Addition of allylstannanes to an oxy-stabilized carbenium ion on a 1,7-dioxaspiro[5.5]undecane ring system

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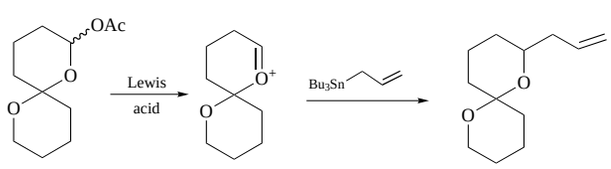
The nucleophilic addition of allylstannanes to (2*R,5*S**,6*S**)-2-acetoxy-5-benzyloxy-1,7-dioxaspiro-[5.5]undecane 1 has been studied. The optimum conditions involve the use of trimethylsilyl trifluoromethanesulfonate in dichloromethane at −78 °C. In the examples studied, substitution of the acetoxy group at C-2 proceeds from an axial direction, however, subsequent ring flipping of the substituted ring occurs as well affording allylated products in which the substituents at both C-2 and C-5 are equatorial.**

The 1,7-dioxaspiro[5.5]undecane ring system is an important structural feature in many biologically active compounds such as the polyether antibiotics, marine and plant toxins, insect pheromones and the antiparasitic agents—the milbemycins and the avermectins.[1] More recently cytotoxic and/or antineoplastic marine organism constituents such as the highly potent spongistatins[2] and the spirolides[3] have been found to contain spiroacetals bearing an allyl unit attached to the terminus of the spiroacetal ring system. We were therefore interested in developing methods to append an allyl unit to C-2 of the 1,7-dioxaspiro-[5.5]undecane ring system.

The majority of synthetic approaches to substituted spiroacetals[1] have involved incorporation of the appropriate substituents into dihydroxy ketone precursors (or synthetic equivalents thereof) which then undergo cyclization to a spiroacetal ring system. Our approach reported herein focuses on further functionalization of a basic 1,7-dioxaspiro[5.5]-undecane framework *via* stereocontrolled addition of allylstannanes to a C-2 centred oxocarbenium ion. A related approach by Mead[4] using allylsilanes as the nucleophilic component has recently been reported and prompted us to publish our work in this area.

Whereas Mead's work focused on the addition of allylsilanes to a C-2 centred spirooxocarbenium ion derived from a 2-methoxy-1,7-dioxaspiro[5.5]undecane ring system our attention focused on the use of a 2-acetoxyspiroacetal to generate the oxocarbenium ion (Scheme 1). In an effort to effect selective

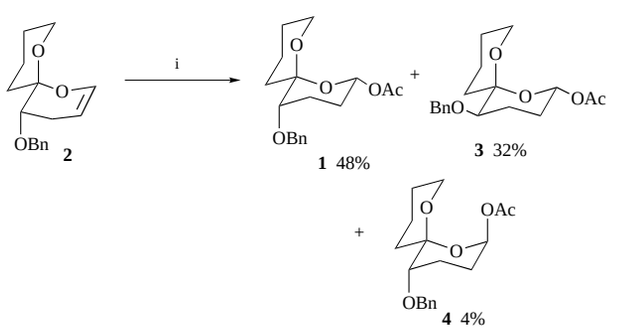


Scheme 1

reaction of the lactol acetate leaving the spiroacetal intact, we also chose to use allylstannanes which being more nucleophilic than allylsilanes[5] would require milder conditions for generation of the electrophilic species. Whilst the use of glycosyl acetates as precursors to oxocarbenium ions in carbohydrate chemistry is well established, use of anomeric spiroacetal acetates in a spirodipyran system has not been studied. The generation of spirooxocarbenium ion intermediates is also rare.[4,6]

In order to probe the stereochemical course of these reactions attention focused on the use of spiroacetal **1** which contained an axial benzyloxy substituent at C-5. Upon treatment with acid, spiroacetal **1** would undergo thermodynamically controlled ring opening/ring closure to afford the more stable spiroacetal in which the benzyloxy group adopts a more favourable equatorial position. Monitoring the stereochemistry at C-5 would therefore provide evidence as to whether addition of the allylstannane to the C-2 centred oxocarbenium ion preceded or followed opening of the spiroacetal ring.

