-1}; δ_H (270 MHz) 7.76 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.65 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *E*-isomer), 7.44-7.24 and 7.13-7.04 (14H, m, H-3 and H-5 of Ts and Ph, both isomers), 6.19 (1H, d, J 12.5 Hz, H-1, *E*-isomer), 6.16 (1H, d, J 5.5 Hz, H-1, *Z*-isomer), 5.76 (2H, m, H-5, both isomers), 5.10 (2H, d with fine coupling, J 17.5 Hz, H-6_E, both isomers), 5.04 (2H, d with fine coupling, J 10.0 Hz, H-6_Z, both

isomers), 4.73 (2H, s, CH_2Ph, *E*-isomer), 4.60 (1H, dd, J 12.5 and 10.0 Hz, H-2, *E*-isomer), 4.56 (1H, d, J 12.5 Hz, CH_2Ph, *Z*-isomer), 4.46 (1H, d, J 12.5 Hz, CH_2Ph, *Z*-isomer), 4.31 (1H, dd, J 10.0 and 5.5 Hz, H-2, *Z*-isomer), 4.26 (1H, td, J 10.0 and 3.5 Hz, H-3, *Z*-isomer), 3.41 (1H, td, J 10.0 and 3.5 Hz, H-3, *E*-isomer), 2.93-2.84 (2H, m, H-4, both isomers), 2.43 (3H, s, Me of Ts, *E*-isomer), 2.42 (3H, s, Me of Ts, *Z*-isomer) and 2.49-2.34 (2H, m, H-4, both diastereomers); *m/z* (EI) 262, 244, 214, 187 $[M\text{-}Ts]^+$, 167, 139, 124, 108 $[BnOH]^+$, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$ (Found: C, 70.07; H, 6.66. $C_{20}H_{22}O_3S$ requires C, 70.15; H, 6.48%).

Preparation of 1-cyclohexyl-1-methoxy-3-(4-tolylsulfonyl)undecene (9a).

To a solution of 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)propene (**13a**) (3.17 g, 10.3 mmol) in THF (51.4 ml) and *t*-BuOH (9.69 ml, 103 mmol, 10 eq) was added *t*-BuOK (10.3 ml of a 1M solution in THF, 10.3 mmol) causing the solution to become golden-yellow. After stirring for 1 h the pale orange solution was quenched with AcOH (10.3 ml of a 1M solution in THF, 10.3 mmol), followed by saturated aqueous $NaHCO_3$ (10 ml) and water (20 ml). The organic layer was separated, the aqueous layer extracted with ether (3 x 30 ml), the combined organic layers washed with saturated aqueous $NaHCO_3$ (30 ml), water (30 ml), brine (30 ml), dried (K_2CO_3) and concentrated under reduced pressure to give crude 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)-2-propene (**8a**) as a pale yellow oil. This oil was redissolved in THF (40.5 ml) and TMEDA (10.1 ml) under a nitrogen atmosphere, cooled to -78°C and *n*-BuLi (4.52 ml of a 2.5M solution in hexanes, 11.3 mmol, 1.1 eq) added, causing the reaction mixture to become bright orange-red in colour. After stirring for 30 min at -78°C a solution of 1-iodooctane (1.86 ml, 10.3 mmol) in THF (10 ml plus 3 ml rinse) was added *via* cannula and the solution allowed to warm to rt, giving a pale yellow cloudy solution. The reaction mixture was poured into water (30 ml), the organic layer separated and the aqueous layer extracted with ether (3 x 60 ml). The combined organic layers were washed with water (60 ml), brine (60 ml), dried (K_2CO_3). Evaporation of the solvents under reduced pressure followed by chromatography (10% ether–petrol), gave a 23:1 *Z:E* mixture of isomers of 1-cyclohexyl-1-methoxy-3-(4-tolylsulfonyl)undecene (**9a**) (3.96 g, 92%) as a colourless oil; R_f 0.52, 50% ether–petrol; ν_{max} (film) 2928, 2854, 1662, 1597, 1312, 1287, 1144, 1086, 815 and 801 cm^{-1}; δ_H (270 MHz) 7.68 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts), 7.24 (2H, d, J 8.0 Hz, H-3 and H-5 of Ts), 4.28 (1H, dd, J 10.5 and 0.5 Hz, H-2), 4.10 (1H, dt, J 10.5 and 3.0 Hz, H-3), 3.07 (3H, s, OMe), 2.37 (3H, s, Me of Ts), 2.07-1.90 (2H, m, H-4 and H-1'), 1.82-1.50 and 1.39-0.95 (23H, m, 1 x H-4, H-5 to H-10 and H-2' to H-6') and 0.83 (3H, t, J 6.5 Hz, H-11); *m/z* (CI) 438 $[M+NH_4]^+$, 421 $[MH]^+$, 265 $[M\text{-}Ts]^+$, 251 $[M\text{-}Ts\text{-}CH_2]^+$, 209 $[M\text{-}Ts\text{-}C_4H_8]^+$, 174, 151, 139, 91 $[C_7H_7]^+$ (Found: $[MH]^+$, 421.2749. $C_{25}H_{40}O_3S$ requires $[MH]^+$, 421.2776).

Preparation of 1-cyclohexyl-1-methoxy-4-phenyl-3-(4-tolylsulfonyl)butene (9b).

This was carried out analogously to the preparation of 1-cyclohexyl-1-methoxy-3-(4-tolylsulfonyl)undecene (**9a**) on a 11.1 mmol scale starting from 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)propene (**13a**) and benzyl bromide to give, after chromatography (30% ether–petrol), a 25:1 *Z:E* mixture of isomers of 1-cyclohexyl-1-methoxy-4-phenyl-3-(4-tolylsulfonyl)butene (**9b**) (3.95 g, 89%) as a colourless oil; R_f 0.34, 50% ether–petrol; ν_{max} (film) 2930, 2854, 1663, 1597, 1452, 1311, 1300, 1288, 1143, 1086, 765 and 743 cm^{-1}; δ_H (270 MHz) 7.80 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts), 7.32 (2H, d, J 8.0 Hz, H-3 and H-5 of Ts), 7.29-7.15 (5H, m, Ph), 4.48-4.41 (2H, m, H-2 and H-4), 3.64-3.58 (1H, m, H-4), 2.90-2.81 (1H, m, H-3), 2.78 (3H, s, OMe), 2.43 (3H, s, Me of Ts), 1.84 (1H, tt, J 11.5 and 3.0 Hz, H-1'), 1.67-1.54 (4H, m, 1 x H-4, H-2' and H-6'), 1.23-1.10 (3H, m, H-3', H-4' or H-5') and 0.97-0.87 (3H, m, H-3', H-4' or H-5'); *m/z* (CI) 416 $[M+NH_4]^+$, 399 $[MH]^+$, 326, 243 $[M\text{-}Ts]^+$, 229 $[M\text{-}Ts\text{-}CH_2]^+$, 174 $[MH\text{-}Ts\text{-}C_5H_{10}]^+$, 153 $[MH\text{-}Ts\text{-}Bn]^+$, 139, 108 and 91 $[C_7H_7]^+$ (Found: $[MH]^+$, 399.5724. $C_{24}H_{30}O_3S$ requires $[MH]^+$, 399.5729).

Preparation of 7-methoxy-9-(4-tolylsulfonyl)-7-heptadecene (9c).

