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(Alkoxyallyl)sulfones as Enal β-Anion Equivalents. Synthesis of 5-Substituted 2(5*H*)-Furanones

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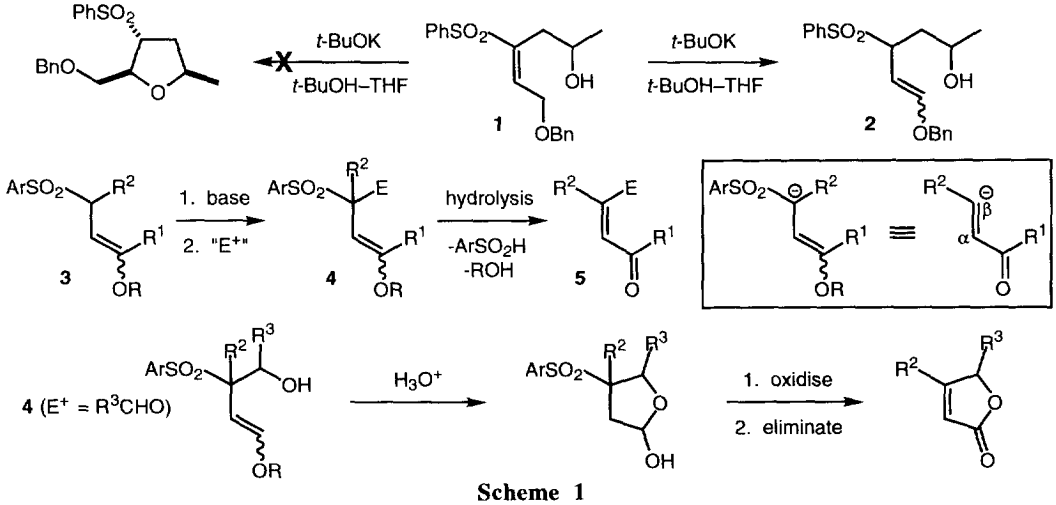
Abstact: 2(5*H*)-Furanones **14** may be prepared in a four-step sequence starting from (alkoxyallyl)sulfone **10** and aldehydes. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

As part of an ongoing programme seeking to exploit the diverse reactivity of the sulfone functional group[1] in the synthesis of oxygen and nitrogen heterocycles, we attempted the 5-*endo*-trig[2] cyclisation reaction of vinylic sulfone **1**. Instead of the expected tetrahydrofuran product,[3] the isomeric enol ether **2** was obtained in almost quantitative yield. It occurred to us that analogous bifunctional compounds **3** would exhibit varied chemistry because of the allylic positioning of the anion-stabilising and nucleofugal sulfonyl group with respect to the electron-rich enol ether.[4] We reasoned that deprotonation of **3** would yield a nucleophilic anion which would react with electrophiles to give derivatives **4**. Hydrolysis would take place with loss of an arylsulfinic acid and an alcohol to provide unsaturated carbonyl compounds **5**. Thus, the conjugate base of **3** would be equivalent synthetically to the enal/enone β-anion synthon;[5] the use of an aldehyde electrophile in such a sequence would yield intermediates possessing functionality suitable for heterocyclisation (Scheme 1). Herein we report in full[6] on the successful application of this strategy to the synthesis of 5-substituted 2(5*H*)-furanones.



Scheme 1

RESULTS AND DISCUSSION

Crucial to the viability of the proposed methodology was a ready source of the parent (alkoxyallyl)sulfone **10**. This was made by base-catalysed isomerisation of vinylic sulfone **9**, which was synthesised as a 2.5:1 *E*:*Z* mixture by Wadsworth–Emmons olefination of 2-benzyloxyethanal **8** with diethyl (4-tolylsulfonyl)methylphosphonate **6**. Aldehyde **8** could be prepared on multi-gram scales by ozonolysis of allyl benzyl ether **7**; the phosphonate coupling partner **6** was generated either *in situ* or in a separate step by phosphorylation of lithiated (tolylsulfonyl)methane.[7] The isomerisation reaction of **9** provided **10** as a ca. 3:1 mixture of *Z*- and *E*-geometric isomers. Compound **10** was only moderately stable; on prolonged storage (> 1 week) decomposition was noticeable, and subsequent chemistry was best carried out on material freshly prepared from the vinylic sulfone precursor.

Treatment of cold tetrahydrofuran solutions of **10** with *n*-butyllithium gave deeply red-coloured anion solutions which were almost completely decolourised on addition of aldehyde. Quenching of the resultant lithium alkoxides was effected by addition of a stoichiometric quantity of acetic acid at -78°C; substantial fragmentation back to aldehyde and sulfone was observed if the reaction mixtures were allowed to warm to temperatures greater than -30°C.[5(v)] No γ-alkylation of lithiated **10** was ever observed in these coupling reactions, in stark contrast with the behaviour of analogous sulf*ide*-containing species.[8] Interestingly, of the four possible diastereomers of **11**, only the *Z*-adducts were obtained, as 1:1 mixtures. We attribute this to intramolecular coordination of lithium in the anion of **10**, which is possible only by a *Z*-oriented benzyloxy group (Figure 1).[9] Conversion of **11** to the requisite lactol intermediates **12** as mixtures of all four diastereomers was accomplished in good to excellent yields by heating with sulfuric acid in aqueous acetonitrile (Table).

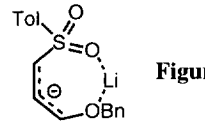
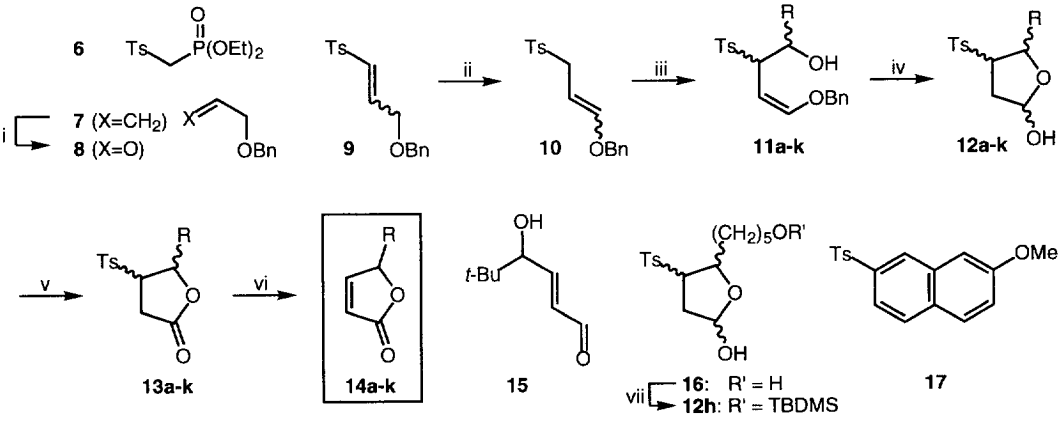


Figure 1



Reagents and conditions: (i) O_3, CH_2Cl_2–*i*-PrOH, -78°C, then 0.5 eq. $(H_2N)_2C{=}S$; (ii) cat. *t*-BuOK, *t*-BuOH–THF; (iii) *n*-BuLi, RCHO, THF, -78°C, then AcOH; (iv) conc. H_2SO_4, 15% aq. MeCN, 65°C; (v) PDC, 4Å mol sieves, CH_2Cl_2; (vi) 0.6 eq. DBU, CH_2Cl_2, -78°C, then AcOH; (vii) TBDMSCl, cat. DMAP, Et_3N, CH_2Cl_2, 0°C.

Scheme 2

Several features of the conversion of **11** into **12** are noteworthy. Firstly, the yield of the *t*-butyl-containing lactol **12d** was noticeably lower than for the other examples, primarily because of competing formation of the *E*-hydroxyenal **15**. We speculate that the bulky nature of the *tert*-butyl group is such that there is substantial relief of steric buttressing on $sp^3 \rightarrow sp^2$ rehybridisation in the elimination step. Secondly, substrate **11h** suffered cleavage of the acetate protecting group under the hydrolysis conditions to give the diol **16**. Attempts to reprotect this compound as the primary monoacetate were low-yielding. Instead, **16** was converted selectively to the silyloxy lactol **12h** by reaction with one equivalent of TBDMSCl under standard conditions. Thirdly, during the search for optimum conditions for the conversion of **11** into **12** it was observed that

exposure of **11k** to anhydrous acetic acid resulted in clean formation of the substituted naphthalene **17**, with no evidence of formation of the alternative regiosiomer. Presumably compound **17** arises from intramolecular trapping of the enol ether-derived oxonium ion by the electron-rich methoxyphenyl ring in a Friedel–Crafts-type alkylation process, followed by loss of benzyl alcohol and water (Scheme 3). Finally, it was observed that two of the four diastereomers of **12** consistently exhibited in the ^{1}H nmr spectrum a sharp doublet (J ca. 12 Hz) corresponding to the OH proton. We speculate that this arises in the 2,4-syn isomers because of intramolecular H-bonding between one of the sulfone oxygen atoms and the lactol hydroxylic hydrogen atom such that the H-2–OH dihedral angle is close to 180° (Figure 2).

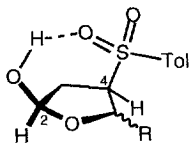
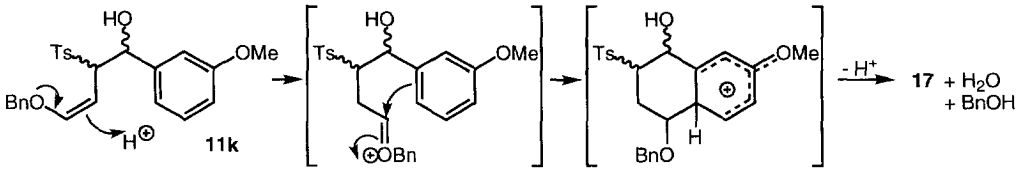


Figure 2



Scheme 3

With the lactols **12** in hand, it remained only to effect oxidation to the γ-lactones **13** and elimination of the elements of tolylsulfinic acid to complete the synthesis of the butenolides **14**. The first of these steps was easily effected by treatment with pyridinium dichromate in dichloromethane, giving **13** as mixtures of 3,4-syn and -anti diastereomers. Elimination of the elements of tolylsulfinic acid from **13** required more extensive optimisation. One of the more striking features of these reactions was the need for only 0.6 equivalents of DBU. Albeit small, this turnover of the base would imply that the driving-force for the elimination is sufficiently large to overcome the presumably very small equilibrium constant for the exchange of proton between $DBUH^+$ and Ts^-. The use of stoichiometric quantities of DBU caused substantial conversion of the initially-formed 2(5*H*)-furanones **14** into the apparently thermodynamically more stable 2(3*H*)-isomers. In the case of **13i** only the undesired 2(3*H*)-furanone could be obtained, and the reactions of substrates **13j** and **13k** resulted in significant decomposition with none of the desired unsaturated lactones being formed. The latter two observations are at variance with those of Ghosez,[5(v)] who has reported the synthesis of similar unsaturated lactones using conditions very similar to those tried here. Attempts to obtain furanones **14j** and **14k** using a wide variety of other bases (KHMDS, *t*-BuOK, KDA, NaH, *i*-Pr_2NEt, pyridine) failed, with highly-coloured reaction mixtures and crude products, and extensive decomposition being observed in all cases. The overall scheme for the synthesis of 2(5*H*)-furanones using the methodology presented above is summarised in Scheme 2 and in the Table.

entry	R	% yield of 11	% yield of 12	% yield of 13	% yield of 14
a	*n*-$C_{11}H_{23}$	99	85	83	91
b	*i*-C_3H_7	90	95	87	87
c	*c*-C_6H_{11}	85	95	86	95
d	*t*-C_4H_9	95	59	85	93
e	(*E*,*E*)-$Me(CH)_4(CH_2)_4$	98	89	82	91
f	$PhCH_2OCH_2$	98	99	81	93
g	$PhCH_2O(CH_2)_2$	96	87	47[a]	90
h	$R'O(CH_2)_5$	78[b]	64[c]	86[d]	94[d]
i	CH_3CH:CH	95	94	83	97[e]
j	C_6H_5	94	92	89	–
k	3-$CH_3OC_6H_4$	95	93	87	–

[a]2(5*H*)-Furanone **14g** also was formed in this reaction (35%). [b]R' = Ac. [c]R' = TBDMS. The yield cited is for the two steps from adduct **11h**. [d]R' = TBDMS. [e]The 2(3*H*)-furanone was formed exclusively.

Table. Synthesis of 2(5*H*)-furanones **14** from (alkoxyallyl)sulfone **10**.

CONCLUSIONS

The results described herein demonstrate that (alkoxyallyl)sulfone **10** is a simple, readily available intermediate which may be combined with aldehydes in the efficient synthesis of 2(5*H*)-furanones **14**. The chemistry is tolerated by a wide range of 5-substituents, with the most notable exceptions being aryl and vinyl groups. We have further explored the utility of **10** and more complex analogues in the high-yielding synthesis of polysubstituted furans.[10]

ACKNOWLEDGEMENTS

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EXPERIMENTAL

General procedures

^{1}H nmr spectra were recorded on either Bruker AM-500, Bruker DRX$_{300}$, Jeol GX-270Q or Bruker WM-250 spectometers, using residual isotopic solvent ($CHCl_3$, δ_H = 7.26 ppm) as an internal reference. Infra-red spectra were recorded on a Perkin-Elmer 881 or Mattson 5000 FTIR spectrometer. Mass spectra were recorded using VG-7070B or Jeol SX-102 instruments. Elemental combustion analysis were performed in the Imperial College Chemistry Department microanalytical laboratory. Melting points were measured on a Reichert hot stage apparatus and are uncorrected. Chromatography refers to flash column chromatography on Merck Kieselgel 60 (230-400 mesh). Tlc refers to thin-layer chromatography performed on pre-coated Merck Kieselgel 60 F_{254} glass-backed plates and visualized with ultraviolet light (254 nm), iodine, acidic ammonium molybdate (IV), acidic ethanolic vanillin, aqueous potassium manganate(VII), 4,4'-bis(dimethylamino)benzhydrol in acetone and acidic methanolic 2,4-dinitrophenylhydrazine, as appropriate. Reactions were carried out at room temperature (rt) unless otherwise stated. Ether and THF were distilled from sodium-benzophenone ketyl; CH_2Cl_2 from phosphorus pentoxide; toluene and TMEDA from sodium wire and DMSO from calcium hydride. Where appropriate, all reagents were purified before use according to standard procedures.[11]

Preparation of 2-benzyloxyethanal (8).