Hydration of alkene **2** followed by acetylation (Scheme 2)



Scheme 2 *Reagents and conditions*: i, THF, H_2O, *p*-TsOH, room temp., then Ac_2O, Et_3N, DMAP (cat.), CH_2Cl_2

afforded 2-acetoxy spiroacetals **1** and **3** with an equatorial acetate group at C-2 as major products, together with spiroacetal **4** where the acetate group was axial, as a minor product. The methine proton, H-5, in spiroacetal **1** resonated as a triplet at $\delta = 3.15$ ppm with the magnitude of the coupling constant, $J = 2.4$ Hz, establishing that the benzyloxy substituent assumed an axial position whilst H-2 resonated as a double doublet at $\delta = 5.69$ ppm with the coupling constants, $J = 9.7$ and 2.8 Hz, establishing that the acetate group occupied an equatorial position. The substrate required for the present work, namely spiroacetal **1**, was easily separated from the other spiroacetals **3** and **4** by flash chromatography and the stereochemistry was confirmed by X-ray crystallography (Fig. 1).

The optimum conditions for reaction of spiroacetal **1** with allyltributylstannane (entry 1, Table 1) involved the use of TMSOTf as the Lewis acid in dichloromethane at −78 °C using 3 equivalents of the stannane. Under these conditions the equatorial C-2 allylated spiroketal **5a** was isolated in 72% yield. The double doublet at $\delta = 3.26$ ppm with coupling constants $J = 11.1$ and 4.9 Hz, assigned to H-5, confirmed that the benzyloxy group at C-5 now occupied a more stable equatorial position.

Whilst the ^{1}H NMR data readily assigned the benzyloxy and allyl groups to equatorial positions, the conformation

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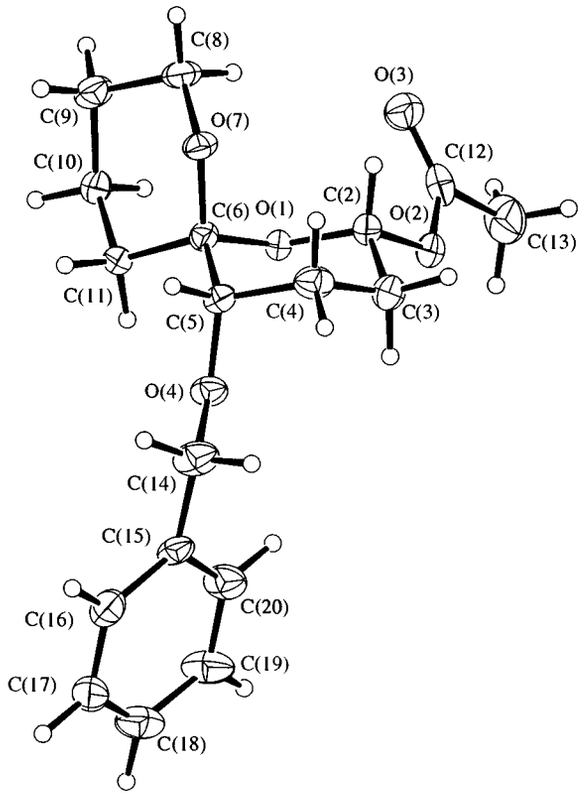
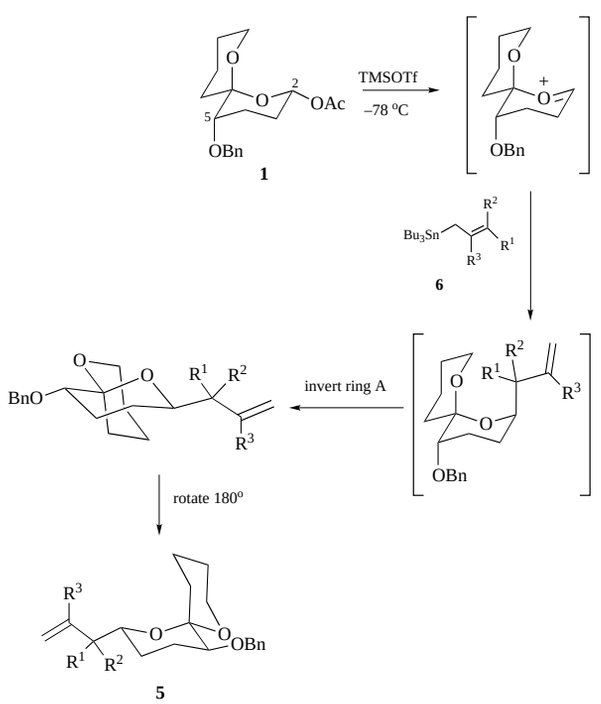