This was carried out analogously to the preparation of 1-cyclohexyl-1-methoxy-3-(4-tolylsulfonyl)undecene (**9a**) on a 3.26 mmol scale starting from 3-methoxy-1-(4-tolylsulfonyl)nonene (**13b**) and 1-iodooctane to give, after chromatography (10% ether–petrol), an 8:1 *Z*:*E* mixture of isomers of 7-methoxy-9-(4-tolylsulfonyl)-7-heptadecene (**9c**) (1.34 g, 97%) as a colourless oil; R_f 0.27, 20% ether–petrol; ν_{max} (film) 3063, 3026, 2953, 2927, 2857, 1666, 1598, 1463, 1378, 1312, 1298, 1287, 1144, 1086, 1065 and 815 cm^{-1}; δ_H (270 MHz) 7.72 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.71 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *E*-isomer), 7.29 (2H, d, J 8.5 Hz, H-3 and H-5 of Ts, *E*-isomer), 7.28 (2H, d, J 8.5 Hz, H-3 and H-5 of Ts, *Z*-isomer), 4.26 (1H, d, J 10.5 Hz, H-8, *Z*-isomer), 4.13 (1H, td, J 10.5 and 3.0 Hz, H-9, *Z*-isomer), 4.08 (1H, d, J 10.5 Hz, H-8, *E*-isomer), 3.58 (1H, td, J 10.5 and 3.0 Hz, H-9, *E*-isomer), 3.49 (3H, s, OMe, *E*-isomer), 3.10 (3H, s, OMe, *Z*-isomer), 2.42 (3H, s, Me of Ts, *E*-isomer), 2.41 (3H, s, Me of Ts, *Z*-isomer), 2.11-1.96 (4H, m, H-6, both isomers), 1.65-1.49 (4H, m, H-10, both isomers), 1.42-1.08 (40H, m, H-2 to H-5 and H-11 to H-16, both isomers) and 0.90-0.81 (12H, m, H-1 and H-17, both isomers); *m/z* (CI) 440 $[M+NH_4]^+$, 423 $[MH]^+$, 349 $[M+NH_4\text{-}Bn]^+$, 267 $[M\text{-}Ts]^+$, 209, 174, 153, 139, 97 (Found: $[MH]^+$, 423.2933. $C_{25}H_{42}O_3S$ requires $[MH]^+$, 423.2921).

Preparation of 6-methoxy-4-(4-tolylsulfonyl)-1,5-dodecadiene (9d).

This was carried out analogously to the preparation of 1-cyclohexyl-1-methoxy-3-(4-tolylsulfonyl)undecene (**9a**) on a 4.07 mmol scale starting from 3-methoxy-1-(4-tolylsulfonyl)nonene (**13b**) and 3-bromopropene to give, after chromatography (20% ether–petrol), a 6:1 *Z*:*E* mixture of isomers of 6-methoxy-4-(4-tolylsulfonyl)-1,5-dodecadiene (**9d**) (1.42 g, 91%) as a colourless oil; R_f 0.45, 50% ether–petrol; ν_{max} (film) 2954, 2930, 2858, 1666, 1643, 1597, 1456, 1310, 1301, 1289, 1195, 1144, 1086, 1058 and 917 cm^{-1}; δ_H (270 MHz) 7.72-7.69 (4H, m, H-2 and H-6 of Ts, both isomers), 7.30-7.25 (4H, m, H-3 and H-5 of Ts, both isomers), 5.71-5.61 (2H, m, H-2, both isomers), 5.09-4.98 (4H, m, H-1, both isomers), 4.28-4.19 (3H, m, H-5, both isomers and H-4, *Z*-isomer), 3.57 (1H, td, J 11.0 and 4.0 Hz, H-4, *E*-isomer), 3.46 (3H, s, OMe, *E*-isomer), 3.06 (3H, s, OMe, *Z*-isomer), 2.89-2.80 (2H, m, H-3, both isomers), 2.39 (3H, s, Me of Ts, *E*-isomer), 2.38 (3H, s, Me of Ts, *Z*-isomer), 2.02-1.94 (6H, m, H-3 and H-7, both isomers), 1.21-1.08 (8H, m, H-8 to H-11, both isomers) and 0.88-0.80 (6H, m, H-12, both isomers); *m/z* (CI) 368 $[M+NH_4]^+$, 351 $[MH]^+$, 328 $[MNH_4\text{-}C_3H_4]^+$, 195 $[M\text{-}Ts]^+$, 181 $[MH\text{-}Ts\text{-}Me]^+$, 174, 156 $[TsH]^+$, 139, 124, 109 (Found: $[MH]^+$, 351.1994. $C_{20}H_{30}O_3S$ requires $[MH]^+$, 351.2005).

Preparation of 2-undecylfuran (6a).

A stirred solution of 1-benzyloxy-3-(4-tolylsulfonyl)pentadecen-4-ol (prepared from **1** by lithiation and addition of dodecanal[1]) (0.344 g, 0.706 mmol) in benzene (7.1 ml) containing p-TSA (1 crystal) was heated under reflux for 4 h. The resultant golden-yellow solution was filtered through a pad consisting of a layer of silica gel and a layer of K_2CO_3 and the pad was washed with ether (50 ml). Removal of the solvents followed by chromatography (petrol), yielded 2-undecylfuran[7] (**6a**) (0.178 g, 88%) as a colourless liquid; R_f 0.47, petrol; ν_{max} (film) 2925, 2854, 2360, 2341, 1597, 1507, 1465, 1378, 1147, 1008, 794 and 725 cm^{-1}; δ_H (270 MHz) 7.37 (1H, dd, J 2.0 and 1.0 Hz, H-5), 6.35 (1H, dd, J 3.0 and 2.0 Hz, H-4), 6.04 (1H, dd, J 3.0 and 1.0 Hz, H-3), 2.62 (2H, t, J 7.5 Hz, H-1'), 1.72-1.57 (2H, m, H-2'), 1.55-0.91 (16H, m, H-3' to H-10') and 0.87 (3H, t, J 6.5 Hz, H-11'); δ_C (68 MHz) 156.66 (C-5), 140.61 (C-2), 110.01 (C-4), 104.49 (C-3), 31.94 (C-1'), 29.73 (C-2'), 29.65 (C-3' and C-4'), 29.57 (C-5'), 29.39 (C-6'), 29.21 (C-7'), 28.06 (C-8'), 27.00 (C-9'), 22.71 (C-12') and 14.12 (C-13'); *m/z* (EI) 222 $[M]^+$, 205, 189, 179 $[M\text{-}C_3H_7]^+$, 165 $[M\text{-}C_4H_8]^+$, 131, 118, 95 $[M\text{-}C_9H_{19}]^+$, 81 $[M\text{-}C_{10}H_{21}]^+$, 57, 41, 29 (Found: C, 80.93; H, 11.67. $C_{15}H_{26}O$ requires C, 81.02; H, 11.79%).

Preparation of 3-heptylfuran (6b).

A stirred solution of 1-benzyloxy-3-(4-tolylsulfonyl)decene (**7a**) (0.950 g, 2.37 mmol) in THF (20.5 ml) at -78°C under a nitrogen atmosphere was treated with *n*-BuLi (1.04 ml of a 2.5M solution in hexanes, 2.61 mmol, 1.1 eq) resulting in the formation of a bright red solution. After 30 min a slurry of paraformaldehyde (0.500 g, 16.6 mmol, 7 eq) in THF (5 ml plus 5 ml rinse) was added *via* cannula and the reaction allowed to warm to rt, causing the colour slowly to become a very pale cloudy yellow. After stirring for a further 10 min, the reaction mixture was quenched with AcOH (2.61 ml of a 1M solution in THF, 2.61 mmol, 1.1 eq), causing the solution to become colourless with a white sediment. The solution was diluted with ether, dried (K_2CO_3), filtered through a plug of Celite® and the solvents evaporated under reduced pressure to give a pale yellow liquid. This was redissolved in CH_2Cl_2 (20.5 ml) under a nitrogen atmosphere, silica gel (11.85 g) added and the pale yellow two-phase system rapidly stirred. After 18 h the reaction mixture was filtered through a small pad of K_2CO_3 which was washed with portions of ether (150 ml). Evaporation of the solvents under reduced pressure followed by chromatography (petrol), yielded 3-heptylfuran[8] (**6b**) (0.375 g, 95%) as a colourless liquid; R_f 0.45, petrol; ν_{max} (film) 2956, 2927, 2857, 1502, 1465, 1161, 1026, 874, 776 and 722 cm^{-1}; δ_H (270 MHz) 7.44 (1H, t, J 1.5 Hz, H-2), 7.30 (1H, d, J 1.0 Hz, H-5), 6.36 (1H, d, J 1.0 Hz, H-4), 2.50 (2H, t, J 7.0 Hz, H-1'), 1.71-1.61 (2H, m, H-2'), 1.55-1.33 (8H, m, H-3' to H-6') and 1.00 (3H, t, J 7.0 Hz, H-7'); δ_C (68 MHz) 142.57 (C-5), 138.72 (C-2), 125.36 (C-4), 111.05 (C-3), 31.86 (C-1'), 30.06 (C-2'), 29.30 (C-3'), 29.16 (C-4'), 24.77 (C-5'), 22.70 (C-6') and 14.11 (C-7'); *m/z* (CI) 184 $[M+NH_4]^+$, 167 $[MH]^+$, 152, 124 $[M-C_3H_6]^+$, 95 $[M-C_5H_{11}]^+$, 82 $[M-C_6H_{12}]^+$, 73, 58 (Found: $[MH]^+$, 167.1436. $C_{11}H_{18}O$ requires $[MH]^+$, 167.1436).