Ozone (O_2 flow rate 3 l h^{-1}) was passed through a solution of 3-benzyloxypropene (**7**) (42.46 g, 0.287 mol) in a mixture of dry CH_2Cl_2 (400 ml) and propan-2-ol (100 ml) at -78°C until a faint pale blue colour persisted. Tlc after 2 h showed complete formation of the hydroperoxide intermediate and the pale yellow solution was purged with oxygen (10 min) and then nitrogen (10 min). Thiourea (10.91 g, 0.143 mol) was added and the resulting suspension was allowed slowly to warm to rt. After 15 h the colourless suspension was diluted with ether (200 ml) and filtered through a short silica gel plug. Concentration under reduced pressure followed by chromatography (50% ether–petrol), gave 2-benzyloxyethanal (**8**) (30.78 g, 90%) as a colourless, viscous liquid with a persistent odour; Rf 0.25, 50% ether–petrol; ν_{max} (film) 2869, 1735, 1604, 1497, 1455, 1374, 1114, 912, 742 and 700 cm^{-1}; δ_H (250 MHz) 9.65 (1H, s, CHO), 7.43-7.21 (5H, m, Ph), 4.6 (2H, s, H-2) and 4.05 (2H, s, CH_2Ph); *m/z* (EI) 150 $[M]^+$, 149 $[M-H]^+$, 121 $[M-CHO]^+$, 107 $[BnO]^+$, 91 $[C_7H_7]^+$, 65 $[C_5H_5]^+$; in agreement with previous data.[12]

Preparation of 3-benzyloxy-1-(4-tolylsulfonyl)propene (9).

n-BuLi (44.4 ml of a 2.5M solution in hexanes, 111 mmol, 1.1 eq) was added to a solution of diethyl (4-tolylsulfonyl)methylphosphonate (**6**) (30.9 g, 101 mmol) in THF (336 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 a solution of 2-benzyloxyethanal (**8**) (14.38 g, 95.8 mmol, 0.95 eq) in THF (40 ml plus 15 ml rinse) was added *via* cannula and the pale yellow reaction mixture allowed to warm to rt. After 1 h the solution was quenched with AcOH (15.1 ml of a 1M solution in THF, 15.1 mmol, 0.15 eq), causing the colour to fade. Water (250 ml) was added to the reaction mixture, the organic phase separated and the aqueous layer extracted with ether (3 x 300 ml). The organic layers were washed with water (3 x 300 ml), brine (300 ml), dried ($MgSO_4$) and the solvents evaporated under reduced pressure. The resulting yellow oil was purified by chromatography (40% ether–petrol), to give 3-benzyloxy-1-(4-tolylsulfonyl)propene (**9**) (27.58 g, 90%) as a 2.5:1 mixture of the *E*- and *Z*-isomers. Small amounts of each isomer were separated; *Z*-isomer; R_f 0.37, 50% ether–petrol; ν_{max} (film) 3035, 2924, 2858, 1598, 1453, 1365, 1310, 1141, 811 and 699 cm^{-1}; δ_H (270 MHz) 7.74 (2H, d, J 9.0 Hz, H-2 and H-6 of Ts), 7.46-7.24 (7H, m, H-3 and H-5 of Ts, Ph), 6.41 (1H, dt, J 11.5 and 4.5 Hz, H-2), 6.26 (1H, dt, J 11.5 and 2.5 Hz, H-1), 4.73 (2H, dd, J 4.5 and 2.5 Hz, H-3), 4.53 (2H, s, CH_2Ph) and 2.43 (3H, s, Me of Ts); *m/z* (EI) 303 $[M+H]^+$, 213, 211 $[M-CH_2Ph]^+$, 196, 139, 107, 91, 77 (Found: $[M-CH_2Ph]^+$, 211.0423. $C_{17}H_{18}O_3S$ requires $[M-CH_2Ph]^+$, 211.0423; *E*-isomer; R_f 0.28, 50% ether–petrol; ν_{max} (film) 3063, 2924, 2858, 1641, 1598, 1453, 1365, 1310, 1201, 1141 and 811 cm^{-1}; δ_H (270 MHz) 7.77 (2H, d, J 9.5 Hz, H-2 and H-6 of Ts), 7.46-7.24 (7H, m, H-3 and H-5 of Ts, Ph), 6.97 (1H, dt, J 14.0 and 4.5 Hz, H-2), 6.66 (1H, dt, J 14.0 and 2.5 Hz, H-1), 4.53 (2H, s, CH_2Ph), 4.20 (2H, dd, J 4.5 and 2.5 Hz, H-3) and 2.44 (3H, s, Me of Ts); *m/z* (EI) 303 $[M+H]^+$, 213, 211 $[M-CH_2Ph]^+$, 196, 139, 107, 91, 77 (Found: $[M-CH_2Ph]^+$, 211.0423. $C_{17}H_{18}O_3S$ requires $[M-CH_2Ph]^+$, 211.0423).

Preparation of 3-benzyloxy-1-(4-tolylsulfonyl)propene (9): formation of Wadsworth–Emmons reagent *in situ*.

A solution of (4-tolylsulfonyl)methane (8.67 g, 50.9 mmol) in THF (20 ml plus 5 ml rinse) was added *via* cannula to a solution of LDA (previously prepared from *i*-Pr_2NH (15.7 ml, 112 mmol, 2.2 eq) and *n*-BuLi (44.8 ml of a 2.5M solution in hexanes, 112 mmol, 2.2 eq)) in THF (81 ml) and TMEDA (20 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 (7.36 ml, 50.9 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-benzyloxyethanal (7.26 g, 48.4 mmol, 0.95 eq) in THF (20 ml plus 10 ml rinse) was added *via* cannula and the pale yellow reaction mixture allowed to warm to rt. After 1 h the solution was quenched with AcOH (10.2 ml of a 1M solution in THF, 10.2 mmol, 0.2 eq) causing the colour to fade. Water (100 ml) was added to the reaction mixture, the organic phase was separated and the aqueous layer extracted with ether (3 x 200 ml). The organic layers were washed with water (3 x 200 ml), brine (200 ml), dried ($MgSO_4$) and the solvents evaporated under reduced pressure. The resulting yellow oil was purified by chromatography (40% ether–petrol), to give 3-benzyloxy-1-(4-tolylsulfonyl)propene (**9**) (13.79 g, 90%) identical in every way to the material prepared as described above.

Preparation of 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene (10).

To a solution of 3-benzyloxy-1-(4-tolylsulfonyl)propene (**9**) (5.82 g, 19.2 mmol) in THF (192 ml) and *t*-BuOH (36.3 ml, 385 mmol, 20 eq) at room temperature was added *t*-BuOK (1.92 ml of a 1M solution in THF, 1.92 mmol, 0.1 eq) causing the solution to turn pale orange and gradually darken to a deep red. After stirring for 5 min the solution was quenched with AcOH (1.92 ml of a 1M solution in THF, 1.92 mmol, 0.1 eq), followed by saturated aqueous $NaHCO_3$ (50 ml) and water (50 ml). The organic layer was separated, the

aqueous layer extracted with ether (3 x 200 ml), the combined organic layers washed with saturated aqueous $NaHCO_3$ (150 ml), water (150 ml), brine (150 ml), dried (K_2CO_3) and concentrated under reduced pressure to give a pale yellow solid. This was purified by chromatography (30% ether–petrol), to give a 3:1 *Z:E* mixture of 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene (**10**) (5.79 g, 100%) as a colourless, crystalline solid; R_f 0.25, 50% ether–petrol; ν_{max} (CH_2Cl_2) 2926, 1658, 1597, 1461, 1317, 1176, 1086, 1041, 896, 736 and 699 cm^{-1}; δ_H (270 MHz) 7.78 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *Z*-isomer), 7.69 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, *E*-isomer), 7.38-7.06 (14H, m, H-3 and H-5 of Ts and Ph, both isomers), 6.35 (1H, br d, J 12.5 Hz, H-1, *E*-isomer), 6.22 (1H, dt, J 6.0 and 1.0 Hz, H-1. *Z*-isomer), 4.79 (1H, dt, J 12.5 and 8.0 Hz, H-2, *E*-isomer), 4.75 (2H, s, CH_2Ph, *E*-isomer), 4.60 (2H, s, J Hz, CH_2Ph, *Z*-isomer), 4.51 (1H, td, J 8.0 and 6.0 Hz, H-2, *Z*-isomer), 3.95 (2H, dd, J 8.0 and 1.0 Hz, H-3, *Z*-isomer), 3.64 (2H, dd, J 8.0 and 1.0 Hz, H-3, *E*-isomer), 2.44 (3H, s, Me of Ts, *E*-isomer) and 2.43 (3H, s, Me of Ts, *Z*-isomer); *m/z* (EI) 302 $[M]^+$, 258, 246, 214, 156 $[TsH]^+$, 147 $[M\text{-}Ts]^+$, 124, 108 $[BnOH]^+$, 91 $[C_7H_7]^+$ (Found (CI): $[M+NH_4]^+$, 320.1320. $C_{17}H_{18}O_3S$ requires $[M+NH_4]^+$, 320.1320).

Preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol (11a).

To a stirred solution of 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene (0.512 g, 1.71 mmol) in THF (17.1 ml) at -78°C under a nitrogen atmosphere was added *n*-BuLi (0.752 ml of a 2.5M solution in hexanes, 1.88 mmol, 1.1 eq) resulting in the formation of a deep red solution. After stirring for 30 min a solution of dodecanal (0.377 ml, 1.71 mmol) in THF (5 ml plus 2 ml rinse) was slowly added *via* cannula causing the colour to become pale yellow. After stirring for 10 min the reaction mixture was quenched by the addition of AcOH (1.88 ml of a 1M solution in THF, 1.88 mmol, 1.1 eq) causing the solution to become colourless, and was allowed to warm to rt. Water (10 ml) was added, the organic layer was separated and the aqueous layer extracted with ether (3 x 30 ml). The combined organic layers were washed with water (30 ml), brine (30 ml), dried (K_2CO_3) and the solvents evaporated under reduced pressure to give a pale yellow liquid. This was purified by chromatography (5%→50% ether–petrol), to yield a >30:>20:<1:<1 mixture of *Z:Z:E:E* diastereomers of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol (**11a**) (0.819 g, 99%) as a colourless, oily solid; R_f 0.35-0.20, 50% ether–petrol; ν_{max} (film) 3525, 3034, 2927, 2855, 1661, 1599, 1498, 1460, 1403, 1369, 1295, 1214, 1142, 1081, 816 and 738 cm^{-1}; δ_H (270 MHz) 7.80-7.72 (4H, m, H-2 and H-6 of Ts, both isomers), 7.40-7,24 and 7.09-6.99 (14H, m, H-3 and H-5 of Ts and Ph, all isomers), 6.25 (1H, d, J 6.0 Hz, H-1, minor diast), 6.13 (1H, d, J 6.0 Hz, H-1, minor diast), 4.73 (1H, dd, J 10.5 and 6.0 Hz, H-2, major diast), 4.57 (1H, d, J 12.5 Hz, CH_2Ph, minor diast), 4.54 (1H, d, J 12.5 Hz, CH_2Ph, major diast), 4.52-4.46 (2H, m, CH_2Ph, minor diast and H-4, minor diast), 4.42 (1H, d, J 12.5 Hz, CH_2Ph, major diast), 4.33 (1H, d, J 10.5 and 8.5 Hz, H-3, major diast), 4.29-4.22 (2H, m, H-4, major diast and H-2, minor diast), 4.19 (1H, br d, J 11.0 Hz, H-3, minor diast), 2.43 (3H, s, Me of Ts, minor diast), 2.42 (3H, s, Me of Ts, major diast), 1.60-1.16 (40H, m, H-5 to H-14, both isomers) and 0.91-0.85 (6H, m, H-15, both isomers); *m/z* (EI) 330 $[M+H\text{-}Ts]^+$, 288, 246, 239, 222, 124, 108 $[BnOH]^+$, 91 $[C_7H_9]^+$, 51 (Found: $[M+H\text{-}Ts]^+$, 330.2560. $C_{29}H_{42}O_4S$ requires $[M+H\text{-}Ts]^+$, 330.2559).

Preparation of 6-benzyloxy-2-methyl-4-(4-tolylsulfonyl)-5-hexen-3-ol (11b).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 1.74 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and isobutyraldehyde to give, after chromatography (40% ether–petrol), a >40:>20:<1:<1 mixture of *Z:Z:E:E* diastereomers of 6-benzyloxy-2-methyl-4-(4-tolylsulfonyl)-5-hexen-3-ol (**11b**) (0.586 g, 90%) as a colourless, oily solid; R_f 0.31, 0.24 and 0.19, 50% ether–petrol; ν_{max} (film) 3515, 3060, 3030, 2959, 2927, 2871, 1657, 1595, 1452, 1365, 1284, 1215, 1126, 1063, 814 and 740 cm^{-1}; δ_H (270 MHz) 7.76 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, major diast), 7.75 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, minor diast), 7.40-7.24 and 7.10-6.98 (14H, m, H-3 and H-5 of Ts and Ph, both diast), 6.22 (1H, d, J 6.0 Hz, H-6, minor diast), 6.13 (1H, d, J 6.0 Hz, H-6, major diast), 4.75

(1H, dd, J 10.5 and 6.0 Hz, H-5, minor diast), 4.52 (1H, d, J 12.0 Hz, CH_2Ph, major diast), 4.44 (1H, d, J 12.5 Hz, CH_2Ph, minor diast), 4.36 (1H, d, J 10.5 Hz, H-4, minor diast), 4.35 (1H, dd, J 10.5 and 9.5 Hz, H-4, major diast), 4.33 (1H, d, J 12.0 Hz, CH_2Ph, major diast), 4.20 (1H, dd, J 10.5 and 6.0 Hz, H-5, major diast), 4.15 (1H, dd, J 9.5 and 2.5 Hz, H-3, major diast), 4.10 (1H, d, J 9.0 Hz, H-3, minor diast), 2.43 (3H, s, Me of Ts, minor diast), 2.42 (3H, s, Me of Ts, major diast), 1.78 (1H, septuple d, J 7.0 and 2.5 Hz, H-2, major diast), 1.65 (1H, m, H-2, minor diast), 1.03 (3H, d, J 7.0 Hz, H-1, major diast), 1.01 (3H, d, J 6.5 Hz, H-1, minor diast), 0.80 (3H, d, J 7.0 Hz, H-1, major diast), 0.78 (3H, d, J 6.5 Hz, H-1, minor diast); *m/z* (CI) 392 $[M+NH_4]^+$, 375 $[M+H]^+$, 374 $[M+NH_4-H_2O]^+$, 331 $[M-i\text{-}Pr]^+$, 278, 265, 239, 157, 111, 108 $[BnOH]^+$, 95, 91 $[C_7H_7]^+$ (Found: $[M+NH_4]^+$, 392.1896. $C_{21}H_{26}O_4S$ requires $[M+NH_4]^+$, 392.1896).

Preparation of 4-benzyloxy-1-cyclohexyl-2-(4-tolylsulfonyl)-3-buten-1-ol (11c).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 2.39 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and cyclohexanecarboxaldehyde to give, after chromatography (30% ether–petrol), a >60:>20:>1:>1 mixture of *Z:Z:E:E* diastereomers of 4-benzyloxy-1-cyclohexyl-2-(4-tolylsulfonyl)-3-buten-1-ol (**11c**) (0.848 g, 85%) as a pale yellow oil; R_f 0.33, 0.26 and 0.22, 50% ether–petrol; ν_{max} (film) 3510, 3058, 3028, 2924, 2850, 1655, 1595, 1493, 1448, 1399, 1300, 1185, 1144, 1083, 913, 890 and 737 cm^{-1}; δ_H (270 MHz) 7.80-7.68 (4H, m, H-2 and H-6 of Ts, both diast), 7.43-7.20 (14H, m, H-3 and H-5 of Ts and Ph, both diast), 6.22 (1H, d, J 5.5 Hz, H-4, minor diast), 6.10 (1H, d, J 5.5 Hz, H-4, major diast), 4.71 (1H, dd, J 16.0 and 7.0 Hz, H-3, major diast), 4.57-4.30 (6H, m, $PhCH_2$, both diast and H-3 and H-2, minor diast), 4.17 (1H, dd, J 11.0 and 5.5 Hz, H-1, major diast), 4.08 (1H, d, J 9.0 Hz, H-2, major diast), 3.96 (1H, d, J 9.0 Hz, H-1, minor diast), 2.40 (3H, s, Me of Ts, major diast), 2.39 (3H, s, Me of Ts, minor diast) and 1.85-0.93 (22H, m, $c\text{-}C_6H_{11}$, both diast); *m/z* (CI) 432 $[M+NH_4]^+$, 414 $[M+H]^+$, 396 $[M-H_2O]^+$, 305, 241, 223, 157, 151, 139, 133, 124, 107 $[BnO]^+$, 91 $[C_7H_7]^+$ (Found: $[M+NH_4]^+$, 432.2210. $C_{24}H_{30}O_4S$ requires $[M+NH_4]^+$, 432.2209).