Preparation of 3-ethyl-2-phenylfuran (6g).

A solution of 1-benzyloxy-3-(4-tolylsulfonyl)pentene (**7b**) (0.742 g, 2.25 mmol) in THF (22.5 ml) at -78°C under a nitrogen atmosphere was treated with *n*-BuLi (0.99 ml of a 2.5M solution in hexanes, 2.47 mmol, 1.1 eq) resulting in the formation of a dark red solution. After stirring for 30 min a solution of benzaldehyde (0.23 ml, 2.25 mmol) in THF (5 ml plus 2 ml rinse) was slowly added *via* cannula, causing the colour to quench to pale yellow. After stirring for a further 10 min, the reaction mixture was quenched with AcOH (2.25 ml of a 1M solution in THF, 2.47 mmol, 1.1 eq), causing the solution to become colourless, followed by saturated aqueous $NaHCO_3$ (10 ml) and allowed to warm to rt. Water (10 ml) was added to the reaction, the organic layer separated and the aqueous layer extracted with ether (3 x 40 ml). The combined organic layers were washed with water (40 ml), brine (40 ml), dried (K_2CO_3) and the solvents removed under reduced pressure to give a pale yellow liquid. This was redissolved in CH_2Cl_2 (22.5 ml) under a nitrogen atmosphere, silica gel (11.25 g) added and the pale yellow two-phase system rapidly stirred. After 16 h the reaction mixture was filtered through a small pad of K_2CO_3 which was washed with portions of ether (100 ml). Evaporation of the solvents under reduced pressure followed by chromatography (petrol), yielded 3-ethyl-2-phenylfuran (**6g**) (0.366 g, 95%) as a colourless liquid; R_f 0.26, petrol; ν_{max} (film) 3054, 2968, 2934, 2876, 1606, 1510, 1485, 1461, 1378, 1162, 1097, 1066, 1025, 949, 911, 889, 846, 766, 738 and 694 cm^{-1}; δ_H (270 MHz) 7.70-7.66 (2H, m, H-2 and H-6 of Ph), 7.50-7.43 (3H, m, H-3 and H-5 of Ph and H-5), 7.32 (1H, tt, J 6.5 and 1.5 Hz, H-4 of Ph), 6.46 (1H, d, J 1.5 Hz, H-4), 2.77 (2H, q, J 7.5 Hz, H-1') and 1.32 (3H, t, J 7.5 Hz, H-2'); *m/z* (EI) 172 $[M]^+$, 157$[M-Me]^+$, 143 $[M-Et]^+$, 129 $[M-C_3H_7]^+$, 115, 91 $[M-C_7H_7]^+$, 77 $[M-C_6H_5]^+$, 51, 39 $[C_3H_3]^+$, 27 (Found: C, 83.31; H, 7.35. $C_{12}H_{12}O$ requires C, 83.69; H, 7.02%).

Preparation of 3-heptyl-2-hexylfuran (6c).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 1.30 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)decene (**7a**) and heptanal to give, after chromatography (petrol), 3-heptyl-2-hexylfuran (**6c**) (0.264 g, 98%) as a colourless liquid; R_f 0.56, petrol; ν_{max} (film) 2927, 2857, 1513,

1466, 1378, 1146, 1051, 893 and 725 cm^{-1}; δ_H (270 MHz) 7.22 (1H, d, J 1.5 Hz, H-5), 6.18 (1H, d, J 1.5 Hz, H-4), 2.55 (2H, t, J 7.5 Hz, H-1'), 2.32 (2H, t, J 7.5 Hz, H-1"), 1.65-1.42 (4H, m, H-2' and H-2"), 1.37-1.21 (14H, m, H-3' to H-5' and H-3" to H-6") and 0.96-0.83 (6H, m, H-6' and H-7"); *m/z* (EI) 250 $[M]^+$, 235 $[M-Me]^+$, 221 $[M-C_2H_5]^+$, 207 $[M-C_3H_7]^+$, 193 $[M-C_4H_9]^+$, 179 $[M-C_5H_{11}]^+$, 166 $[M-C_6H_{13}]^+$, 151 $[M-C_7H_{16}]^+$, 137 $[M-C_8H_{18}]^+$, 123 $[M-C_9H_{20}]^+$, 95 $[M-C_{11}H_{24}]^+$, 82 $[M-C_{12}H_{24}]^+$, 39 $[C_3H_3]^+$, 29 $[HCO]^+$ (Found: C, 81.25; H, 11.98. $C_{17}H_{30}O$ requires C, 81.54; H, 12.07%).

Preparation of 3-heptyl-2-phenylfuran (6d).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 1.21 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)decene (**7a**) and benzaldehyde to give, after chromatography (petrol), 3-heptyl-2-phenylfuran[9] (**6d**) (0.250 g, 85%) as a colourless liquid; R_f 0.35, petrol; ν_{max} (film) 2924, 2853, 1738, 1605, 1511, 1462, 1376, 1160, 1060, 889, 766, 728 and 691 cm^{-1}; δ_H (270 MHz) 7.65-7.58 (2H, m, H-1 and H-5 of Ph), 7.46-7.37 (2H, m, H-2 and H-4 of Ph), 7.39 (1H, d, J 2.0 Hz, H-5), 7.29-7.20 (1H, m, H-3 of Ph), 6.38 (1H, d, J 2.0 Hz, H-4), 2.66 (2H, t, J 8.0 Hz, H-1'), 1.70-1.58 (2H, m, H-2'), 1.56-1.21 (8H, m, H-3' to H-6') and 0.88 (3H, t, J 6.5 Hz, H-7'); *m/z* (EI) 242 $[M]^+$, 157 $[M-C_6H_{13}]^+$, 144 $[M-C_7H_{14}]^+$, 129, 115, 91, 77, 55, 41 $[M-C_3H_5]^+$, 39 $[M-C_3H_3]^+$, 28 $[CHO]^+$ (Found: C, 84.16; H, 8.99. $C_{17}H_{22}O$ requires C, 84.25; H, 9.15%).

Preparation of 2-cyclohexyl-3-heptylfuran (6e).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 0.652 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)decene (**7a**) and cyclohexanecarboxaldehyde to give, after chromatography (petrol), 2-cyclohexyl-3-heptylfuran (**6e**) (0.140 g, 86%) as a colourless liquid; R_f 0.41, petrol; ν_{max} (film) 2928, 2854, 1512, 1450, 1376, 1239, 1148, 1099, 1054, 886 and 731 cm^{-1}; δ_H (270 MHz) 7.21 (1H, d, J 1.5 Hz, H-5), 6.18 (1H, d, J 1.5 Hz, H-4), 2.62 (1H, tt, J 11.5 and 3.5 Hz, H-1'), 2.35 (2H, t, J 7.5 Hz, H-1"), 1.86-1.20 (20H, m, H-2' to H-6' and H-2" to H-6") and 0.90 (3H, t, J 7.0 Hz, H-7"); *m/z* (EI) 233 $[M]^+$, 219 $[M-C_2H_5]^+$, 205, 191 $[M-C_4H_9]^+$, 177 $[M-C_5H_{11}]^+$, 163 $[M-C_6H_{13}]^+$, 149 $[M-C_7H_{15}]^+$, 121 $[M-C_9H_{19}]^+$, 95 $[M-C_{11}H_{21}]^+$, 82 $[M-C_{12}H_{20}]^+$, 77, 55, 41, 29 $[HCO]^+$ (Found: C, 82.43; H, 11.59. $C_{17}H_{28}O$ requires C, 82.20; H, 11.36%).

Preparation of 2-[5-(*tert*-butyldiphenylsilyloxy)pentyl]-3-heptylfuran (6f).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 3.04 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)decene (**7a**) and 6-(*tert*-butyldiphenylsilyloxy)hexanal to give, after chromatography (1% ether–petrol), 2-[5-(*tert*-butyldiphenylsilyloxy)pentyl]-3-heptylfuran (**6f**) (1.45 g, 97%) as a colourless liquid; R_f 0.33, 1% ether–petrol; ν_{max} (film) 3070, 2929, 2857, 1510, 1464, 1429, 1387, 1109, 893, 823, 736, 704 and 612 cm^{-1}; δ_H (270 MHz) (4H, m, H-2 and H-6 of Ph), 7.46-7.34 (6H, m, H-3 to H-5 of Ph), 7.22 (1H, d, J 2.0 Hz, H-5), 6.18 (1H, d, J 2.0 Hz, H-4), 3.66 (2H, t, J 6.5 Hz, H-5'), 2.55 (2H, t, J 7.5 Hz, H-1'), 2.31 (2H, t, J 7.5 Hz, H-1"), 1.66-1.22 (16H, m, H-2' to H-4' and H-2" to H-6"). 1.05 (9H, s, *t*-Bu) and 0.89 (3H, t, J 6.5 Hz, H-7"); *m/z* (EI) 433 $[M-t\text{-}Bu]^+$, 391 $[M-C_7H_{15}]^+$, 355, 269, 217, 199, 183, 139, 135, 95, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 57, 43 (Found: C, 78.11; H, 9.55. $C_{32}H_{46}O_2Si$ requires C, 78.31; H, 9.45%).

Preparation of 2-[5-(*tert*-butyldiphenylsilyloxy)pentyl]-3-ethylfuran (6h).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 1.23 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)pentene (**7b**) and 6-(*tert*-butyldiphenylsilyloxy)hexanal to give, after chromatography (1% ether–petrol), 2-[5-(*tert*-butyldiphenylsilyloxy)pentyl]-3-ethylfuran (**6h**) (0.461 g,

97%) as a colourless liquid; R_f 0.27, 1% ether–petrol; ν_{max} (film) 3070, 2933, 2859, 1590, 1511, 1467, 1428, 1388, 1260, 1109, 944, 892, 822, 736 and 704 cm^{-1}; δ_H (270 MHz) 7.71-7.66 (4H, m, H-2 and H-6 of Ph), 7.46-7.35 (6H, m, H-3 to H-5 of Ph), 7.23 (1H, d, J 1.5 Hz, H-5), 6.21 (1H, d, J 1.5 Hz, H-4), 3.66 (2H, t, J 6.5 Hz, H-5'), 2.56 (2H, t, J 7.5, H-1'), 2.35 (2H, q, J 7.5 Hz, H-1"), 1.66-1.55 and 1.45-1.27 (6H, m, H-2' to H-4'), 1.13 (3H, t, J 7.5 Hz, H-2") and 1.06 (9H, s, *t*-Bu); *m/z* (EI) 420 $[M]^+$, 405 $[M\text{-}Me]^+$, 377 $[M\text{-}C_3H_7]^+$, 370, 363 [M-*t*-Bu), 285, 199, 183, 165 [M-TBDPS]$^+$, 147, 139, 91 $[M\text{-}C_7H_7]^+$, 77 $[M\text{-}C_6H_5]^+$ (Found: C, 77.89; H, 8.48. $C_{27}H_{36}O_2Si$ requires C, 77.89; H, 8.48%).

Preparation of 3-benzylfuran (6i).

This was carried out analogously to the preparation of 3-heptylfuran (**6b**) on a 2.65 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)-4-phenylbutene (**7c**) and paraformaldehyde to give, after chromatography (petrol), 3-benzylfuran[10] (**6b**) (0.412 g, 98%) as a colourless liquid; R_f 0.19, petrol; ν_{max} (film) 3028, 2912, 1604, 1494, 1454, 1154, 1066, 1023, 874, 781, 765, 726 and 705 cm^{-1}; δ_H (500 MHz) 7.50-7.08 (6H, m, H-5 and Ph), 6.31 (1H, m, H-4) and 3.84 (2H, s, CH_2Ph); δ_C (68 MHz) 143.13 (C-5), 140.44 (C-1 of Ph), 139.68 (C-2), 128.66 (C-3 and C-5 of Ph), 128.54 (C-2 and C-6 of Ph), 126.26 (C-4), 124.34 (C-4 of Ph), 111.35 (C-3) and 31.25 (CH_2Ph); *m/z* (CI) 159 $[MH]^+$, 129 $[M\text{-}CHO]^+$, 115, 108, 91 $[C_7H_7]^+$, 81 $[M\text{-}Bn]^+$, 78, 71 $[C_6H_5]^+$ (Found: $[MH]^+$, 159.0809. $C_{11}H_{10}O$ requires $[MH]^+$, 159.0810).

Preparation of 3-benzyl-2-hexylfuran (6j).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 2.43 mmol scale starting from 1-benzyloxy-4-phenyl-3-(4-tolylsulfonyl)butene (**7c**) and heptanal to give, after chromatography (petrol), 3-benzyl-2-hexylfuran (**6j**) (0.559 g, 95%) as a colourless liquid; R_f 0.20, petrol; ν_{max} (film) 3062, 3027, 2928, 2856, 1603, 1511, 1455, 1377, 1141, 1051, 891 and 727 cm^{-1}; δ_H (270 MHz) 7.31-7.27 and 7.22-7.14 (5H, m, Ph), 7.24 (1H, d, J 2.0 Hz, H-5), 6.13 (1H, d, J 2.0 Hz, H-4), 3.71 (2H, s, CH_2Ph), 2.60 (2H, t, J 7.5 Hz, H-1'), 1.66-1.55 (2H, m, H-2'), 1.39-1.23 (6H, m, H-3' to H-5') and 0.88 (3H, t, J 6.5 Hz, H-6'); *m/z* (EI) 242 $[M]^+$, 171 $[M\text{-}C_5H_{11}]^+$, 157 $[M\text{-}C_6H_{13}]^+$, 153, 151 $[M\text{-}Bn]^+$, 143, 141, 128, 115, 91 $[C_7H_7]^+$, 81, 65 $[C_3H_3O]^+$, 55 $[C_3H_3O]^+$, 43 (Found: C, 83.97; H, 9.29. $C_{17}H_{22}O$ requires C, 84.25; H, 9.15%).

Preparation of 3-benzyl-2-cyclohexylfuran (6k).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 1.86 mmol scale starting from 1-benzyloxy-4-phenyl-3-(4-tolylsulfonyl)butene (**7c**) and cyclohexanecarboxaldehyde to give, after chromatography (petrol), 3-benzyl-2-cyclohexylfuran (**6k**) (0.417 g, 93%) as a colourless liquid; R_f 0.36, petrol; ν_{max} (film) 3062, 3027, 2930, 2853, 1604, 1511, 1494, 1450, 1239, 1146, 1074, 1052, 1030, 881, 817, 731 and 707 cm^{-1}; δ_H (270 MHz) 7.31-7.13 (5H, m, Ph), 7.22 (1H, d, J 1.5 Hz, H-5), 6.10 (1H, d, J 1.5 Hz, H-4), 3.74 (2H, s, CH_2Ph), 2.67 (1H, tt, J 11.5 and 3.5 Hz, H-1') and 1.89-1.46 and 1.41-1.17 (10H, m, H-2' to H-6'); *m/z* (EI) 240 $[M]^+$, 197 $[M\text{-}Pr]^+$, 184 $[M\text{-}Bu]^+$, 169 $[M\text{-}C_5H_{11}]^+$, 157 $[M\text{-}C_6H_{11}]^+$, 149 $[M\text{-}Bn]^+$, 141, 128, 115, 91 $[C_7H_7]^+$, 81, 77 $[C_6H_5]^+$, 65, 55 $[C_3H_3O]^+$, 51, 43 (Found: C, 85.59; H, 8.23. $C_{17}H_{20}O$ requires C, 85.31; H, 8.00%).

Preparation of 2-hexyl-3-(2-propenyl)furan (6p).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 0.722 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-hexadiene (**7g**) and heptanal to give, after chromatography (petrol), 2-hexyl-3-(2-propenyl)furan[11] (**6p**) (0.133 g, 95%) as a colourless liquid; R_f 0.39, petrol; ν_{max} (film) 3080, 2926, 2856, 1731, 1640, 1511, 1466, 1379, 1261, 1143, 1049, 992, 913, 888 and 726 cm^{-1}; δ_H (270

MHz) 7.23 (1H, d, J 2.0 Hz, H-5), 6.17 (1H, d, J 2.0 Hz, H-4), 5.96-5.81 (1H, m, H-2'), 5.08-4.98 (2H, m, H-3$_Z$' and H-3$_E$'), 3.11-3.08 (2H, m, H-1'), 2.55 (2H, t, J 7.5 Hz, H-1"), 1.67-1.55 (2H, m, H-2"), 1.51-1.29 (6H, m, H-3" to H-5") and 0.95-0.83 (3H, m, H-6"); *m/z* (EI) 192 $[M]^+$, 163 $[M\text{-}Et]^+$, 151 $[M\text{-}Pr]^+$, 135, 121 $[M\text{-}C_5H_{11}]^+$, 107, 91 $[M\text{-}C_7H_7]^+$, 77 $[M\text{-}C_6H_5]^+$, 41, 39 $[C_3H_3]^+$ (Found: C, 81.25; H, 10.59. $C_{13}H_{20}O$ requires C, 81.20; H, 10.48%).