Preparation of 6-benzyloxy-2,2-dimethyl-4-(4-tolylsulfonyl)-5-hexen-3-ol (11d).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 3.89 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and pivalaldehyde to give, after chromatography (50% ether–petrol), a >20:>20:<1:<1 mixture of *Z:Z:E:E* diastereomers of 6-benzyloxy-2,2-dimethyl-4-(4-tolylsulfonyl)-5-hexen-3-ol (**11d**) (1.44 g, 95%) as a colourless oil; R_f 0.33 and 0.23, 50% ether–petrol; ν_{max} (film) 3510, 2957, 1657, 1597, 1454, 1366, 1287, 1140, 1068, 815, 736 and 700 cm^{-1}; δ_H (270 MHz) 7.80-7.72 (4H, m, H-2 and H-6 of Ts, both diast), 7.42-7.21 and 7.10-7.02 (14H, m, H-3 and H-5 of Ts and Ph, both diast), 6.10 (1H, d, J 6.0 Hz, H-6), 6.02 (1H, d, J 5.5 Hz, H-6), 4.83 (1H, dd, J 10.5 and 6.5 Hz, H-5), 4.72 (1H, dd, J 12.5 and 5.5 Hz, H-5), 4.56-4.20 (7H, m, CH_2Ph, both diast, 2 x H-4 and H-3), 4.05 (1H, dd, J 10.5 and 6.5 Hz, H-3), 2.45 (3H, s, Me of Ts), 2.43 (3H, s, Me of Ts), 0.95 (9H, s, H-1) and 0.92 (9H, s, H-1); *m/z* (EI) 331 $[M-t\text{-}Bu]^+$, 297 $[M-Bn]^+$, 278, 259, 246, 231, 214, 139, 124, 109 $[BnOH]^+$, 91 $[C_7H_7]^+$, 79 (Found: $[M-t\text{-}Bu]^+$, 331.1004. $C_{22}H_{28}O_4S$ requires $[M-t\text{-}Bu]^+$, 331.1004).

Preparation of (9*E*,11*E*)-1-benzyloxy-3-(4-tolylsulfonyl)-1,9,11-tridecatrien-4-ol (11e).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 4.91 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and (*E,E*)-6,8-decadienal[13] to give, after chromatography (30%→50% ether–petrol), a >40:>20:<1:<1 mixture of *Z:Z:E:E* diastereomers of (9*E*,11*E*)-1-benzyloxy-3-(4-tolylsulfonyl)-1,9,11-tridecatrien-4-ol (**11e**) (2.20 g, 98%) as a colourless oil; R_f 0.44, 0.33, 0.28 and 0.18, 50% ether–petrol; ν_{max} (film) 3514, 3015, 2926, 1655, 1599, 1447, 1369, 1287, 1136, 1073, 990, 812 and 742 cm^{-1}; δ_H (270 MHz) 7.81-7.61 (4H, m, H-2 and H-6 of Ts, both diast), 7.38-7.21 (14H, m, H-3 and H-5 of Ts and Ph, both diast), 6.25 (1H, d, J 6.1 Hz, H-1, minor diast), 6.13 (1H, d,

J 6.0 Hz, H-1, major diast), 6.07-5.83 (2H, m, H-10 and H-11, both diast) 5.59-5.47 (2H, m, H-9 and H-12, both diast), 4.73 (1H, dd, J 10.0 and 6.0 Hz, H-2, major diast), 4.60-4.16 (9H, m, $PhCH_2$, H-3 and H-4, both diast and H-2, minor diast), 4.02 (1H, br s, OH, major diast), 3.12 (1H, br s, OH, minor diast), 2.43 (3H, s, Me of Ts, minor diast) 2.42 (3H, s, Me of Ts, major diast), 2.06-2.00 (4H, m, H-5, both diast), 1.79 (3H, d, J 6.5 Hz, H-13, major diast), 1.72 (3H, d, J 6.5 Hz, H-13, minor diast), 1.59-1.21 (12H, m, H-6 to H-8, both diast); *m/z* (CI) 364 $[M+NH_4-H_2O]^+$, 363 $[M-Bn]^+$, 346 $[M-BnOH]^+$, 299 $[M-Ts]^+$, 281 $[M-Ts-H_2O]^+$, 256, 246, 190 $[M-Ts-OBn]^+$, 124, 108, 94, 91 $[C_7H_7]^+$ (Found: $[M+NH_4-H_2O]^+$, 364.1946. $C_{27}H_{34}O_4S$ requires $[M+NH_4-H_2O]^+$, 364.1946).

Preparation of 1,5-bis(benzyloxy)-3-(4-tolylsulfonyl)-4-penten-2-ol (11f).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 1.19 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and 2-benzyloxyethanal to give, after chromatography (40% ether–petrol), a 5:5:1:1 mixture of *Z:Z:E:E* diastereomers of 1,5-bis(benzyloxy)-3-(4-tolylsulfonyl)-4-penten-2-ol (**11f**) (0.528 g, 98%) as a colourless oil; R_f 0.40 and 0.35, 80% ether–petrol; ν_{max} (film) 3500, 3031, 2923, 1660, 1598, 1497, 1454, 1366, 1302, 1208, 1147, 816, 740, 699 and 667 cm^{-1}; δ_H (270 MHz) 7.76 (4H, d, J 8.5 Hz, H-2 and H-6 of Ts, both *Z*-diast), 7.68 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *E*-diast), 7.64 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts, *E*-diast), 7.48-7.20 and 7.09-6.98 (48H, m, H-3 and H-5 of Ts and Ph, all diast), 6.28 (1H, d, J 6.0 Hz, H-5, *Z*-diast), 6.20 (1H, d, J 12.5 Hz, H-5, *E*-diast), 6.17 (1H, d, J 12.5 Hz, H-5, *E*-diast) 6.14 (1H, d, J 6.0 Hz, H-5, *Z*-diast), 4.95 (H, dd, J 12.5 and 10.5 Hz, H-4, *E*-diast), 4.82-4.36 (26H, m, CH_2Ph and H-2, all diast, 3 x H-4, 2 x *Z*-diast and 1 x *E*-diast, 2 x OH, *Z*-diast and *E*-diast and H-3, *Z*-diast), 4.29 (1H, dd, J 10.5 and 6.0 Hz, H-3, *Z*-diast, 4.11 (1H, d, J 0.5 Hz, OH, *E*-diast), 3.95 (1H, br s, OH, *Z*-diast), 3.72 (1H, dd, J 10.5 and 8.5 Hz, H-3, *E*-diast), 3.66 (1H, dd, J 10.0 and 3.0 Hz, H-1, *Z*-diast), 3.63-3.61 (3H, m, H-1, 2 x *Z*-diast and *E*-diast), 3.58 (1H, dd, J 10.5 and 1.5 Hz, H-1, *E*-diast), 3.51 (1H, dd, J 10.0 and 5.0 Hz, H-1, *Z*-diast), 3.50-3.44 (3H, m, 2 x H-1, *E*-diast and *Z*-diast and H-3, *E*-diast), 2.44 (3H, s, Me of Ts, *E*-diast), 2.43 (3H, s, Me of Ts, *E*-diast), 2.41 (3H, s, Me of Ts, *Z*-diast), 2.40 (3H, s, Me of Ts, *Z*-diast); *m/z* (EI) 345 $[M-OBn]^+$, 189, 181, 163, 150, 136, 124, 107 $[BnO]^+$, 91 $[C_7H_7]^+$ (Found: $[M-OBn]^+$, 345.1160. $C_{26}H_{28}O_5S$ requires $[M-OBn]^+$, 345.1161).

Preparation of 1,6-bis(benzyloxy)-4-(4-tolylsulfonyl)-5-hexen-3-ol (11g).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 4.93 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and 3-benzyloxypropanal to give, after chromatography (40%→80% ether–petrol), a >20:>20:<1:<1 mixture of *Z:Z:E:E* diastereomers of 1,6-bis(benzyloxy)-4-(4-tolylsulfonyl)-5-hexen-3-ol (**11g**) (2.22 g, 96%) as a colourless oil; R_f 0.18 and 0.11, 50% ether–petrol; ν_{max} (film) 3503,3030, 2865, 1956, 1658, 1598, 1494, 1453, 1366, 1287, 1144, 816, 740, 701 and 667 cm^{-1}; δ_H (500 MHz) 7.79-7.72 (4H, m, H-2 and H-6 of Ts), 7.38-7.00 (24H, m, H-3 and H-5 of Ts and Ph, both diast), 6.27 (1H, d, J 6.0 Hz, H-6), 6.16 (1H, d, J 6.0 Hz, H-6), 4.76-4.34 (10H, m, CH_2Ph, H-3, H-5 and OH, both diast), 4.29 (1H, dd, J 10.5 and 6.0 Hz, H-4), 4.23 (1H, dd, J 10.5 and 1.0 Hz, H-4), 3.83-3.53 (4H, m, H-1, both diast), 2.44 (3H, s, Me of Ts), 2.42 (3H, s, Me of Ts) and 2.07-1.63 (4H, m, H-2, both diast); *m/z* (EI) 358 $[M-BnOH]^+$, 278, 246, 214, 202, 172, 139, 124, 100, 91 $[C_7H_7]^+$, 81 (Found: $[M-BnOH]^+$, 358.1239. $C_{27}H_{30}O_5S$ requires $[M-BnOH]^+$, 358.1239).

Preparation of 1-acetoxy-9-benzyloxy-7-(4-tolylsulfonyl)-8-nonen-6-ol (11h).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 2.54 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and 6-acetoxyhexanal to give, after chromatography (30%→70% ether–petrol), a >40:>20:<1:<1 mixture of *Z:Z:E:E* diastereomers of 1-acetoxy-9-benzyloxy-7-(4-tolylsulfonyl)-8-nonen-6-ol (**11h**) (0.913 g, 78%) as a colourless oil; R_f 0.31, 0.27

and 0.22, 70% ether–petrol; ν_{max} (film) 3505, 2939, 2864, 1735, 1660, 1597, 1494, 1457, 1367, 1244, 1142, 1080, 817, 741, 703 and 664 cm^{-1}; δ_H (270 MHz) 7.72 (4H, m, H-2 and H-6 of Ts, both diast), 7.38-7.16 and 7.06-6.93 (14H, m, H-3 and H-5 of Ts, Ph), 6.23 (1H, d, J 6.5 Hz, H-9, minor diast), 6.12 (1H, d, J 6.5 Hz, H-9, major diast), 4.69 (1H, dd, J 11.0 and 6.5 Hz, H-8, major diast), 4.60-4.51 (3H, m, H-6, major diast and CH_2Ph, minor diast), 4.47 (1H, d, J 14.5 Hz, CH_2Ph, major diast), 4.38 (1H, d, J 14.5 Hz, CH_2Ph, major diast), 4.34-4.10 (4H, m, H-7, both diast, H-6 and H-8, minor diast), 4.00 (4H, m, H-1, both diast), 3.44 (4H, dd, J 13.0 and 6.5 Hz, H-5, both diast), 2.40 (3H, s, Me of Ts) 2.39 (3H, s, Me of Ts), 2.03 (6H, s, Me of ester, both diast), 1.67-1.46 (4H, m, H-8, both diast), 1.43-1.24 (4H, m, H-7, both diast) and 1.22-1.10 (4H, m, H-6, both diast); *m/z* (CI) 478 $[M+NH_4]^+$, 461 $[M+H]^+$, 318, 278, 246, 214, 197, 157, 139, 137, 107 $[BnO]^+$, 91 $[C_7H_7]^+$, 79, 43 (Found: $[M+NH_4]^+$, 478.2260. $C_{25}H_{32}O_6S$ requires $[M+NH_4]^+$, 478.2263).

Preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-heptadien-4-ol (11i).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 1.66 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and crotonaldehyde to give, after chromatography (30% ether–petrol), a 7:7:1:1 mixture of *Z:Z:E:E* diastereomers of 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-heptadien-4-ol (**11i**) (0.590 g, 95%) as a pale yellow oil; R_f 0.16,0.13 and 0.09, 50% ether–petrol; ν_{max} (film) 3494, 3059, 3029, 2919, 1656, 1595, 1491, 1449, 1399, 1365, 1285, 1212, 1183, 1142, 1082, 1026, 966, 814, 738 and 700 cm^{-1}; δ_H (500 MHz) 7.77-7.62 (8H, m, H-2 and H-6 of Ts all diast), 7.37-7.00 (28H, m, H-3 and H-5 of Ts and Ph, all diast), 6.24 (1H, d, J 6.0 Hz, H-1, *Z*-diast), 6.18 (1H, d, J 13.0 Hz, H-1, *E*-diast), 6.11 (1H, d, J 6.0 Hz, H-1, *Z*-diast), 6.09 (1H, d, J 13.0 Hz, H-1, *E*-diast), 5.77-5.69 (4H, m, H-1, H-6, all diast), 5.42-5.34 (4H, m, H-5, all diast), 4.98 (1H, dd, J 13.0 and 10.5 Hz, H-4, *E*-diast), 4.92 (1H, dd, J 12.5 and 6.5 Hz, H-4, *Z*-diast), 4.75-4.69 (2H, m, H-4, *E*- and *Z*-diast), 4.66 (1H, t, J 7.5 Hz, H-3, *Z*-diast), 4.53 (2H, s, CH_2Ph, *Z*-diast), 4.50 (2H, s, CH_2Ph, *E*-diast), 4.45 (2H, s, CH_2Ph, *Z*-diast), 4.42 (2H, s, CH_2Ph, *E*-diast), 4.41 (1H, dd, J 13.0 and 7.5 Hz, H-2, *E*-diast), 4.35 (1H, dd, J 11.0 and 8.5 Hz, H-2, *Z*-diast), 4.25 (1H, dd, J 10.5 and 1.0 Hz, H-2, *Z*-diast), 4.22 (1H, dd, J 10.5 and 3.0 Hz, H-2, *E*-diast), 4.18 (1H, dd, J 10.5 and 6.0 Hz, *Z*-diast), 4.04-3.96 (3H, m, OH, 2 x *E*- and 1 x *Z*-diast), 3.92 (1H, d, J 9.0 Hz, OH, *Z*-diast), 3.47 (1H, dd, J 11.0 and 8.0 Hz, H-3, *E*-isomer), 3.38 (1H, dd, J 10.5 and 3.0 Hz, H-3, *E*-isomer), 2.45 (3H, s, Me of Ts, *E*-isomer), 2.43 (3H, s, Me of Ts), 2.42 (3H, s, Me of Ts, *Z*-isomer), 2.41 (3H, s, Me of Ts, *Z*-isomer) and 1.75-1.64 (12H, m, H-7, all isomers); *m/z* (CI) 390 $[M+NH_4]^+$, 373 $[M+H]^+$, 354 $[M-H_2O]^+$, 278, 246, 214, 163, 139, 124, 108 $[BnOH]^+$, 91 $[C_7H_7]^+$ (Found: $[M+NH_4]^+$, 390.1739. $C_{21}H_{24}O_4S$ requires $[M+NH_4]^+$, 390.1739).

Preparation of 1-benzyloxy-4-phenyl-3-(4-tolylsulfonyl)-1-buten-4-ol (11j).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 1.47 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and benzaldehyde to give, after chromatography (45% ether–petrol), a 3:3:1:1 mixture of *Z:Z:E:E* diastereomers of 1-benzyloxy-4-phenyl-3-(4-tolylsulfonyl)-1-buten-4-ol (**11j**) (0.565 g, 94%) as a pale yellow oil; R_f 0.18 and 0.15, 50% ether–petrol; ν_{max} (film) 3491, 3059, 3028, 2871, 1654, 1595, 1491, 1450, 1399, 1364, 1286, 1217, 1139, 1083, 1056, 1028, 814 and 738 cm^{-1}; δ_H (270 MHz) 7.83-7.66 (8H, m, H-2 and H-6 of Ts, all diast), 7.40-7.00, 6.90-6.83 and 6.78-6.72 (48H, m, H-3 and H-5 of Ts and Ph, all diast), 6.07 (1H, d, J 6.0 Hz, H-4, *Z*-diast), 5.84 (1H, d, J 13.0 Hz, H-4, *E*-diast), 5.78 (1H, d, J 13.0 Hz, H-4, *E*-diast), 5.77 (1H, d, J 6.0 Hz, H-4, *Z*-diast), 5.73 (1H, s, H-1, *Z*-diast), 5.72 (1H, s, H-1, *E*-diast), 5.23 (1H, d, J 9.5 Hz, H-1, *Z*-diast), 5.17 (1H, d, J 9.0 Hz, H-1, *E*-diast), 5.07 (1H, dd, J 13.0 and 10.5 Hz, H-3, *E*-diast), 4.81 (1H, dd, J 10.5 and 6.0 Hz, H-3, *Z*-diast), 4.64 (1H, dd, J 10.5 and 9.5 Hz, H-2, *Z*-diast), 4.60 (2H, s, CH_2Ph, *E*-diast), 4.43 (1H, m, H-2, *Z*-diast), 4.37-4.26 (6H, m, CH_2Ph, 2 x *Z*- and 1 x *E*-diast), 4.06 (1H, dd, J 10.5 an 6.0 Hz, H-3, *Z*-diast), 3.69-3.62 (2H, m, H-3 and H-2, *E*-diast), 3.44 (1H, dd, J 10.5 and 1.5 Hz, H-2, *E*-diast), 2.45 (3H, s, Me of

Ts, *E*-diast), 2.44 (6H, s, Me of Ts, 2 x *Z*-diast) and 2.43 (3H, s, Me of Ts, *E*-diast); *m/z* (CI) 426 $[M+NH_4]^+$, 409 $[M+H]^+$, 390 $[M-H_2O]$, 324, 299, 289, 271, 243, 206, 180, 155, 144, 139, 124, 106, 91 $[C_7H_7]^+$ (Found: $[M+NH_4]^+$, 426.1739. $C_{24}H_{24}O_4S$ requires $[M+NH_4]^+$, 426.1739).

Preparation of 1-benzyloxy-4-(3-methoxyphenyl)-3-(4-tolylsulfonyl)-1-buten-4-ol (11k).

This was carried out analogously to the preparation of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol on a 5.93 mmol scale starting from 3-benzyloxy-1-(4-tolylsulfonyl)-2-propene and 3-methoxybenzaldehyde to give, after chromatography (30%→50% ether–petrol), a 3:3:1:1 mixture of *Z:Z:E:E* diastereomers of 1-benzyloxy-4-(3-methoxyphenyl)-3-(4-tolylsulfonyl)-1-buten-4-ol (**11k**) (2.48 g, 95%) as a colourless, oily solid; R_f 0.21, 0.15 and 0.10, 50% ether–petrol; ν_{max} (film) 3491, 3058, 3029, 2988, 1655, 1597, 1488, 1452, 1433, 1400, 1285, 1184, 1082, 1042, 942, 874, 813 and 735 cm^{-1}; δ_H (500 MHz) 7.82-7.65 (8H, m, H-2 and H-6 of Ts, all diast), 7.49-7.00 and 6.98-6.65 (44H, m, H-3 and H-5 of Ts, Ph and 3-MeOPh all diast), 6.07 (1H, d, J 6.0 Hz, H-4, *Z*-diast), 5.88 (1H, d, J 12.5 Hz, H-4, *E*-diast), 5.82 (1H, d, J 12.5 Hz, H-4, *E*-diast), 5.80 (1H, d, J 6.0 Hz, H-4, *Z*-diast), 5.72 (1H, s, H-1, *Z*-diast), 5.59 (1H, d, J 5.0 Hz, H-1, *E*-diast), 5.50 (1H, s, H-1, *E*-diast), 5.21 (1H, d, J 9.5 Hz, H-1, *Z*-diast), 4.80 (1H, dd, J 10.5 and 6.2 Hz, H-3, *Z*-diast), 4.72 (1H,d, J 11.5 Hz, H-2, *E*-diast), 4.64 (1H, dd, J 11.0 and 9.5 Hz, H-2, *Z*-diast, 4.49-4.42 (1H, m, H-2, *Z*-diast), 4.34 (1H, s, CH_2Ph, *Z*-diast), 4.33 (1H, s, CH_2Ph, *Z*-diast), 4.29 (1H, s, CH_2Ph, *E*-diast), 4.27 (1H, s, CH_2Ph, *E*-diast), 4.14 (1H, dd, J 11.0 and 7.0 Hz, H-3, *E*-diast), 4.09 (1H, dd, J 11.0 and 6.0 Hz, H-3, *Z*-diast), 3.80-3.60 (14H, m, MeO, all diast, H-2 and H-3, *E*-diast), 2.44 (3H, s, Me of Ts, *Z*-diast), 2.39 (3H, s, Me of Ts, *E*-diast), 2.37 (3H, s, Me of Ts, *Z*-diast) and 2.35 (3H, s, Me of Ts, *E*-diast); *m/z* (CI) 456 $[M+NH_4]^+$, 239 $[M+H]^+$, 420 $[M-H_2O]^+$, 340 $[M-Bn]^+$, 330 $[M-MeOPh]^+$, 312 $[M-MeOPh-H_2O)$, 264, 174, 147, 144, 139, 135 $[BnOC_2H_4]^+$, 107 $[BnO]^+$, 91 $[C_7H_7]^+$ (Found: $[M+NH_4]^+$, 456.1845. $C_{24}H_{26}O_5S$ requires $[M+NH_4]^+$, 456.1844).

Preparation of 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran (12a).

A stirred solution of 1-benzyloxy-3-(4-tolylsulfonyl)-1-pentadecen-4-ol (**11a**) (0.720 g, 1.48 mmol) in 15% aqueous MeCN (30 ml) containing concentrated H_2SO_4 (2.96 ml) was heated at 65°C for 4 h. The yellow reaction mixture was quenched with solid $NaHCO_3$, then water (20 ml) and the aqueous layer extracted with EtOAc (3 x 40 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (50 ml), water (50 ml), brine (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a pale yellow oil. Purification by chromatography (35%→55% ether–petrol), gave a 2:2:1:1 mixture of diastereomers of 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran (**12a**) (0.498 g, 85%) as an oily solid; R_f 0.17 and 0.13, 50% ether–petrol; ν_{max} (film) 3389, 3028, 2921, 2851, 1595, 1490, 1462, 1400, 1377, 1352, 1314, 1300, 1181, 1149, 1087, 1042 and 814 cm^{-1}; δ_H (270 MHz) 7.82-7.74 (8H, m, H-2 and H-6 of Ts), 7.43-7.32 (8H, m, H-3 and H-5 of Ts), 5.59-5.55 (1H, m, H-2), 5.51-5.43 (2H, m, H-2), 5.38 (1H, ddd, J 11.0, 6.0 and 1.5 Hz, H-2), 4.69 (1H, d, J 6.0 Hz, OH), 4.61 (1H, d, J 11.0 Hz), 4.53-4.45 (2H, m, H-5), 4.40 (1H, m, H-5), 4.16 (1H, m, H-5), 3.91 (1H, q, J 8.0 Hz, H-4), 3.68-3.58 (2H, m, H-4), 3.38 (1H, m, H-4), 2.47 (3H, s, Me of Ts), 2.46 (3H, s, Me of Ts), 2.45 (3H, s, Me of Ts), 2.44 (3H, s, Me of Ts), 2.14-1.87 (8H, m, H-3), 1.64-1.10 (80H, m, H-6 to H-15) and 0.90-0.84 (12H, m, H-16); *m/z* (EI) 305 $[M-Bn]^+$, 289 $[M-C_7H_7O]^+$, 275, 251, 235, 223 $[M-C_{11}H_{23}-H_2O]^+$, 222, 151, 139, 124, 123, 109, 91 $[C_7H_7]^+$, 81 (Found: $[M-C_{11}H_{23}-H_2O]^+$, 223.0434. $C_{22}H_{36}O_4S$ requires $[M-C_{11}H_{23}-H_2O]^+$, 223.0428).

Preparation of 2-hydroxy-5-isopropyl-4-(4-tolylsulfonyl)tetrahydrofuran (12b).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 1.48 mmol scale starting from 6-benzyloxy-2-methyl-4-(4-tolylsulfonyl)-5-hexen-3-ol (**11b**) to give, after chromatography (30%→70% ether–petrol), a 3:3:1:1 mixture of diastereomers of 2-hydroxy-5-isopropyl-4-(4-

tolylsulfonyl)tetrahydrofuran (**12b**) (0.507 g, 90%) as an oily solid; R_f 0.36 and 0.24, 70% ether–petrol; ν_{max} (film) 3402, 1654, 1595, 1540, 1420, 1325, 1289, 1256, 1142, 1083, 1017, 866, 849, 817 and 713 cm^{-1}; δ_H (270 MHz) 7.84-7.75 (8H, m, H-2 and H-6 of Ts), 7.43-7.33 (8H, m, H-3 and H-5 of Ts), 5.53 (1H, dd, J 5.5 and 3.0 Hz, H-2, major diast), 5.51-5.45 (2H, m, H-2, major and minor diast), 5.38 (1H, dd, J 12.0 and 6.5 Hz, H-2, minor diast), 4.87 (1H, d, J 12.0 Hz, OH, minor diast), 4.74 (1H, d, J 12.0 Hz, OH, minor diast), 4.41 (1H, dd, J 5.0 and 4.0 Hz, H-5, minor diast), 4.22 (1H, t, J 6.0 Hz, H-5, minor diast), 4.06 (1H, dd, J 9.0 and 5.0 Hz, H-5, major diast), 3.81 (1H,ddd, J 8.5, 5.0 and 4.0 Hz, H-4, major diast), 3.69 (1H, m, H-4, minor diast), 3.64 (1H, dd, J 11.0 and 5.0 Hz, H-5, major diast), 3.58 (1H, dd, J 8.0 and 5.0 Hz, H-4, major diast), 3.46 (1H, ddd, J 10.5, 4.0 and 1.5 Hz, H-4, minor diast), 2.88-2.78 (2H, m, OH, major diast). 2.72-2.30 (19H, m, 2 x H-6, major diast, 5 x H-3, 3 x major and 2 x minor diast, Me of Ts, all diast), 2.15 (1H, d, J 15.5 Hz, H-3, minor diast), 2.06 (1H, ddd, J 14.0, 8.5 and 2.0 Hz, H-3, minor diast), 2.00 (1H, ddd, J 14.0, 8.0 and 3.0 Hz, H-3, major diast), 1.82 (1H, octet, J 6.0 Hz, H-6, major diast), 1.57 (1H, m, H-6, minor diast), 1.13 (3H, d, J 6.5 Hz, CHC*H*$_3$ major diast), 1.07 (3H, d, J 6.5 Hz, CHC*H*$_3$, major diast), 1.06 (3H, d, J 6.5 Hz, CHC*H*$_3$, major diast), 1.05 (3H, d, J 6.5 Hz, CHC*H*$_3$, major diast), 0.92 (3H, d, J 6.5 Hz, CHC*H*$_3$, minor diast), 0.87 (3H, d, J 6.5 Hz, CHC*H*$_3$, minor diast), 0.75 (3H, d, J 6.0 Hz, CHC*H*$_3$, minor diast), 0.73 (3H, d, J 6.0 Hz, CHC*H*$_3$, minor diast); *m/z* (EI) 241 $[M\text{-}CHMe_2]^+$, 221, 177, 155 $[Ts]^+$, 149, 139, 111, 95, 91 $[C_7H_7]^+$ (Found: $[M\text{-}CHMe_2]^+$, 241.0538. $C_{14}H_{20}O_4S$ requires $[M\text{-}CHMe_2]^+$, 241.0534).

Preparation of 5-cyclohexyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (12c).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 1.75 mmol scale starting from 4-benzyloxy-1-cyclohexyl-2-(4-tolylsulfonyl)-3-buten-1-ol (**11c**) to give, after chromatography (30-70% ether–petrol), a 3:3:1:1 mixture of diastereomers of 5-cyclohexyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12c**) (0.543 g, 95%) as a colourless solid; mp 110°C (dec), R_f 0.28 and 0.22, 70% ether–petrol; ν_{max} (CH_2Cl_2) 3454, 2928, 2851, 2365, 2356, 2339, 2331, 1674, 1596, 1539, 1495, 1441, 1289, 1143, 1085, 1032, 890, 815, 714 and 664 cm^{-1}; δ_H (270 MHz) 7.85-7.73 (4H, m, H-2 and H-6 of Ts, all diast), 7.45-7.35 (4H, m, H-3 and H-5 of Ts, all diast), 5.56 (1H, m, H-2, major diast), 5.48 (1H, m, H-2, major diast), 5.43 (1H, d, J 4.5 Hz, H-2, minor diast), 5.08 (1H, d, J 6.5 Hz, H-2, minor diast), 4.87 (1H, d, J 13.5 Hz, OH, major diast), 4.73 (1H, d, J 13.5 Hz, OH, minor diast), 4.43 (1H, dd, J 7.0 and 4.5 Hz, H-5, minor diast), 4.23 (1H, t, J 7.0 Hz, H-5, minor diast), 4.17-4.07 (2H, m, H-5, major diast), 3.82 (1H, q, J 4.0 Hz, H-4, major diast), 3.71 (1H, dd, J 13.5 and 5,5 Hz, H-4, minor diast), 3.55-3.48 (1H, m, H-4, minor diast), 3.07 (1H, q, J 7.0 Hz, H-4, major diast), 2.87-2.71 (2H, m, OH, minor and major diast), 2.58 (1H, dd, J 7.0 and 4.5 Hz, H-3, minor diast), 2.54 (1H, dd, J 7.0 and 4.5 Hz, H-3, major diast), 2.53 (3H, s, Me of Ts, major diast), 2.52 (3H, s, Me of Ts, major diast), 2.51 (3H, s, Me of Ts, minor diast), 2.50 (3H, s, Me of Ts, minor diast), 2.37 (1H, dd, J 7.0 and 4.5 Hz, H-3, minor diast), 2.23 (1H, dd, J 10.0 and 5.5 Hz, H-3, major diast), 2.15-2.02 (2H, m, 2 x H-3, major and minor diast), 2.00 (1H, dd, J 7.0 and 4.0 Hz, H-3, minor diast). 1.93 (1H, dd, J 7.0 and 4.5 Hz, H-3, minor diast), 1.87-1.42 (20H, m, H-6, H-7 and H-11, all diast) and 1.82-1.40 (24H, m, H-8 to H-10, all diast); *m/z* (EI) 342 $[M+NH_4]^+$, 325 $[M+H]^+$, 246, 241, 183, 168 $[M\text{-}Ts]^+$, 157, 150, 139, 124, 91 $[C_7H_7]^+$, 86, 83 (Found: $[M+NH_4]^+$, 342.1740. $C_{17}H_{24}O_4S$ requires $[M+NH_4]^+$, 342.1739).