Preparation of 2-phenyl-3-(2-propenyl)furan (6q).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 0.515 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-hexadiene (**7g**) and benzaldehyde to give, after chromatography (petrol), 2-phenyl-3-(2-propenyl)furan (**6q**) (0.090 g, 96%) as a colourless liquid; R_f 0.31, petrol; ν_{max} (film) 3078, 3005, 2979, 2913, 1607, 1512, 1486, 1445, 1413, 1292, 1189, 1158, 1060, 1031, 992, 915, 886, 773, 736, 694, 670 and 609 cm^{-1}; δ_H (270 MHz) 7.63-7.58 (2H, m, H-2 and H-6 of Ph), 7.46-7.36 (3H, m, H-3 and H-5 of Ph and H-5), 7.34-7.35 (1H, m, H-4 of Ph), 6.37 (1H, d, J 1.5 Hz, H-4), 6.10-5.95 (1H, m, H-2'), 5.17-5.13 (1H, m, H-3$_Z$'), 5.12-5.08 (1H, m, H-3$_E$') and 3.45-3.41 (2H, m, H-1'); *m/z* (EI) 184 $[M]^+$, 169 $[M\text{-}Me]^+$, 155 $[M\text{-}Et]^+$, 141, 128, 115, 102, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 51, 39 $[C_3H_3]^+$, 28 $[CO]^+$ (Found: C, 84.91; H, 6.63. $C_{13}H_{12}O$ requires C, 84.75; H, 6.63%).

Preparation of 2-cyclohexyl-3-(2-propenyl)furan (6r).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 0.910 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-hexadiene (**7g**) and cyclohexanecarboxaldehyde to give, after chromatography (petrol), 2-cyclohexyl-3-(2-propenyl)furan (**6r**) (0.157 g, 91%) as a colourless liquid; R_f 0.31, petrol; ν_{max} (film) 3079, 2930, 2854, 1639, 1511, 1449, 1239, 1147, 1051, 1025, 992, 912, 891, 772, 722 and 679 cm^{-1}; δ_H (270 MHz) 7.22 (1H, d, J 2.0 Hz, H-5), 6.16 (1H, d, J 2.0 Hz, H-4), 5.97-5.82 (1H, m, H-2'), 5.07-4.98 (2H, m, H-3'$_Z$ and H-3'$_E$), 3.13 (2H, dt, J 6.0 and 1.5 Hz, H-1'), 2.62 (1H, tt, J 11.5 and 3.5 Hz, H-1") and 1.85-1.17 and 0.89-0.84 (10H, m, H-2" to H-6"); *m/z* (EI) 190 $[M]^+$, 175 $[M\text{-}Me]^+$, 161 $[M\text{-}Et]^+$, 147 $[M\text{-}C_3H_7]^+$, 133 $[M\text{-}C_4H_9]^+$, 119 $[M\text{-}C_5H_{11}]^+$, 105 $[M\text{-}C_6H_{13}]^+$, 91 $[M\text{-}C_7H_7]^+$, 86, 84 $[M\text{-}C_4H_4O]^+$ (Found: C, 82.04; H, 9.69. $C_{13}H_{18}O$ requires C, 82.06; H, 9.53%).

Preparation of 2-[5-(*tert*-butyldiphenylsilyloxy)pentyl]-3-(2-propenyl)furan (6s).

This was carried out analogously to the preparation of 3-ethyl-2-phenylfuran (**6g**) on a 3.79 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-hexadiene (**7g**) and 6-(*tert*-butyldiphenylsilyloxy)hexanal to give, after chromatography (1% ether–petrol), 2-[5-(*tert*-butyldiphenylsilyloxy)pentyl]-3-(2-propenyl)furan (**6s**) (1.58 g, 97%) as a colourless liquid; R_f 0.26, 1% ether–petrol; ν_{max} (film) 3079, 2931, 2855, 1638, 1511, 1466, 1450, 1390, 1260, 1109, 994, 912, 891, 774, 736, 722, 704 and 679 cm^{-1}; δ_H (270 MHz) 7.73-7.64 (4H, m H-2 and H-4 of Ph), 7.45-7.35 (6H, m, H-3 to H-5 of Ph), 7.23 (1H, d, J 1.5 Hz, H-5), 6.19 (1H, d, J 1.5 Hz, H-4), 5.97-5.83 (1H, m, H-2"), 5.05-4.96 (2H, m, H-3"$_Z$ and H-3"$_E$), 3.66 (2H, t, J 6.5 Hz, H-5'), 3.17 (2H, dt, J 6.0 Hz and 1.5 Hz, H-1"), 2.53 (2H, t, J 7.5 Hz, H-1'), 1.69-1.53 and 1.47-1.29 (6H, m, H-2' to H-4') and 1.01 (9H, s, *t*-Bu); *m/z* (EI) 432 $[M]^+$, 417 $[M\text{-}Me]^+$, 403 $[M\text{-}Et]^+$, 389 $[M\text{-}Pr]^+$, 375 $[M\text{-}t\text{-}Bu]^+$, 297, 211, 177, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 39 $[C_3H_3]^+$, 29 $[HCO]^+$ (Found: C, 77.57; H, 8.47. $C_{28}H_{36}O_2Si$ requires C, 77.73; H, 8.39%).

Preparation of 2-hexyl-3-isopropylfuran (6l).

To a solution of 1-benzyloxy-4-methyl-3-(4-tolylsulfonyl)pentene (**7d**) (2.44 g, 7.09 mmol) in THF (71 ml) at -78°C under a nitrogen atmosphere was added *n*-BuLi (3.12 ml of a 2.5M solution in hexanes, 7.80 mmol, 1.1 eq) resulting in the formation of a blood-red solution. After stirring for 30 min heptanal (1.14 ml of a

6.2M solution in THF, 7.09 mmol) was slowly added causing the colour to slowly quench to a very pale yellow. After stirring for a further 10 min, the reaction mixture was quenched with AcOH (7.80 ml of a 1M solution in THF, 7.80 mmol, 1.1 eq), resulting in the solution to become colourless, followed by saturated aqueous $NaHCO_3$ (10 ml) and allowed to warm to rt. Water (20 ml) was added to the reaction mixture, the organic layer separated and the aqueous layer extracted with ether (3 x 60 ml). The combined organic layers were washed with water (60 ml), brine (60 ml), dried (K_2CO_3) and the solvents evaporated under reduced pressure to give a pale yellow liquid. This was redissolved in CH_2Cl_2 (23.7 ml) under a nitrogen atmosphere, silica gel (35.45 g) added followed by concentrated H_2SO_4 (1 drop) and the pale yellow two-phase system rapidly stirred. After 9 h the reaction mixture was filtered through a small pad of K_2CO_3 which was washed with portions of ether (120 ml). Evaporation of the solvents under reduced pressure followed by chromatography (petrol), yielded 2-hexyl-3-isopropylfuran (**6l**) (1.29 g, 93%) as a colourless liquid; R_f 0.39, petrol; ν_{max} (film) 2959, 2929, 2871, 2860, 1513, 1466, 1381, 1363, 1147, 1065, 896, 728 and 699 cm^{-1}; δ_H (270 MHz) 7.27 (1H, d, J 2.0 Hz, H-5), 6.29 (1H, d, J 2.0 Hz, H-4), 2.85 (1H, septet, J 7.0 Hz, H-1''), 2.63 (2H, t, J 7.5 Hz, H-1'), 1.72-1.61 (2H, m, H-2'), 1.50-1.26 (6H, m, H-3' to H-5'), 1.21 (6H, d, J 7.0 Hz, H-2'') and 0.95 (3H, t, J 6.5 Hz, H-6'); δ_C (68 MHz) 149.89 (C-2), 139.85 (C-5), 125.39 (C-3), 108.63 (C-4), 31.70 (C-1'), 29.01 (C-2'). 28.85 (C-3'), 26.12 (C-4'), 24.52 (C-5'), 23.93 (C-2''), 22.68 (C-1'') and 14.08 (C-6'); *m/z* (CI) 195 $[MH]^+$, 179 $[M\text{-}Me]^+$, 123 $[M\text{-}C_5H_{11}]^+$, 109 $[M\text{-}C_6H_{13}]^+$, 58, 44 (Found: C, 80.12; H, 11.32. $C_{13}H_{22}O$ requires C, 80.12; H, 11.41%).