Preparation of 5-*t*-butyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (12d).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 3.53 mmol scale starting from 6-benzyloxy-2,2-dimethyl-4-(4-tolylsulfonyl)-5-hexen-3-ol (**11d**) to give, after chromatography (20%→50% ether–petrol), a 6:4:2:1 mixture of diastereomers (A:B:C:D) of 5-*t*-butyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12d**) (0.620 g, 59%) as a colourless solid; R_f 0.33 and 0.31, 70% ether–petrol; ν_{max} (film) 3455, 2959, 1686, 1597, 1446, 1401, 1366, 1307, 1175, 1142, 1086, 1052, 982,

856, 817, 710 and 671 cm^{-1}; δ_H (270 MHz) 7.80-7.71 (8H, m, H-2 and H-6 of Ts, all diast), 7.40-7.27 (8H, m, H-3 and H-5 of Ts, all diast), 5.49-5.43 (4H, m, H-2, all diast), 5.02 (1H, d, J 12.5 Hz, OH, diast A), 4.91 (1H, d, J 12.5 Hz, OH, diast D), 4.31 (1H, d, J 3.0 Hz, H-2, diast A), 4.16 (1H, d, J 5.0 Hz, H-2, diast C), 4.11 (1H, d, J 3.0 Hz, H-2, diast B), 4.05 (1H, d, J 5.0 Hz, H-2, diast D), 3.78-3.68 (2H, m, H-4, diast C and D), 3.54-3.45 (2H, m, H-4, diast A and B), 2.62 (1H, m, H-3, diast C), 2.56 (1H, m, H-3, diast B), 2.50-2.23 (20H, Me of Ts, all diast and H-3, diast A and D), 1.97-1.82 (2H, m, H-3, diast B and C), 0.94 (9H, s, H-6, diast C), 0.81 (9H, s, H-6, diast B), 0.73 (9H, s, H-6, diast D), 0.69 (9H, s, H-6, diast A); *m/z* (EI) 241 $[M\text{-}t\text{-}Bu]^+$, 214, 199, 182, 124, 109, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 57 (Found: $[M\text{-}t\text{-}Bu]^+$, 241.0534. $C_{15}H_{22}O_4S$ requires $[M\text{-}t\text{-}Bu]^+$, 241.0535).

Preparation of (*E*,*E*)-2-hydroxy-5-(5,7-nonadienyl)-4-(4-tolylsulfonyl)tetrahydrofuran (12e).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 4.53 mmol scale starting from (9*E*,11*E*)-1-benzyloxy-3-(4-tolylsulfonyl)-1,9,11-tridecatrien-4-ol (**11e**) to give, after chromatography (70% ether–petrol), a 2:2:1:1 mixture of diastereomers of (*E*,*E*)-2-hydroxy-5-(5,7-nonadienyl)-4-(4-tolylsulfonyl)tetrahydrofuran (**12e**) (1.56 g, 89%); as a colourless oil; R_f 0.31 and 0.24, 70% ether–petrol; ν_{max} (film) 3015, 2932, 2733, 1690, 1597, 1494, 1449, 1301, 1147, 988, 816, 709 and 667 cm^{-1}; δ_H (270 MHz) 7.80-7.74 (8H, m, H-2 and H-6 of Ts, all diast), 7.41-7.27 (8H, m, H-3 and H-5 of Ts, all diast), 6.02-5.92 (8H, m, H-6' and H-7', all diast), 5.60-5.44 (12H, m, H-2, H-5' and H-8', all diast), 4.61-4.39 (4H, m, H-5, all diast), 3.91 (1H, q, J 7.0 Hz, H-4, major diast), 3.69-3.57 (2H, m, H-4, minor diast), 2.46 (3H, s, Me of Ts, major diast), 2.45 (3H, s, Me of Ts, major diast), 2.42 (3H, s, Me of Ts, minor diast), 2.39 (3H, s, Me of Ts, minor diast), 2.26-1.89 (16H, m, H-3 and H-1', all diast), 1.78-1.14 (36H, m, H-2' to H-4' and H-9', all diast); *m/z* (CI) 364 $[M+NH_4\text{-}H_2O]^+$, 346 $[M\text{-}H_2O]^+$, 354, 331, 281, 220, 208 $[M\text{-}Ts]^+$, 205, 190 $[M\text{-}TsH\text{-}H_2O]^+$, 108, 93, 81, 77 $[C_7H_7]^+$, 67 (Found: $[M+NH_4\text{-}H_2O]^+$, 364.1946. $C_{20}H_{28}O_4S$ requires $[M+NH_4\text{-}H_2O]^+$, 364. 1946).

Preparation of 5-benzyloxymethyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (12f).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 1.17 mmol scale starting from 1,5-bis(benzyloxy)-3-(4-tolylsulfonyl)-4-penten-2-ol (**11f**) to give, after chromatography (20%→50% ether–petrol), a 2:2:1:1 mixture of diastereomers of 5-benzyloxymethyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12f**) (0.418 g, 97%) as a colourless oil; R_f 0.50 and 0.40, ether; ν_{max} (film) 3452, 3084, 3059, 3028, 2922, 2863, 1655, 1595, 1450, 1313, 1287, 1207, 1146, 1086, 1027, 914, 815, 738 and 699 cm^{-1}; δ_H (270 MHz) 7.80-7.70 (8H, m, H-2 and H-6 of Ts, all diast), 7.42-7.20 (28H, m, H-2 and H-6 of Ts, Ph, all diast), 5.64 (1H, d, J 5.0 Hz, H-2, major diast), 5.54 (1H, dd, J 11.5 and 5.0 Hz, H-2, minor diast), 5.44-5.38 (2H, m, H-2, major and minor diast), 4.78-4.44 (14H, m, CH_2Ph, 4 x major and 3 x minor diast, 3 x OH, H-5, all diast), 4.36 (1H, d, J 12.0 Hz, CH_2Ph, minor diast), 4.15 (1H, dd, J 10.5 and 3.0 Hz, H-6, major diast), 4.10 (1H, dd, J 10.5 and 4.5 Hz, H-6, minor diast), 4.06-3.97 (3H, m, H-6, major and minor diast and H-4, major diast), 3.93 (1H, ddd, J 9.5, 8.0 and 6.0 Hz, H-4, major diast), 3.80 (1H, ddd, J 10.5, 4.5 and 2.5 Hz, H-4, minor diast), 3.76 (1H, td, J 8.5 and 7.0 Hz, H-4, minor diast), 3.66 (1H, dd, J 10.0 and 2.5 Hz, H-6, major diast), 3.51 (1H, dd, J 11.0 and 3.5 Hz, H-6, minor diast), 3.37 (1H, dd, J 10.5 and 2.5 Hz, H-6, major diast), 3.22 (1H, dd, J 11.0 and 3.5 Hz, H-6, minor diast), 3.12 (1H, s, OH), 2.52-2.30 (18H, m, Me of Ts, all diast and H-3, 3 x major and 3 x minor diast), 2.08 (1H, m, H-3, major diast) and 1.95 (1H, m, H-3, major diast); *m/z* (EI) 360, 342 $[M\text{-}H_2O]^+$, 278, 267, 253 $[M\text{-}OBn]^+$, 246, 241, 139, 124, 107 $[BnO]^+$, 91 $[C_7H_7]^+$ (Found: $[M\text{-}H_2O]^+$, 344.1076. $C_{19}H_{22}O_5S$ requires $[M\text{-}H_2O]^+$, 344.1082).

Preparation of 5-[2-benzyloxyethyl]-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (12g).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 4.67 mmol scale starting from 1,6-bis(benzyloxy)-4-(4-tolylsulfonyl)-5-hexen-3-ol (**11g**) to give, after chromatography (20%→50% ether–petrol), a 2:2:1:1 mixture of diastereomers of 5-[2-benzyloxyethyl]-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12g**) (1.53 g, 87%) as a pale yellow oil; R_f 0.17 and 0.13, 70% ether–petrol; ν_{max} (film) 3457, 3033, 2928, 2866, 1684, 1598, 1487, 1448, 1366, 1302, 1206, 1142, 1087, 814, 743, 701 and 666 cm^{-1}; δ_H (270 MHz) 7.78-7.71 (8H, m, H-2 and H-6 of Ts, all diast), 7.41-7.23 (28H, m, H-2 and H-6 of Ts and Ph, all diast), 5.58 (1H, d, J 5.0 Hz, H-2, minor diast), 5.50 (2H, m, H-2, major diast), 5.44 (1H, m, H-2, minor diast), 4.71-4.39 (14H, m, CH_2Ph, H-5, all diast and OH, major and minor diast), 3.92-3.39 (8H, m, H-2' and H-4, all diast), 2.94 (1H, s, OH, major diast), 2.59 (1H, s, OH, minor diast), 2.46 (3H, s, Me of Ts, major diast), 2.45 (3H, s, Me of Ts, minor diast), 2.44 (3H, s, Me of Ts, major diast), 2.43 (3H, s, Me of Ts, minor diast), 2.17-1.62 (8H, m, H-1', all diast); *m/z* (EI) 278, 230, 220 [M+H-Ts]$^+$, 205, 203, 129, 114, 107 [BnO]$^+$, 91 [C_7H_7]$^+$, 79, 55 (Found: [M+H-Ts]$^+$, 220.1099. $C_{20}H_{24}O_5S$ requires [M+H-Ts]$^+$, 220.1099).

Preparation of 5-[5-(*t*-butyldimethylsilyloxy)pentyl]-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (12h).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 1.98 mmol scale starting from 1-acetoxy-9-benzyloxy-7-(4-tolylsulfonyl)-8-nonen-6-ol (**11h**) to give, after chromatography (100% ether→50% EtOAc–petrol), a 2:2:1:1 mixture of diastereomers of 2-hydroxy-5-(5-hydroxypentyl)-4-(4-tolylsulfonyl)tetrahydrofuran (**16**) (0.491 g, 75%) as an oily solid; R_f 0.10, ether; ν_{max} (film) 3409, 2935, 2860, 2358, 1597, 1541, 1458, 1291, 1145, 1083, 816 and 667 cm^{-1}. A portion of this material (0.360 g, 1.10 mmol) in CH_2Cl_2 (1 ml plus 1 ml rinse) was added to a stirred mixture of TBDMSCl (0.165 g, 1.096 mmol), DMAP (6.69 mg, 0.0548 mmol, 0.05 eq) and Et_3N (168 µl, 1.21 mmol, 1.1 eq) *via* cannula. After 2 h the pale yellow reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 ml) and the layers separated. The aqueous layer was extracted with EtOAc (3 x 10 ml), the combined organic layers washed with water (2 x 10 ml), brine (10 ml), dried (Na_2SO_4) and the solvents removed under reduced pressure. Chromatography (80% ether–petrol) gave a 4:4:1:1 mixture of diastereomers of 5-[5-(*t*-butyldimethylsilyloxy)pentyl]-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12h**) (0.414 g, 85%) as a colourless oil; R_f 0.50 and 0.40, 90% ether–petrol; ν_{max} (film) 3471, 2931, 2857, 1597, 1462, 1389, 1360, 1302, 1256, 1147, 1089, 836, 777, 709 and 667 cm^{-1}; δ_H (270 MHz) 7.78-7.76 (8H, m, H-2 and H-6 of Ts, all diast), 7.38-7.25 (8H, m, H-3 and H-5 of Ts, all diast), 5.53 (1H, d, J 5.0 Hz, H-2, major diast), 5.47-5.38 (2H, m, H-2, major and minor diast), 5.37-5.31 (1H, m, H-2, minor diast), 4.64-4.56 (1H, m, H-5, minor diast), 4.51-4.28 (4H, m, 2 x H-5, major diast and OH, major and minor diast), 4.21-4.09 (1H, m, H-5, minor diast), 3.89 (1H, q, J 8.2 Hz, H-4, major diast), 3.66-3.47 (12H, m, H-5', all diast, 2 x H-4 and 2 x OH, major and minor diast), 3.35 (1H, q, J 6.5 Hz, H-4, minor diast), 2.53-2.28 (12H, m, Me of Ts, all diast), 2.28-2.15 (1H, m, H-3, minor diast), 2.10-1.85 (7H, m, H-3, major and minor diast), 1.62-1.16 (32H, m, H-1' to H-4', all diast), 0.84 (36H, s, *t*-Bu, all diast) and 0.01 (24H, s, MeSi, all diast); *m/z* (EI) 385 [M-*t*-Bu]$^+$, 325, 253, 230, 229, 227, 211, 131, 124, 101, 91 [C_7H_7]$^+$, 75 (Found: [M-*t*-Bu]$^+$, 385.1505. $C_{22}H_{38}O_5SSi$ requires [M-*t*-Bu]$^+$, 385.1505).

Preparation of (*E*)-2-hydroxy-5-propenyl-4-(4-tolylsulfonyl)tetrahydrofuran (12i).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 2.38 mmol scale starting from 1-benzyloxy-3-(4-tolylsulfonyl)-1,5-heptadien-4-ol (**11i**) to give, after chromatography (30%→70% ether–petrol), a 2:2:1:1 mixture of diastereomers of (*E*)-2-hydroxy-5-propenyl-4-(4-tolylsulfonyl)tetrahydrofuran (**12i**) (0.631 g, 94%) as a colourless oil; R_f 0.24 and 0.18, 70% ether–petrol;

ν_{max} (film) 3464, 3028, 2921, 2854, 1684, 1637, 159, 1491, 1445, 1300, 1146, 1085, 1035, 967, 887 and 815 cm^{-1}; δ_H (270 MHz) 7.91-7.70 (8H, m, H-2 and H-6 of Ts, all diast), 7.40-7.27 (8H, m, H-3 and H-5 of Ts, all diast), 5.83 (1H, d, J 6.5 Hz, H-2, minor diast), 5.77 (1H, d, J 6.5 Hz, H-2, major diast), 5.71-5.60 (4H, m, H-2', all diast), 5.66 (1H, d, J 6.5 Hz, H-2, minor diast), 5.62 (1H, d, J 5.0 Hz, H-2, major diast), 5.51 (1H, m, H-5, major diast), 5.48-5.33 (4H, m, H-1', all diast), 5.15 (1H, d, J 7.0 Hz, H-5, minor diast), 5.03 (1H, d, J 7.0 Hz, H-5, minor diast), 4.85-4.78 (4H, m, H-4, H-5, major diast, 2 x OH, major diast), 4.71 (1H, t, J 7.5 Hz, H-4, minor diast), 4.57 (1H, t, J 7.1 Hz, H-4, major diast), 3.83-3.72 (1H, m, H-3, major diast), 3.49-3.43 (1H, m, H-3, major diast), 2.61 (1H, dd, J 9.0 and 5.0 Hz, H-3, minor diast), 2.53 (1H, dd, J 9.0 and 4.5 Hz, H-3, major diast), 2.49-2.43 (16H, m, Me of Ts, all diast, 2 x H-3, minor diast and 2 x OH, minor diast), 2.20 (1H, dd, J 12.5 and 7.5 Hz, H-3 minor diast), 2.11 (1H, dd, J 13.5 and 8.0 Hz, H-3 major diast), 1.72 (3H, dd, J 6.5 and 0.5 Hz, H-3', minor diast), 1.68 (3H, d, J 6.5 Hz, H-3', major diast), 1.63 (3H, d, J 6.0 Hz, H-3', minor diast), 1.51 (3H, d, J 6.0 Hz, H-3', major diast); *m/z* (CI) 282 $[M+NH_4-H_2O]^+$, 264 $[M-H_2O]^+$, 256, 183, 139, 124, 97, 91 $[C_7H_7]^+$, 79, 69, 41 (Found: $[M+NH_4-H_2O]^+$, 282.1164. $C_{14}H_{18}O_4S$ requires $[M+NH_4-H_2O]^+$, 282.1164).

Preparation of 2-hydroxy-5-phenyl-4-(4-tolylsulfonyl)tetrahydrofuran (12j).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 1.35 mmol scale starting from 1-benzyloxy-4-phenyl-3-(4-tolylsulfonyl)-1-buten-4-ol (**11j**) to give, after chromatography (30%→70% ether–petrol), a 5:5:1:1 mixture of diastereomers of 2-hydroxy-5-phenyl-4-(4-tolylsulfonyl)tetrahydrofuran (**12j**) (0.396 g, 92%) as an oily solid; R_f 0.26 and 0.11, 70% ether–petrol; ν_{max} (film) 3460, 3060, 2923, 1595, 1491, 1448, 1400, 1378, 1301, 1289, 1182, 1145, 1085, 1041, 845, 814, 740 and 701 cm^{-1}; δ_H (270 MHz) 7.83-7.66 (8H, m, H-2 and H-6 of Ts, all diast), 7.843-7.00 (28H, m, H-3 and H-5 of Ts and Ph, all diast), 5.90 (1H, d, J 5.0 Hz, H-2, minor diast), 5.76 (1H, dd, J 12.0 and 5.0 Hz, H-2, major diast), 5.68 (1H, t, J 4.0 Hz, H-2, minor diast), 5.63 (1H, dd, J 12.0 and 5.0 Hz, H-2, major diast), 5.60 (1H, d, J 4.0 Hz, H-5, major diast), 5.52 (1H, d, J 7.5 Hz, H-5, minor diast), 5.39 (1H, d, J 7.0 Hz, H-5, major diast), 5.25 (1H, d, J 6.0 Hz, H-5, minor diast), 5.01 (1H, d, J 12.5 Hz, OH, major diast), 4.91 (1H, d, J 12.0 Hz, OH, major diast), 4.28 (1H, q, J 7.5 Hz, H-4, minor diast), 4.03 (2H, m, H-4 and OH, minor diast), 3.66 (1H, ddd, J 10.0, 4.0 and 2.5 Hz, H-4, major diast), 3.39 (1H, t, J 7.0 Hz, H-4, major diast), 3.15 (1H, s, OH, minor diast), 2.97-2.87 (3H, m H-3, 2 x major and 1 x minor diast), 2.77 (1H, ddd, J 15.0, 8.5 and 6.0 Hz, H-3, minor diast), 2.67 (1H, ddd, J14.0, 9.5 and 5.0 Hz, H-3, minor diast), 2.54-2.35 (13H, m, Me of Ts, all diast, H-3, major diast), 2.32 (1H, ddd, J 14.0, 8.5 and 1.5 Hz, H-3, major diast) and 2.26 (1H, ddd, J 13.0, 7.5 and 1.5 Hz, H-3, major diast); *m/z* (EI) 318 $[M]^+$, 289 $[M-CHO]^+$, 274 $[M-CO_2]^+$, 212 $[M-PhCHO]^+$, 162 $[M-Ts]^+$, 133, 105 $[PhCO]^+$, 91 $[C_7H_7]^+$, 84, 77 $[C_6H_5]^+$ (Found: $[M]^+$, 318.0917 . $C_{17}H_{18}O_4S$ requires $[M]^+$, 318.0925).

Preparation of 2-hydroxy-5-(3-methoxyphenyl)-4-(4-tolylsulfonyl)tetrahydrofuran (12k).

This was prepared in a similar manner to 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 2.37 mmol scale starting from 1-benzyloxy-4-(3-methoxyphenyl)-3-(4-tolylsulfonyl)-1-buten-4-ol (**11k**) to give, after chromatography (10%→70% ether–petrol), a 3:3:1:1 mixture of diastereomers of 2-hydroxy-5-(3-methoxyphenyl)-4-(4-tolylsulfonyl)tetrahydrofuran (**12k**) (0.746 g, 90%) as an oily solid; R_f 0.24 and 0.18, 70% ether–petrol; ν_{max} (film) 3465, 3057, 2927, 2835, 1597, 1489, 145, 1287, 1146, 1084, 1040, 874, 814, 786 and 700 cm^{-1}; δ_H (500 MHz) 7.83-7.67 (8H, m, H-2 and H-6 of Ts, all diast), 7.42-6.50 (24H, m, H-3 and H-5 of Ts and MeOPh, all diast), 5.73 (1H, d, J 4.0 Hz, H-2, major diast), 5.63 (1H, d, J 4.5 Hz, H-2, minor diast), 5.55 (1H, d, J 4.0 Hz, H-2, major diast), 5.32 (1H, d, J 6.5 Hz, H-2, minor diast), 4.95 (1H, s, OH, minor diast), 4.82 (1H, s, OH, minor diast), 4.66 (1H, dd, J 11.5 and 4.5 Hz, H-4, minor diast), 4.48 (1H, dd, J 11.5 and 4.5 Hz, H-4, major diast), 4.33 (1H, t, J 11.5 Hz, H-4, minor diast), 4.00 (1H, dd, J 11.5 and 4.5 Hz, H-4, major diast), 3.82-3.62 (14H, m, OMe, all diast and OH, major diast), 3.29-3.25 (2H, m, H-

3, major diast), 3.18 (1H, dd, J 15.0 and 1.5 Hz, H-3, minor diast), 2.94 (1H, dd, J 14.0 and 8.0 Hz, H-3, minor diast) and 2.65-2.19 (16H, m, Me of Ts, all diast, H-3, 2 x major, 2 x minor diast); *m/z* (CI) 366 $[M+NH_4]^+$, 349 $[M+H]^+$, 348 $[M+NH_4-H_2O]^+$, 312, 274, 246, 210, 195, 174, 145, 124, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$ (Found: $[M+NH_4]^+$, 366.1380. $C_{18}H_{20}O_5S$ requires $[M+NH_4]^+$, 366.1375).

Preparation of 4-(4-tolylsulfonyl)-2-oxo-5-undecyltetrahydrofuran (13a).

A solution of 2-hydroxy-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran (**12a**) (0.481 g, 1.21 mmol) in CH_2Cl_2 (19.2 ml plus 5 ml rinse) was added *via* cannula to a stirred mixture of PDC (0.684 g, 1.82 mmol, 1.5 eq) and 4Å molecular sieves (1.13 g) under a nitrogen atmosphere. The initially orange suspension rapidly became dark brown-black in colour. After 4 h the reaction mixture was diluted with ether (30 ml) and the mixture filtered through a plug of silica gel, which was thoroughly washed with EtOAc (300 ml). Removal of the solvents followed by chromatography (50% ether–petrol), gave a 1:1 mixture of diastereomers of 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran (**13a**) (0.399 g, 83%) as a colourless, oily solid; R_f 0.40 and 0.27, 80% ether–petrol; ν_{max} (film) 2929, 2855, 1784, 1651, 1597, 1467, 1324, 1304, 1147, 1087, 1017, 816, 715 and 676 cm^{-1}; δ_H (270 MHz) 7.81-7.76 (4H, m, H-2 and H-6 of Ts, both diast), 7.44-7.38 (4H, m, H-3 and H-5 of Ts, both diast), 4.85 (1H, dt, J 7.0 and 5.5 Hz, H-5), 4.79 (1H, ddd, J 10.5, 7.0 and 3.0 Hz, H-5), 3.98 (1H, td, J 8.5 and 7.0 Hz, H-4), 3.61 (1H, ddd, J 10.0, 6.5 and 5.5 Hz, H-4), 2.99 (1H, dd, J 18.5 and 6.5 Hz, H-3), 2.97 (1H, dd, J 17.5 and 8.5 Hz, H-3), 2.78 (1H, dd, J 18.5 and 10.0 Hz, H-3), 2.58 (1H, dd, J 17.5 and 8.5 Hz, H-3), 2.50-2.42 (7H, m, Me on Ts, both diast and H-6), 2.24-2.01 (3H, m, H-6), 1.68-1.60 (4H, m, H-7, both diast), 1.46-1.20 (32H, m, H-8 to H-15, both diast) and 0.91-0.85 (6H, m, H-16); *m/z* (EI) 395 $[M+H]^+$, 377, 239 $[M-Ts]^+$, 221, 203, 179, 157, 139, 109, 97, 91 $[C_7H_7]^+$, 81, 69, 55, 43 (Found: $[M-Ts]^+$, 239.0378. $C_{22}H_{34}O_4S$ requires $[M-Ts]^+$, 239.0378).

Preparation of 5-isopropyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (13b).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 0.758 mmol scale starting from 2-hydroxy-5-isopropyl-4-(4-tolylsulfonyl)tetrahydrofuran (**12b**) to give, after chromatography (80% ether–petrol), a 4:1 mixture of diastereomers of 5-isopropyl-2-oxo-4-(4-tolylsulfonyl)-tetrahydrofuran (**13b**) (0.186 g, 87%) as an oily solid; R_f 0.32 and 0.22, 80% ether–petrol; ν_{max} (film) 1794, 1503, 1315, 1300, 1256, 1203, 1185, 1159, 1139, 1085, 1036, 1017, 987, 950, 820. 728, 710, 683 and 657 cm^{-1}; δ_H (270 MHz) 7.80-7.75 (4H, m, H-2 and H-6 of Ts, both diast), 7.44-7.37 (4H, m, H-3 and H-5 of Ts, both diast), 4.71 (1H, dd, J 5.5 and 3.5 Hz, H-5, minor diast), 4.37 (1H, dd, J 8.0 and 6.0 Hz, H-5, major diast), 3.97 (1H, ddd, J 8.5, 6.0 and 4.5 Hz, H-4, major diast), 3.66 (1H, d, J 10.0 and 3.5 Hz, H-4, minor diast), 2.96 (1H, dd, J 19.0 and 4.5 Hz, H-3, minor diast), 2.85-2.74 (3H, m, H-3, major and minor diast and C*H*CH_3, major diast), 2.68 (1H, dd, J 18.0 and 8.5 Hz, H-3, major diast), 2.44 (3H, s, Me of Ts, minor diast), 2.43 (3H, s, Me of Ts, major diast), 1.86 (1H, m, C*H*CH_3, minor diast), 1.15 (6H, d, J 6.5 Hz, CHC*H*$_3$, major diast), 0.92 (3H, s, CHC*H*$_3$, minor diast) and 0.89 (3H, s, CHC*H*$_3$, minor diast); *m/z* (EI) 246, 239 $[M-CHMe_2]^+$, 219, 183, 155, 139, 124, 91 $[C_7H_7]^+$, 84, 77 $[C_6H_5]^+$, 55, 43 (Found: $[M-CHMe_2]^+$, 239.0378. $C_{14}H_{18}O_4S$ requires $[M-CHMe_2]^+$, 239.0378).

Preparation of 5-cyclohexyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (13c).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 0.660 mmol scale starting from 5-cyclohexyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12c**) to give, after chromatography (50% ether–petrol), a 6:1 mixture of diastereomers of 5-cyclohexyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13c**) (0.184 g, 86%) as an oily solid; R_f 0.46 and 0.33, 80% ether–petrol; ν_{max} (film) 2929, 2856, 1784, 1596, 1451, 1313, 1147, 1085, 1011, 814, 726 and 662 cm^{-1}; δ_H (270 MHz) 7.93

(2H, d, J 8.0 Hz, H-2 and H-6 of Ts, minor diast), 7.78 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts, major diast), 7.50-7.33 (4H, m, H-3 and H-5 of Ts, both diast), 4.77-4.66 (1H, m, H-5, major diast), 4.49-4.38 (1H, m, H-5, minor diast), 4.00-3.93 (1H, m, H-4, minor diast), 3.78-3.67 (1H, m, H-4, major diast), 3.00-2.85 (2H, m, H-3, major and minor diast), 2.81-2.57 (2H, m, H-3, major and minor diast), 2.51 (3H, s, Me of Ts, minor diast), 2.55 (3H, s, Me of Ts, major diast) and 1.81-0.81 (22H, m, C_6H_{11}, both diast); *m/z* (EI) 322 $[M]^+$, 277, 258, 239 $[M\text{-}c\text{-}C_6H_{11}]^+$, 183, 167 $[M\text{-Ts}]^+$, 155, 91, 84, 55 (Found: $[M\text{-}c\text{-}C_6H_{11}]^+$, 239.0378. $C_{17}H_{22}O_4S$ requires $[M\text{-}c\text{-}C_6H_{11}]^+$, 239.0378).

Preparation of 5-*t*-butyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (13d).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 1.62 mmol scale starting from 5-*t*-butyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12d**) to give, after chromatography (40%→70% ether–petrol), 5-*t*-butyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13d**) (0.412 g, 85%) as a colourless solid; mp 118-119°C, R_f 0.31 and 0.26, 80% ether–petrol; ν_{max} (CH_2Cl_2) 2953, 1781, 1603, 1579, 1310, 1164, 1027, 994 and 812 cm^{-1}; δ_H (270 MHz) 7.70-7.26 (4H, m, H-2 and H-6 of Ts, both diast), 7.38-7.31 (4H, m, H-3 and H-5 of Ts, both diast), 4.52 (1H, d, J 1.0 Hz, H-5, major diast), 4.41 (1H, d, J 5.5 Hz, H-5, minor diast), 3.94 (1H, dt, J 11.5 and 4.5 Hz, H-4, minor diast), 3.69 (1H, dt, J 10.0 and 2.5 Hz, H-4, major diast), 2.89 (1H, dd, J 19.5 and 2.2 Hz, H-3, major diast), 2.75 (1H, dd, J 19.5 and 10.0 Hz, H-3, major diast), 2.60 (2H, d, J 6.0 Hz, H-3, minor diast), 2.42 (6H, s, Me of Ts, both diast) and 0.80 (18H, s, H-6, both diast); *m/z* (EI) 296 $[M]^+$, 281 $[M\text{-Me}]^+$, 239 $[M\text{-}t\text{-Bu}]^+$, 214, 155, 139 $[M\text{-Ts}]^+$, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 57, 44 (Found: C, 60.76; H, 6.74. $C_{15}H_{20}O_4S$ requires C, 60.79; H, 6.80%).