Preparation of 2-hexyl-3-phenylfuran (6n).

This was prepared in an analogous manner to 2-hexyl-3-isopropylfuran (**6l**) on a 1.03 mmol scale starting from 1-benzyloxy-3-phenyl-3-(4-tolylsulfonyl)propene (**7f**) and heptanal to give, after chromatography (petrol), 2-hexyl-3-phenylfuran (**6n**) (0.207 g, 88%) as a colourless liquid; R_f 0.41, petrol; ν_{max} (film) 2927, 2856, 1612, 1518, 1465, 1146, 1050, 955, 893, 766, 732 and 698 cm^{-1}; δ_H (270 MHz) 7.48-7.39 (4H, m, H-2, H-3, H-5 and H-6 of Ph), 7.37 (1H, d, J 2.0 Hz, H-5), 7.36-7.02 (1H, m, H-7 of Ph), 6.52 (1H, d, J 2.0 Hz, H-4), 2.81 (2H, t, J 4.5 Hz, H-1'), 1.79-1.68 (2H, m, H-2'), 1.56-1.24 (6H, m, H-3' to H-5') and 0.91 (3H, t, J 6.5 Hz, H-6'); *m/z* (EI) 228 $[M]^+$, 157 $[M\text{-}C_5H_{11}]^+$, 129, 115, 91 $[M\text{-}C_7H_7]^+$, 77 $[M\text{-}C_6H_5]^+$, 57, 51, 43 (Found: C, 83.92; H, 8.97. $C_{16}H_{20}O$ requires C, 84.17; H, 8.83%).

Preparation of 2,3-diphenylfuran (6o).

This was prepared in an analogous manner to 2-hexyl-3-isopropylfuran (**6l**) on a 1.73 mmol scale starting from 1-benzyloxy-3-phenyl-3-(4-tolylsulfonyl)propene (**7f**) and benzaldehyde to give, after chromatography (petrol), 2,3-diphenylfuran (**6o**) (0.341 g, 90%) as a colourless liquid; R_f 0.32, petrol; ν_{max} (film) 3059, 2957, 1603, 1502, 1443, 1235, 1156, 1069, 942, 890, 704, 742 and 895 cm^{-1}; δ_H (270 MHz) 7.60-7.23 (10H, m, Ph), 7.52 (1H, d, J 2.0 Hz, H-5) and 6.59 (1H, d, J 2.0 Hz, H-4); δ_C (68 MHz) 148.62 (C-5), 141.62 (C-4), 134.44 (Ph), 131.28 (Ph), 128.77 (Ph), 128.71 (Ph), 128.46 (Ph), 127.61 (Ph), 127.21 (Ph), 126.36 (Ph), 122.37 (C-2) and 114.07 (C-2); *m/z* (EI) 220 $[M]^+$, 191, 164, 157, 115, 95, 77 $[C_6H_5]^+$, 63, 57, 51, 41, 39 $[C_3H_3]^+$, 29 $[HCO]^+$ (Found: C, 87.37; H, 5.61. $C_{16}H_{12}O$ requires C, 87.25; H, 5.49%).

Preparation of (*E*)-3-ethenyl-2-(2-phenylethenyl)furan (6m).

A solution of LDA (prepared from *i*-Pr_2NH (0.309 ml, 2.20 mmol, 1.1 eq) and *n*-BuLi (0.88 ml of a 2.5M solution in hexanes, 2.20 mmol, 1.1 eq) was added to a solution of (3*E*)-1-(benzyloxy)-3-(4-tolylsulfonyl)-1,3-pentadiene (**7e**) (0.838 g, 2.00 mmol) in THF (20.0 ml) at -78°C under a nitrogen atmosphere resulting in the formation of a red-orange solution. After stirring for 30 min a solution of (*E*)-3-phenyl-2-propenal (0.252 ml, 7.09 mmol) in THF (10 ml) was slowly added, causing the colour slowly to become a bright yellow. After stirring for a further 10 min, the reaction mixture was quenched with AcOH

(2.20 ml of a 1M solution in THF, 2.20 mmol, 1.1 eq), causing the solution to become yellow, followed by saturated aqueous $NaHCO_3$ (5 ml) and allowed to warm to rt. Water (10 ml) was added to the reaction mixture, the organic layer separated and the aqueous layer extracted with ether (3 x 20 ml). The combined organic layers were washed with water (20 ml), brine (20 ml), dried (K_2CO_3) and the solvents evaporated under reduced pressure to give a pale yellow liquid. This was redissolved in CH_2Cl_2 (20.0 ml) under a nitrogen atmosphere, silica gel (10.0 g) added and the pale yellow two-phase system rapidly stirred. After 21 h the reaction mixture was filtered through a small pad of K_2CO_3 which was washed with portions of ether (120 ml). Evaporation of the solvents under reduced pressure followed by chromatography (petrol), yielded (*E*)-3-ethenyl-2-(2-phenylethenyl)furan (**6m**) (0.314 g, 63%) as an oily, putrid-smelling, yellow solid; R_f 0.14, petrol; ν_{max} (film) 3058, 3039, 3025, 2956, 2922, 2870, 1627, 1448, 1432, 1063, 981, 953, 891, 742, 691, 585 cm^{-1}; δ_H (270 MHz) 7.52-7.47 (2H, m, H-3 and H-5 of Ph), 7.39-7.23 (3H, m, H-2 and H-6 of Ph and H-5), 7.06-6.98 (3H, m, H-4 of Ph, H-1' and H-2'), 6.78 (1H, ddd, J 17.5, 11.0 and 1.0 Hz, H-1''), 6.60 (1H, dd, J 2.0 and 1.0 Hz, H-4), 5.51 (1H, dd, J 17.5 and 1.5 Hz) and 5.24 (1H, dd, J 11.0 and 1.5 Hz); *m/z* (EI) 196 $[M]^+$, 167, 151, 128, 115, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 51, 39 $[C_3H_3]^+$ (Found: $[M]^+$, 196.0882. $C_{14}H_{12}O$ requires $[M]^+$, 196.0888).

Preparation of 5-hexyl-2-phenylfuran (6u).

To a solution of a mixture of (*E*)- and (*Z*)-3-methoxy-3-phenyl-1-(4-tolylsulfonyl)propene ((*E*)- and (*Z*)-**13c**) and (*Z*)-1-methoxy-1-phenyl-3-(4-tolylsulfonyl)propene (**8c**) (1.39 g, 4.59 mmol) in THF (45.9 ml) and *t*-BuOH (4.33 ml, 45.9mmol, 10 eq) was added *t*-BuOK (4.59 ml of a 1M solution in THF, 4.59 mmol) causing the solution to become dark red in colour. After stirring for 1 h the dark red solution was quenched with AcOH (4.59 ml of a 1M solution in THF, 4.59 mmol), followed by saturated aqueous $NaHCO_3$ (10 ml) and water (20 ml). The organic layer was separated, the aqueous layer extracted with ether (3 x 30 ml), the combined organic layers washed with saturated aqueous $NaHCO_3$ (30 ml), water (30 ml), brine (30 ml), dried (K_2CO_3) and concentrated under reduced pressure to give crude **8c** as a pale yellow oil. This oil was redissolved in THF (45.9 ml) under a nitrogen atmosphere, cooled to -78°C and *n*-BuLi (2.02 ml of a 2.5M solution in hexanes, 5.05 mmol, 1.1 eq) added dropwise resulting in the formation of a green-black solution. After stirring for 30 min, heptanal (0.74 ml of a 6.2M solution in THF, 4.59 mmol) was slowly added, causing the colour to slowly quench to very pale yellow. After stirring for a further 10 min, the reaction mixture was quenched with AcOH (5.05 ml of a 1M solution in THF, 5.05 mmol, 1.1 eq), causing the solution to become colourless, followed by saturated aqueous $NaHCO_3$ (20 ml) and allowed to warm to rt. Water (20 ml) was added to the reaction mixture, the organic layer separated and the aqueous layer extracted with ether (3 x 50 ml). The combined organic layers were washed with water (50 ml), brine (50 ml), dried (K_2CO_3) and the solvents evaporated under reduced pressure to give a pale yellow liquid. This was redissolved in CH_2Cl_2 (45.9 ml) under a nitrogen atmosphere, silica gel (22.95 g) added and the pale yellow two-phase system rapidly stirred. After 18 h the reaction mixture was filtered through a small pad of K_2CO_3 which was washed with portions of ether (180 ml). Evaporation of the solvents under reduced pressure followed by chromatography (petrol) yielded 5-hexyl-2-phenylfuran (**6u**) (0.949 g, 87%) as a colourless liquid; R_f 0.33, petrol; ν_{max} (film) 3081, 3061, 3039, 3028, 2954, 2858, 1610, 1595, 1579, 1548, 1021, 783, 758, 691 and 661 cm^{-1}; δ_H (270 MHz) 7.78-7.71 (2H, m, H-2 and H-6 of Ph), 7.50-7.41 (2H, m, H-3 and H-5 of Ph), 7.33-7.26 (1H, m, H-4 of Ph), 6.64 (1H, d, J 3.0 Hz, H-3), 6.15 (1H, d, J 3.0 Hz, H-4), 2.78 (2H, t, J 7.5 Hz, H-1'), 1.85-1.74 (2H, m, H-2'), 1.58-1.40 (6H, m, H-3' to H-5') and 1.01 (3H, t, J 6.5 Hz, H-6'); δ_C (68 MHz) 156.83 (C-5), 152.06 (C-2), 131.57 (C-6), 129.05 (C-3 and C-5 of Ph), 127.19 (C-4 of Ph), 123.56 (C-2 and C-6 of Ph), 107.06 (C-3), 105.52 (C-4), 31.61 (C-1'), 29.57 (C-2'), 28.95 (C-3'), 27.34 (C-4') 22.52 (C-5') and 14.31 (C-6'); *m/z* (EI) 228 $[M]^+$, 157 $[M\text{-}C_5H_{11}]^+$, 128, 115, 105, 86, 84, 77 $[C_6H_5]^+$, 49 (Found: $[M]^+$, 228.1514. $C_{16}H_{20}O$ requires $[M]^+$, 228.1514) (Found: C, 84.19; H, 8.86. $C_{16}H_{20}O$ requires C, 84.17; H, 8.86%).

Preparation of 2-hexyl-5-isobutylfuran (6t).

This was carried out analogously to the preparation of 5-hexyl-2-phenylfuran (**6u**) on a 2.82 mmol scale starting from (*E*)-3-methoxy-1-(4-tolylsulfonyl)nonene (**13b**) and 3-methylbutanal to give, after chromatography (petrol), 2-hexyl-5-isobutylfuran (**6t**) (0.551 g, 94%) as a colourless oil; R_f 0.33, petrol; ν_{max} (film) 3103, 2956, 2929, 2870, 2861, 1566, 1465, 1431, 1384, 1367, 1169, 1012, 965 and 778 cm^{-1}; δ_H (270 MHz) 5.97 (2H, s, H-3 and H-4), 2.69 (2H, t, J 7.5 Hz, H-1"), 2.57 (2H, d, J 7.0 Hz, H-1'), 2.06 (1H, nonet, J 6.5 Hz, H-2'), 1.73 (2H, m, H-2"), 1.52-1.40 (6H, m, H-3" to H-5") and 1.12-1.00 (9H, m, H-6" and H-3'); δ_C (68 MHz) 154.67 (C-2 or C-5), 153.61 (C-2 or C-5), 105.99 (C-3 and C-4), 104.86 (C-3 or C-4), 37.33 (C-1"), 31.68 (C-1'), 28.93 (C-2'), 28.18 (C-3'), 28.14 (C-4'), 28.03 (C-5'), 22.65 (C-6'), 22.38 (C-3") and 14.08 (C-2"); *m/z* (CI) 209 $[MH]^+$, 165 $[M-C_3H_7]^+$, 137 $[M-C_5H_{11}]^+$, 107, 95, 81 $[C_5H_5O]^+$, 58 (Found: C, 80.53; H, 11.33. $C_{14}H_{24}O$ requires C, 80.71; H, 11.61%).

Preparation of 4-benzyl-2-cyclohexylfuran (6w).

This was carried out analogously to the preparation of 3-heptylfuran (**6b**) on a 3.66 mmol scale starting from 1-cyclohexyl-1-methoxy-4-phenyl-3-(4-tolylsulfonyl)butene (**9b**) and paraformaldehyde to give, after chromatography (petrol) 2-cyclohexyl-4-benzylfuran (**6w**) (0.830 g, 94%) as a colourless liquid; R_f 0.38, petrol; ν_{max} (film) 3028, 2938, 2853, 1604, 1546, 1495, 1451, 1110, 941 and 703 cm^{-1}; δ_H (270 MHz) 7.40-7.25 (5H, m, Ph), 7.13 (1H, s, H-5), 5.90 (1H, s, H-3), 3.80 (2H, s, CH_2Ph), 2.69-2.59 (1H, m, H-1'), 2.11-1.02 (2H, m, H-2' or H-4'), 1.88-1.73 (2H, m, H-2' or H-4') and 1.55-1.26 (6H, m, H-3' to H-5'); δ_C (68 MHz) 161.56 (C-1, of Ph), 140.73 (C-2), 137.49 (C-5), 128.78 (C-2 and C-6 or C-3 and C-5 of Ph), 128.53 (C-2 and C-6 or C-3 and C-5 of Ph), 126.19 (C-3), 124.71 (C-4), 104.66 (C-4 of Ph), 37.49 (CH_2Ph), 31.68 (C-1'), 31.62 (C-2' and C-6'), 26.32 (C-4') and 26.12 (C-3'and C-5'); *m/z* (CI) 241 $[MH]^+$, 211 $[M-C_2H_5]^+$, 197 $[M-C_3H_7]^+$, 184 $[M-C_4H_8]^+$, 171 $[M-C_5H_9]^+$, 149 [M-Bn]$^+$, 128, 108 $[M-C_{10}H_{12}]^+$, 91 $[C_7H_7]^+$ (Found: $[MH]^+$, 241.1592. $C_{17}H_{20}O$ requires $[MH]^+$, 241.1592).

Preparation of 4-benzyl-2-cyclohexylfuran (6w): *in situ* alkylation method.

To a solution of 3-cyclohexyl-3-methoxy-1-(4-tolylsulfonyl)propene (**13a**) (0.257 g, 0.834 mmol) in THF (4.21 ml) and *t*-BuOH (0.787 ml, 8.34 mmol, 10 eq) was added *t*-BuOK (0.834 ml of a 1M solution in THF, 0.834 mmol) causing the solution to become golden-yellow. After stirring for 1 h the pale orange solution was quenched with AcOH (0.834 ml of a 1M solution in THF, 0.834 mmol), followed by saturated aqueous $NaHCO_3$ (4 ml) and water (4 ml). The organic layer was separated, the aqueous layer extracted with ether (3 x 10 ml), and the combined organic layers washed with saturated aqueous $NaHCO_3$ (10 ml), water (10 ml), brine (10 ml), dried (K_2CO_3) and concentrated under reduced pressure to give crude **8a** as a pale yellow oil. The oil was redissolved in THF (6.72 ml) and TMEDA (1.73 ml) under a nitrogen atmosphere, cooled to -78°C and *n*-BuLi (0.367 ml of a 2.5M solution in hexanes, 0.918 mmol, 1.1 eq) resulting in the formation of a bright orange solution. After 30 min a solution of $PhCH_2Br$ (99.2 µl, 0.834 mmol) in THF (2 ml plus 1 ml rinse) was added *via* cannula and the reaction allowed to warm to rt.. After 1 h the yellow solution was recooled to -78°C and *n*-BuLi (0.367 ml of a 2.5M solution in hexanes, 0.918 mmol, 1.1 eq) was added, followed 30 min later by a slurry of paraformaldehyde (0.175 g, 5.84 mmol, 7 eq) in THF (5 ml plus 2 ml rinse). The reaction was allowed to warm to rt, causing the colour slowly to become a very pale cloudy yellow. After stirring for a further 10 min, the reaction mixture was quenched with AcOH (1.00 ml of a 1M solution in THF, 1.00 mmol, 1.2 eq), resulting in the solution becoming colourless with a white sediment. The solution was diluted with ether (20 ml), dried (K_2CO_3), filtered through a plug Celite® and the solvents evaporated under reduced pressure to give a pale yellow liquid. This was redissolved in CH_2Cl_2 (8.43 ml) under a nitrogen atmosphere, silica gel (4.17 g) added and the pale yellow two-phase system rapidly stirred. After 18 h the reaction mixture was filtered through a small pad of K_2CO_3 which was washed with portions of ether (50 ml). Evaporation of

the solvents under reduced pressure followed by chromatography (petrol) gave 4-benzyl-2-cyclohexylfuran (**6w**) (0.174 g, 87%) identical in every respect to the material prepared using the stepwise method.