Preparation of (*E*,*E*)-5-(5,7-nonadienyl)-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (13e).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 2.52 mmol scale starting from (*E*,*E*)-2-hydroxy-5-(5,7-nonadienyl)-4-(4-tolylsulfonyl)tetrahydrofuran (**12e**) to give, after chromatography (60%→80% ether–petrol), a 1:1 mixture of diastereomers (A:B) of (*E*,*E*)-5-(5,7-nonadienyl)-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13e**) (0.753 g, 82%) as a colourless oil. Small amounts of each isomer were separated; diastereomer A, R_f 0.29, 80% ether–petrol; ν_{max} (film) 2929, 1788, 1597, 1493, 1446, 1322, 1146, 1086, 990, 817, 714 and 664 cm^{-1}; δ_H (270 MHz) 7.76 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts), 7.38 (2H, d, J 8.0 Hz, H-3 and H-5 of Ts), 5.83-5.26 (2H, m, H-6' and H-7'), 5.63-5.37 (2H, m, H-5' and H-8'), 4.78-4.82 (1H, m, H-5), 3.62 (1H, td, J 10.0 and 6.0 Hz, H-4), 2.96 (1H, dd, J 19.0 and 10.0 Hz, H-3), 2.75 (1H, dd, J 19.0 and 10.0 Hz, H-3), 2.43 (3H, s, Me of Ts), 2.31-1.90 (2H, m, H-1'), 1.70 (3H, d, J 7.0 Hz, H-9'), 1.64-1.52 (2H, m, H-2') and 1.43-1.22 (4H, m, H-3' and H-4'); *m/z* (EI) 206 $[M\text{-Ts}]^+$, 177, 151, 137, 124, 91 $[C_7H_7]^+$, 81, 41, 28 (Found: C, 66.61; H, 7.22. $C_{20}H_{26}O_4S$ requires C, 66.27; H, 7.23%). Diastereomer B, R_f 0.20, 80% ether–petrol; ν_{max} (film) 2929, 1788, 1597, 1493, 1446, 1322, 1146, 1086, 990, 817, 714 and 664 cm^{-1}; δ_H (270 MHz) 7.75 (2H, d, J 8.0 Hz, H-2 and H-6 of Ts), 7.37 (2H, d, J 8.0 Hz, H-3 and H-5 of Ts), 6.03-5.93 (2H, m, H-6' and H-7'), 5.65-5.41 (2H, m, H-5' and H-8'), 4.82-4.71 (1H, m, H-5), 4.04-3.89 (1H, m, H-4), 2.95 (1H, dd, J 17.0 and 7.5 Hz, H-3), 2.57 (1H, dd, J 17.0 and 10.0 Hz, H-3), 2.44 (3H, s, Me of Ts), 2.30-1.93 (2H, m, H-1'), 1.79-1.55 (5H, m, H-2' and H-9') and 1.55-1.41 (4H, m, H-3' and H-4'); *m/z* (EI) 206 $[M\text{-Ts}]^+$, 177, 151, 137, 124, 91 $[C_7H_7]^+$, 81, 41, 28 (Found: C, 66.53; H, 7.34. $C_{20}H_{26}O_4S$ requires C, 66.27; H, 7.23%).

Preparation of 5-benzyloxymethyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (13f).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 0.671 mmol scale starting from 5-benzyloxymethyl-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12f**) to give, after chromatography (60% ether–petrol), a 1:1 mixture of diastereomers of 5-benzyloxymethyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13f**) (0.195 g, 81%) as a colourless oil; R_f 0.26 and 0.13, 80% ether–petrol;

ν_{max} (film) 3033, 2928, 2859, 1790, 1598, 1494, 1456, 1365, 1313, 1285, 1143, 1118, 1030, 813, 743, 703 and 662 cm^{-1}; δ_H (270 MHz) 7.75 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts), 7.74 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts), 7.52-7.21 (14H, m, H-3' and H-6' of Ts and Ph, both diast), 5.02 (1H, m, H-5), 4.93 (1H, m, H-5), 4.66 (1H, d, J 12.0 Hz, CH_2Ph), 4.53 (1H, d, J 12.0 Hz, CH_2Ph), 4.52 (1H, d, J 12.0 Hz, CH_2Ph), 4.43 (1H, d, J 12.0 Hz, CH_2Ph), 4.20-3.94 (4H, m, H-4 and H-1', both diast), 3.76 (1H, dd, J 11.5 and 3.0 Hz, H-1'), 3.49 (1H, dd, J 11.5 and 3.0 Hz, H-1'), 3.07 (1H, dd, J 18.0 and 9.0 Hz, H-3), 2.90 (1H, d, J 2.0 Hz, H-3), 2.87 (1H, s, H-3), 1.45 (3H, s, Me of Ts) and 1.43 (3H, s, Me of Ts); *m/z* (EI) 360 $[M]^+$, 278, 253 $[M\text{-}BnO]^+$, 246, 237, 214, 205 $[M\text{-}Ts]^+$, 139, 124, 107 $[BnO]^+$, 99 $[M+H\text{-}Ts\text{-}BnO]^+$, 91 $[C_7H_7]^+$, 88 (Found: $[M\text{-}BnO]^+$, 253.0531. $C_{19}H_{20}O_5S$ requires $[M\text{-}BnO]^+$, 253.0535).

Preparation of 5-[2-benzyloxyethyl]-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (13g) and 5-[2-benzyloxyethyl]-2(5*H*)-furanone (14g).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 3.23 mmol scale starting from 5-[2-benzyloxyethyl]-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12g**) to give, after chromatography (30%→60% ether–petrol), a combination of a 2:1 mixture of diastereomers of 5-[2-benzyloxyethyl]-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13g**) (0.569 g, 47%) and 5-[2-benzyloxyethyl]-2(5*H*)-furanone[14] (**14g**) (0.245 g, 35%), both as colourless oils; **13g**: R_f 0.35 and 0.24, 80% ether–petrol; ν_{max} (film) 2867, 2291, 1788, 1595, 1450, 1362, 1320, 1146, 1087, 816 and 741 cm^{-1}; δ_H (270 MHz) 7.78-7.70 (4H, m, H-2 and H-6 of Ts, both diast), (14H, m, H-3 and H-5 of Ts and Ph, both diast), 5.29-5.03 (2H, m, H-5, both diastereomers), 4.48 (2H, d, J 12.0 Hz, CH_2Ph, minor diast), 4.47 (2H, d, J 12.0 Hz, CH_2Ph, major diast), 4.06-3.92 (4H, m, H-2', both diast), 3.97-3.65 (1H, m, H-4, minor diast), 3.62-3.47 (1H, m, H-4, major diast), 2.97 (1H, dd, J 18.5 and 6.3 Hz, H-3, major diast), 2.83 (1H, dd, J 18.5 and 10.0 Hz, H-3, major diast), 2.73-2.61 (2H, m, H-3, minor diast), 2.46 (3H, s, Me of Ts, minor diast), 2.45 (3H, s, Me of Ts, major diast) and 2.00-1.91 (4H, m, H-1', both diast); *m/z* (EI) 374 $[M]^+$, 286, 267 $[M\text{-}OBn]^+$, 246, 219 $[M\text{-}Ts]^+$, 214, 182, 146, 124, 112 $[M\text{-}Ts\text{-}OBn]^+$, 107 $(OBn)^+$, 91 $[C_7H_7]^+$, 84 (Found: C, 64.32; H, 6.21. $C_{20}H_{22}O_5S$ requires C, 64.15; H, 5.92%); **14g**: R_f 0.38, 80% ether–petrol; ν_{max} (film) 2866, 1755, 1601, 1451, 1362, 1164, 1101, 1017, 904, 817, 744 and 701 cm^{-1}; δ_H (270 MHz) 7.51 (1H, dd, J 5.5 and 1.5 Hz, H-4), 7.48-7.27 (5H, m, Ph), 6.07 (1H, dd, J 5.5 and 2.0 Hz, H-3), 5.26-5.20 (1H, m, H-5), 4.53 (1H, d, J 12.0 Hz, CH_2Ph), 4.48 (1H, d, J 12.0 Hz, CH_2Ph), 3.73-3.56 (2H, m, H-2'), 2.35-2.01 (1H, m, H-1') and 1.99-1.87 (1H, m, H-1'); *m/z* (EI) 218 $[M]^+$, 188, 159, 146, 140, 133, 127 $[M\text{-}Bn]^+$, 112 $[M+H\text{-}OBn]^+$, 91 $[C_7H_7]^+$, 84 (Found: C, 71.84; H, 6.41. $C_{13}H_{14}O_3$ requires C, 71.54; H, 6.47%).

Preparation of 5-(5-*t*-butyldimethylsilyloxypentyl)-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (13h).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 0.511 mmol scale starting from 5-[5-(*t*-butyldimethylsilyloxy)pentyl]-2-hydroxy-4-(4-tolylsulfonyl)tetrahydrofuran (**12h**) to give, after chromatography (30%→70% ether–petrol), a 1:1 mixture of diastereomers of 5-(5-*t*-butyldimethylsilyloxypentyl)-4-(4-tolylsulfonyl)-2-oxotetrahydrofuran (**13h**) (0.194 g, 86%) as a colourless oil; R_f 0.68 and 0.55, ether; ν_{max} (film) 2937, 2860, 1787, 1598, 1462, 1318, 1254, 1151, 1096, 837, 776 and 666 cm^{-1}; δ_H (270 MHz) 7.79-7.76 (4H, m, H-2 and H-6 of Ts, both diast), (4H, m, H-3 and H-5 of Ts, both diast), 4.86-4.78 (2H, m, H-5, both diast), 3.98 (1H, q, J 8.0 Hz, H-4), 3.63-3.55 (5H, m, H-5', both diast and H-4), 3.02-2.91 (2H, m, H-3), 2.76 (1H, dd, J 18.5 and 11.0 Hz, H-3), 2.59 (1H, dd, J 18.5 and 8.5 Hz, H-3), 2.47 (3H, s, Me of Ts), 2.46 (3H, s, Me of Ts), 1.67-1.21 (16H, m, H-1' to H-4', both diast), 0.88 (18H, s, *t*-Bu, both diast) and 0.04 (12H, s, SiMe, both diast); *m/z* (EI) 383 $[M\text{-}t\text{-}Bu]^+$, 269, 246, 241 $[M\text{-}TsH\text{-}Me]^+$, 227 $[M\text{-}TsH\text{-}t\text{-}Bu]^+$, 124, 107, 91 $[C_7H_7]^+$, 75 (Found: $[M\text{-}t\text{-}Bu]^+$, 383.1348. $C_{22}H_{36}O_5SSi$ requires $[M\text{-}t\text{-}Bu]^+$, 383.1348).

Preparation of (*E*)-2-oxo-5-propenyl-4-(4-tolylsulfonyl)tetrahydrofuran (13i).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 1.50 mmol scale starting from (*E*)-2-hydroxy-5-propenyl-4-(4-tolylsulfonyl)tetrahydrofuran (**12i**) to give, after chromatography (70% ether–petrol), a 7:1 mixture of diastereomers of (*E*)-2-oxo-5-propenyl-4-(4-tolylsulfonyl)tetrahydrofuran (**13i**) (0.345 g, 83%) as a colourless, oily solid; R_f 0.33 and 0.19, 80% ether–petrol; ν_{max} (film) 2926, 1786, 1597, 1448, 1318, 1150, 1087, 970, 812, 718 and 662 cm^{-1}; δ_H (270 MHz) 7.79-7.72 (4H, m, H-2 and H-6 of Ts, both diast), 7.42-7.23 (4H, m, H-3 and H-5 of Ts, both diast), 5.88-5.82 (1H, octet, J 4.0 Hz, H-7, minor diast), 5.82-5.72 (1H, octet, J 4.0 Hz, H-7, major diast), 5.34-5.25 (2H, m, H-6, both diast), 5.23-5.11 (2H, m, H-5, both diast), 3.72-3.68 (2H, m, H-5, both diast), 3.10 (1H, dd, J 18.0 and 9.0 Hz, H-3, minor diast), 3.03 (1H, dd, J 18.0 and 7.0 Hz, H-3, major diast), 2.81 (1H, dd, J 18.0 and 9.0 Hz, H-3, minor diast), 2.68 (1H, dd, J 18.0 and 7.0 Hz, H-3, major diast), 2.48 (6H, s, Me of Ts, both diast) and 1.68-1.50 (6H, d, J 7.0 Hz, H-8, both diast); *m/z* (EI) 281 $[M+H]^+$, 267 $[M-Me]^+$, 239 $[M-C_3H_5]^+$, 214, 193, 139, 124 $[M-TsH]^+$, 91 $[C_7H_7]^+$, 69, 41 (Found: $[M+H]^+$, 281.0848. $C_{14}H_{16}O_4S$ requires $[M+H]^+$, 281.0848).

Preparation of 2-oxo-5-phenyl-4-(4-tolylsulfonyl)tetrahydrofuran (13j).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 0.873 mmol scale starting from 2-hydroxy-5-phenyl-4-(4-tolylsulfonyl)tetrahydrofuran (**12j**) to give, after chromatography (50% ether–petrol), a 1:1 mixture of diastereomers of 2-oxo-5-phenyl-4-(4-tolylsulfonyl)tetrahydrofuran (**13j**) (0.247 g, 89%) as an oily pale yellow solid; R_f 0.59 and 0.24, 80% ether–petrol; ν_{max} (film) 3047, 2925, 2859, 1789, 1730, 1678, 1598, 1501, 1452, 1410, 1317, 1226, 1153, 1087, 1024, 816, 750, 740 and 666 cm^{-1}; δ_H (270 MHz) 7.78 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts), 7.40-7.14 (16H, m, H-2', H-3', H-5' and H-6' of Ts and Ph, both diast), 5.92 (1H, d, J 4.0 Hz, H-5), 5.81 (1H, d, J 4.0 Hz, H-5), 4.36 (1H, ddd, J 13.5, 7.0 and 6.0 Hz, H-4), 3.90 (1H, ddd, J 10.0, 5.0 and 4.0 Hz, H-4), 3.33 (1H, dd, J 18.0 and 6.0 Hz, H-3), 3.04 (1H, dd, J 18.5 and 5.0 Hz, H-3), 2.93 (1H, dd, J 18.0 and 13.5 Hz, H-3), 2.89 (1H, dd, J 18.5 and 10.0 Hz, H-3), 2.46 (3H, s, Me of Ts) and 2.39 (3H, s, Me of Ts); *m/z* (EI) 316 $[M]^+$, 314, 246, 210, 196, 193, 180, 165, 160 [M-TsH), 105, 91 $C_7H_7]^+$, 77 $[C_6H_5]^+$, 65 (Found: $[M]^+$, 316.0770. $C_{17}H_{16}O_4S$ requires $[M]^+$, 316.0769).