Preparation of 5-hexyl-2-isobutyl-3-octylfuran (6x).

This was carried out analogously to the preparation of 2-hexyl-3-isopropylfuran (**6l**) on a 2.61 mmol scale starting from 7-methoxy-9-(4-tolylsulfonyl)-7-heptadecene (**9c**) (1.00 g, 2.61 mmol) and 3-methylbutanal to give, after chromatography (petrol) 5-hexyl-2-isobutyl-3-octylfuran (**6x**) (0.736 g, 97%) as a colourless liquid; R_f 0.47, petrol; ν_{max} (film) 2955, 2927, 2856, 1464, 1380, 1367, 796 and 723 cm^{-1}; δ_H (270 MHz) 5.77 (1H, s, H-4), 2.50 (2H, t, J 7.0 Hz, H-1'''), 2.37 (2H, d, J 7.0 Hz, H-1'), 2.25 (2H, t, J 7.5 Hz, H-1''), 1.92 (1H, septet, J 7.0 Hz, H-2'), 1.65-1.52 (2H, m, H-2'''), 1.50-1.46 (2H, m, H-2'), 1.44-1.22 (16H, m, H-3'' to H-7'' and H-3''' to H-5''') and 1.01-0.84 (12H, m, H-3', H-8'' and H-6'''); δ_C (68 MHz) 158.09 (C-2 or C-5), 148.04 (C-2 or C-5), 119.88 (C-4), 104.08 (C-3), 37.27, 35.06, 31.96, 31.64, 30.66, 29.57, 29.53, 29.33, 28.56, 26.27, 26.03, 25.00, 22.73, 22.44 and 14.14; *m/z* (CI) 321 $[MH]^+$, 277 $[M\text{-}C_3H_7]^+$, 265 $[M\text{-}C_4H_7]^+$, 249 $[M\text{-}C_5H_{11}]^+$, 221 $[M\text{-}C_7H_{15}]^+$, 179 $[M\text{-}C_{10}H_{21}]^+$, 166 $[M\text{-}C_{11}H_{22}]^+$, 121 $[M\text{-}C_{14}H_{31}]^+$, 109 $[M\text{-}C_{15}H_{32}]^+$, 95 $[M\text{-}C_{16}H_{42}]^+$, 58 (Found: C, 82.20; H, 12.51. $C_{22}H_{40}O$ requires C, 82.43; H, 12.58%).

Preparation of 2-cyclohexyl-5-hexyl-3-(2-propenyl)furan (6y).

This was carried out analogously to the preparation of 2-hexyl-3-isopropylfuran (**6l**) on a 3.31 mmol scale starting from 6-methoxy-4-(4-tolylsulfonyl)-1,5-dodecadiene (**9d**) and cyclohexanecarboxaldehyde to yield, after chromatography (petrol), 2-cyclohexyl-5-hexyl-3-(2-propenyl)furan (**6y**) (0.861 g, 95%) as a colourless liquid; R_f 0.45, petrol; ν_{max} (film) 3079, 3004, 2929, 2855, 1639, 1574, 1449, 1234, 1102, 1052, 993, 911, 802 and 787 cm^{-1}; δ_H (270 MHz) 6.10-5.97 (1H, m, H-2'), 5.91 (1H, s, H-4), 5.23-5.15 (2H, m, H-3'), 3.24 (2H, d, J 6.0 Hz, H-1'), 2.79-2.67 (3H, m, H-1'' and H-1'''), 1.99-1.68 (10H, m, H-2'' to H-8'' and H-2'''), 1.50-1.46 (8H, m, H-4'' and H-3''' to H-5''') and 1.07-1.02 (3H, m, H-6'''); δ_C (68 MHz) 153.53, 153.46, 137.71, 115.08, 114.65, 106.64 (C-3'), 36.17, 31.97, 31.73, 29.44, 29.07, 28.17, 28.06, 26.68, 26.10. 22.70 and 14.12; *m/z* (CI) 275 $[MH]^+$, 231 $[M\text{-}C_3H_7]^+$, 217 $[M\text{-}C_4H_9]^+$, 203 $[M\text{-}C_5H_{11}]^+$, 191, 161 $[M\text{-}C_8H_{17}]^+$, 147 $[M\text{-}C_9H_{19}]^+$, 131 $[M\text{-}C_{10}H_{23}]^+$, 121 $[M\text{-}C_{11}H_{21}]^+$, 105 $[M\text{-}C_{12}H_{25}]^+$, 91 $[C_7H_7]^+$ (Found: C, 83.14; H, 10.71. $C_{19}H_{30}O$ requires C, 83.15; H, 11.02%).

Preparation of 2-cyclohexyl-5-isobutyl-4-octylfuran (6v).

This was carried out analogously to the preparation of 2-hexyl-3-isopropylfuran (**6l**) on a 2.76 mmol scale starting from 1-cyclohexyl-1-methoxy-3-(4-tolylsulfonyl)undecene (**9a**) and 3-methylbutanal to yield, after chromatography (petrol), 2-cyclohexyl-5-isobutyl-4-octylfuran (**6v**) (0.813 g, 93%) as a colourless liquid; R_f 0.43, petrol; ν_{max} (film) 2953, 2929, 2856, 1570, 1463, 1451, 1367, 1286, 1208, 1134, 1014, 967 and 891 cm^{-1}; δ_H (270 MHz) 5.84 (1H, s, H-3), 2.64-2.60 (1H, m, H-1'''), 2.47 (2H, d, J 7.0 Hz, H-1'), 2.36 (2H, t, J 7.0 Hz, H-1''), 2.11-1.97 (5H, m, H-2', 1 x H-2'' and 1 x H-6''' and H-6'''), 1.89-1.30 (18H, m, H-3''to H-7'', 1 x H-2'' and 1 x H-6'' and H-3''' to H-5'') and 1.06-0.96 (9H, m, H-3' and H-8''); δ_C (68 MHz) 158.09 (C-2 or C-5), 148.04 (C-2 or C-5), 119.88 (C-4), 104.08 (C-3), 37.27, 35.06, 31.96, 31.64, 30.66, 29.53, 29.33, 28.56, 26.27, 26.03, 25.00, 22.73, 22.44 and 14.14; *m/z* (CI) 319 $[MH]^+$, 275 $[M\text{-}i\text{-}Pr]^+$, 263 $[M\text{-}C_4H_7]^+$, 219 $[M\text{-}C_7H_{15}]^+$, 177 $[M\text{-}C_{10}H_{21}]^+$, 164 $[M\text{-}C_{11}H_{22}]^+$, 121 $[M\text{-}C_{14}H_{29}]^+$, 58 (Found: C, 82.71; H, 12.05. $C_{22}H_{38}O$ requires C, 82.95; H, 12.02%).

Preparation of 2-cyclohexyl-5-isobutyl-4-octylfuran (6v): *in situ* alkylation method.

This was carried out on a 1.53 mmol scale analogously to the preparation of 4-benzyl-2-cyclohexylfuran (**6w**) *via* the *in situ* alkylation method using method C for furan formation, starting from 3-cyclohexyl-3-

methoxy-1-(4-tolylsulfonyl)propene (**13a**), 1-iodooctane and 3-methylbutanal. After chromatography (petrol) there was obtained 2-cyclohexyl-5-isobutyl-4-octylfuran (**6v**) (0.405 g, 83%), identical in every respect to the material prepared using the stepwise method.

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(*Received in UK* 12 *September* 1996; *accepted* 10 *October* 1996)