Preparation of 5-(3-methoxyphenyl)-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (13k).

This was prepared analogously to 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran on a 0.980 mmol scale starting from 2-hydroxy-5-(3-methoxyphenyl)-4-(4-tolylsulfonyl)tetrahydrofuran (**12k**) to give, after chromatography (50% ether–petrol), a 1:1 mixture of diastereomers of 5-(3-methoxyphenyl)-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13k**) (0.297 g, 87%) as a pale yellow, oily solid; R_f 0.38 and 0.21, 80% ether–petrol; ν_{max} (film) 3096, 3068, 2964, 2929, 1790, 1602, 1497, 1466, 1324, 1291, 1268, 1148, 1086, 963, 778, 726, 704 and 663 cm^{-1}; δ_H (270 MHz) 7.78 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts), 7.76 (2H, d, J 8.5 Hz, H-2 and H-6 of Ts), 7.38 (2H, d, J 8.5 Hz, H-3 and H-5 of Ts), 7.34 (2H, d, J 8.5 Hz, H-3 and H-5 of Ts), 7.21 (2H, d, J 9.0 Hz, H-4 of MeOPh, both diast), 6.83 (2H, dd, J 9.0 and 2.5 Hz, H-5 of MeOPh, both diast), 6.72 (2H, d, J 9.0 Hz, H-6 of MeOPh, both diast), 6.63 (2H, s, H-2 of MeOPh, both diast), 5.95 (1H, d, J 4.5 Hz, H-5), 5.83 (1H, d, J 4.5 Hz, H-5), 4.29 (1H, ddd, J 13.0, 5.5 and 4.5 Hz, H-4), 3.90 (1H, ddd, J 9.0, 4.5 and 4.5 Hz, H-4), 3.30 (1H, dd, J 18.0 and 5.5 Hz, H-3), 3.03 (1H, dd, J 18.0 and 4.5 Hz, H-3), 2.91 (1H, dd, J 18.0 and 13.0 Hz, H-3), 2.89 (1H, dd, J 18.0 and 9.0 Hz, H-3), 2.44 (3H, s, Me of Ts) and 2.35 (3H, s, Me of Ts); *m/z* (EI) 346 $[M]^+$, 307, 293, 279, 190 $[M-TsH]^+$, 167, 149 $[M+H-MeOPh-Bn]^+$, 135, 107 $(MeOPh]^+$, 91 $[C_7H_7]^+$, 71, 57 (Found: $[M]^+$, 346.0875. $C_{18}H_{18}O_5S$ requires $[M]^+$, 346.0875).

Preparation of 5-undecyl-2(5*H*)-furanone (14a).

To a solution of 2-oxo-4-(4-tolylsulfonyl)-5-undecyltetrahydrofuran (**13a**) (0.131 g, 0.794 mmol) in CH_2Cl_2 (7.9 ml) at -78°C under a nitrogen atmosphere was added DBU (71.2 µl, 0.476 mmol, 0.6 eq) causing the reaction to become golden-yellow in colour. After 3 h the solution was quenched with AcOH (0.48 ml of a 1M solution in THF, 0.476 mmol, 0.6 eq) and allowed to warm to rt. After the addition of water (5 ml), the organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 x 10 ml). The combined organic layers were washed with water (2 x 10 ml), dried ($MgSO_4$), concentrated under reduced pressure and purified by chromatography (50% ether–petrol), to give 5-undecyl-2(5*H*)-furanone[15] (**14a**) (65 mg, 93%) as a colourless solid; mp 36°C, R_f 0.45, 70% ether–petrol; ν_{max} (CH_2Cl_2) 2922, 2855, 1743, 1597, 1473, 1361, 1323, 1175, 1107, 1094, 1008, 904, 828, 718 and 704 cm^{-1}; δ_H (270 MHz) 7.45 (1H, dd, J 5.5 and 1.5 Hz, H-4), 6.10 (1H, dd, J 5.5 and 2.0 Hz, H-3), 5.03 (1H, ddt, J 7.0, 5.5 and 1.5 Hz, H-5), 1.75-1.18 (20H, m, H-6 to H-15) and 0.87 (3H, t, J 6.0 Hz, H-16); *m/z* (EI) 238 $[M]^+$, 178, 167 $[M-C_5H_{11}]^+$, 165, 151, 140 $[M+H-C_7H_{15}]^+$, 125 $[M-C_8H_{17}]^+$, 122, 111 $[M-C_9H_{19}]^+$, 97 $[M-C_{10}H_{21}]^+$, 84 $[M+H-C_{11}H_{23}]^+$, 57, 55, 43, 41 (Found: $[M]^+$, 238.1926. $C_{15}H_{26}O_2$ requires $[M]^+$, 238.1933).

Preparation of 5-isopropyl-2(5*H*)-furanone (14b).

This was prepared analogously to 5-undecyl-2(5*H*)-furanone on a 0.522 mmol scale starting from 5-isopropyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13b**) to give, after chromatography (50% ether–petrol), 5-isopropyl-2(5*H*)-furanone[16] (**14b**) (57.0 mg, 87%) as a colourless oil; R_f 0.35, 70% ether–petrol; ν_{max} (film) 2965, 2930, 1758, 1600, 1466, 1295, 1164, 1129, 1092, 1033, 994, 914, 891, 833 and 814 cm^{-1}; δ_H (270 MHz) 7.44 (1H, dd, J 6.0 and 1.5 Hz, H-4), 6.12 (1H, dd, J 6.0 and 2.0 Hz, H-3), 4.94 (1H, dt, J 6.0 and 2.0 Hz, H-5), 2.01 (1H, octet, J 6.0 Hz, H-6) and 1.00 (6H, d, J 6.0 Hz, H-7); *m/z* (EI) 126 $[M]^+$, 111 $[M-Me]^+$, 109, 97 $[M-C_2H_5]^+$, 91, 84 $[M+H-i-Pr]^+$, 71, 57, 55, 43, 41 (Found: $[M]^+$, 126.0681. $C_7H_{10}O_2$ requires $[M]^+$, 126.0681).

Preparation of 5-cyclohexyl-2(5*H*)-furanone (14c).

This was prepared analogously to 5-undecyl-2(5*H*)-furanone on a 0.434 mmol scale starting from 5-cyclohexyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13c**) to give, after chromatography (40% ether–petrol), 5-cyclohexyl-2(5*H*)-furanone[17] (**14c**) (68.8 mg, 95%) as a colourless solid; mp 38-39°C, R_f 0.52, 70% ether–petrol; ν_{max} (CH_2Cl_2) 2923, 2856, 2335, 1745, 1600, 1557, 1450, 1332, 1170, 1114, 1034, 979, 910 and 831 cm^{-1}; δ_H (270 MHz) 7.47 (1H, dd, J 5.5 and 1.5 Hz, H-4), 6.11 (1H, dd, J 5.5 and 2.0 Hz, H-3), 4.84 (1H, dt, J 5.5 and 1.5 Hz, H-5), 1.84-1.50 (7H, m, 2 x H-6, H-7 and H-11 and 1 x H-8 and H-10) and 1.35-1.01 (4H, m, 2 x H-9 and 1 x H-8 and H-10); *m/z* (EI) 166 $[M]^+$, 145, 124 $[M-C_3H_6]^+$, 111 $[M+H-C_4H_8]^+$, 97 $[M+H-C_5H_{10}]^+$, 84 $[M+H-C_6H_{11}]^+$, 55, 41 (Found: C, 72.12; H, 8.41. $C_{10}H_{14}O_2$ requires C, 72.26; H, 8.49%).

Preparation of 5-*t*-butyl-2(5*H*)-furanone (14d).

This was prepared analogously to 5-undecyl-2(5*H*)-furanone on a 1.23 mmol scale starting from 5-*t*-butyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13d**) to give, after chromatography (40% ether–petrol), 5-*t*-butyl-2(5*H*)-furanone[18] (**14d**) (0.161 g, 93%) as a colourless solid; mp 58-59°C, R_f 0.42, 70% ether–petrol; ν_{max} (CH_2Cl_2) 2966, 2873, 1825, 1798, 1753, 1601, 1470, 1369, 1331, 1195, 1172, 1100, 1058, 1011, 993, 912, 887, 830 and 706 cm^{-1}; δ_H (270 MHz) 7.45 (1H, d, J 5.5 Hz, H-4), 6.16 (1H, dd, J 5.5 and 1.5 Hz, H-3), 4.71 (1H, d, J 1.5 Hz, H-5) and 0.99 (9H, s, *t*-Bu); *m/z* (EI) 140 $[M]^+$, 125 $[M-Me]^+$, 97 $[M-C_3H_7]^+$, 84 [M-*t*-Bu], 57, 41, 29 (Found: C, 68.41; H, 8.63. $C_8H_{12}O_2$ requires C, 68.55; H, 8.63%).

Preparation of (*E*,*E*)-5-(5,7-nonadienyl)-2(5*H*)-furanone (14e).

This was prepared analogously to 5-undecyl-2(5*H*)-furanone on a 1.25 mmol scale starting from (*E*,*E*)-5-(5,7-nonadienyl)-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13e**) to give, after chromatography (50% ether–petrol), (*E*,*E*)-5-(5,7-nonadienyl)-2(5*H*)-furanone (**14e**) (0.235 g, 91%) as a colourless oil; R_f 0.38, 70% ether–petrol; ν_{max} (film) 2930, 2857, 1755, 1601, 1441, 1331, 1163, 1104, 990, 818 and 705 cm^{-1}; δ_H (270 MHz) 7.42 (1H, dd, J 6.0 and 1.5 Hz, H-4), 6.01 (1H, dd, J 6.0 and 2.0 Hz, H-3), 6.00-5.87 (2H, m, H-6' and H-7'), 5.56-5.40 (2H, m, H-5' and H-8'), 4.97 (1H, td, J 3.7 and 1.7 Hz, H-5), 2.12-1.97 (2H, m, H-1'), 1.78-1.46 (5H, m, H-2' and H-9') and 1.44-1.20 (4H, m, H-3' and H-4'); *m/z* (EI) 206 $[M]^+$, 177 $[M+H-C_2H_4]^+$, 161, 151, 107, 93, 81, 79, 67, 41 (Found: C, 75.94; H, 8.95. $C_{13}H_{18}O_2$ requires C, 75.69; H, 8.79%).

Preparation of 5-benzyloxymethyl-2(5*H*)-furanone (14f).

This was prepared analogously to 5-undecyl-2(5*H*)-furanone on a 0.345 mmol scale starting from 5-benzyloxymethyl-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13f**) to give, after chromatography (50% ether–petrol), 5-benzyloxymethyl-2(5*H*)-furanone[19] (**14f**) (61.5 mg, 93%) as a colourless oil; R_f 0.31, 70% ether–petrol; ν_{max} (film) 2863, 1751, 1601, 1493, 1449, 1362, 1328, 1263, 1205, 1161, 1127, 1099, 1027, 955, 922, 890, 866, 818, 742, 699 and 675 cm^{-1}; δ_H (270 MHz) 7.49 (1H, dd, J 6.0 and 1.5 Hz, H-4), 7.40-7.25 (5H, m, Ph), 6.17 (1H, dd, J 6.0 and 2.0 Hz, H-3), 5.17 (1H, tt, J 5.0 and 2.0 Hz, H-5), 4.57 (2H, s, CH_2Ph), 3.74 (1H, dd, J 10.5 and 5.5 Hz, H-1') and 3.67 (1H, dd, J 10.5 and 5.0 Hz, H-1'); *m/z* (EI) 204 $[M]^+$, 174, 160 $[M-CO_2]^+$, 149, 128, 121, 115, 108 $[BnOH]^+$, 107 $[BnO]^+$, 105, 98 $[M+H-OBn]^+$, 97 $[M-OBn]^+$, 77 $[C_6H_5]^+$ (Found: $[M]^+$, 204.0786. $C_{12}H_{12}O_2$ requires $[M]^+$, 204.0786).

Preparation of 5-[2-benzyloxyethyl]-2(5*H*)-furanone (14g).

This was prepared analogously to 5-undecyl-2(5*H*)-furanone on a 1.49 mmol scale starting from 5-[2-benzyloxyethyl]-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13g**) to give, after chromatography (60% ether–petrol), 5-[2-benzyloxyethyl]-2(5*H*)-furanone (**14g**) (0.294 g, 90%) as a colourless oil, identical in every way to material produced in the preparation of the starting material **13g** described above.

Preparation of 5-(5-*t*-butyldimethylsilyloxypentyl)-2(5*H*)-furanone (14h).

This was prepared analogously to 5-undecyl-2(5*H*)-furanone on a 0.248 mmol scale starting from 5-(5-*t*-butyldimethylsilyloxypentyl)-2-oxo-4-(4-tolylsulfonyl)tetrahydrofuran (**13h**) to give, after chromatography (40% ether–petrol), 5-[5-*t*-butyldimethylsilyloxypentyl]-2(5*H*)-furanone (**14h**) (66.3 mg, 94%) as a colourless oil; R_f 0.53, 70% ether–petrol; ν_{max} (film) 3094, 2930, 2858, 2316, 1758, 1601, 1542, 1465, 1385, 1330, 1254, 1161, 1101, 1026, 915, 894, 836, 776, 705 and 661 cm^{-1}; δ_H (270 MHz) 7.44 (1H, dd, J 6.0 and 1.5 Hz, H-4), 6.11 (1H, dd, J 6.0 and 2.0 Hz, H-3), 5.03 (1H, tdd, J 7.5, 5.5 and 1.5 Hz, H-5), 3.60 (2H, t, J 6.0 Hz, H-5'), 1.77-1.21 (8H, m, H-1' to H-4'), 0.89 (9H, s, *t*-Bu) and 0.04 (6H, s, MeSi); *m/z* (EI) 284 $[M]^+$, 227 $[M-t\text{-}Bu]^+$, 209, 199, 157, 135, 107, 101, 75, 73, 55 (Found: $[M-t\text{-}Bu]^+$, 227.1103. $C_{15}H_{28}O_3Si$ requires $[M-t\text{-}Bu]^+$, 227.1103).

Preparation of (*E*)-5-propenyl-2(3*H*)-furanone (14i).

This was prepared analogously to 5-undecyl-2(5*H*)-furanone on a 0.515 mmol scale starting from (*E*)-2-oxo-5-propenyl-4-(4-tolylsulfonyl)tetrahydrofuran (**13i**) to give, after chromatography (40% ether–petrol), 5-propenyl-2(3*H*)-furanone[20] (**14i**) (62.2 mg, 97%) as a colourless oil; R_f 0.58, 70% ether–petrol; ν_{max} (film) 2925, 2855, 1737, 1633, 1459, 1378, 1262, 1124, 801 and 741 cm^{-1}; δ_H (270 MHz) 6.20 (1H, dq, J 15.0 and

7.0 Hz, H-2'), 5.91 (1H, d, J 15.0 Hz, H-1'), 5.10 (1H, t, J 0.5 Hz, H-4), 3.27 (2H, br s, H-3) and 1.84 (3H, d, J 7.0 Hz, H-3'); *m/z* (EI) 124 $[M]^+$, 102, 83 $[M-C_3H_5]^+$, 81, 75, 73, 69, 55, 32 (Found: $[M]^+$, 124.0524. $C_7H_8O_2$ requires $[M]^+$, 124.0524).

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