Fig. 1 A labelled ORTEP[23] projection of **1** with thermal ellipsoids depicted at the 25% level

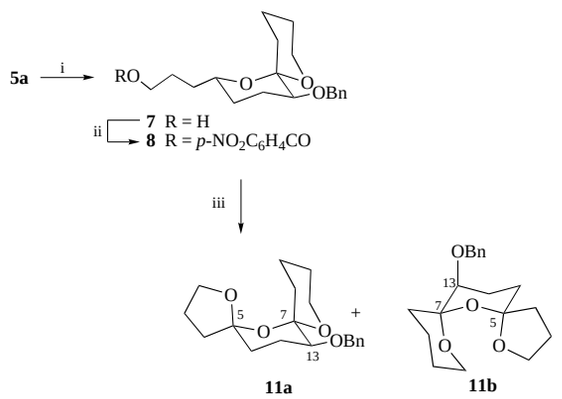


a $R^1 = R^2 = R^3 = H$
b $R^1 = R^2 = H$; $R^3 = Me$
c $R^1 = R^2 = Me$; $R^3 = H$
d $R^1 = C_6H_5$; $R^2 = R^3 = H$
e $R^1 = Me$; $R^2 = R^3 = H$
f $R^1 = R^3 = H$; $R^2 = OSiBu^tMe_2$
g $R^1 = R^2 = H$; $R^3 = CH_2CH_2OSiBu^tPh_2$
h $R^1 = R^2 = H$; $R^3 = CH_2CH_2OH$

that the spiroacetals adopted needed addressing. In order to address this issue spiroacetal **5a** underwent hydroboration with diborane in THF providing alcohol **7** which was then converted to its *p*-nitrobenzoate derivative **8** in order to provide crystals suitable for X-ray diffraction. The resultant crystal structure for **8** (Fig. 2) confirmed that although the substituents at C-5 and C-2 adopted equatorial positions, the conformation of the

Table 1 Reaction of spiroacetal **1** with allylstannanes and TMSOTf in CH_2Cl_2 at −78 °C

Entry	Allylstannane	Product(s)	Time	Yield (%)
1	**6a**	**5a**	8 h	72
2	**6b**	**5b**	8 h	67
3	**6c**	**5c**	10 h	52
4	**6d**	**5d**	16 h	37
5	**6e**	**5e**	16 h	65
6	**6f**	**5f**	16 h	28
7	**6g**	**5g**	6 h	58



Scheme 3 *Reagents and conditions*: i, BH_3·THF, NaOH, H_2O_2, 0 °C to room temp., 68%; ii, *p*-$NO_2C_6H_4COCl$, Et_3N, DMAP (cat.), CH_2Cl_2, 89%; iii, $PhI(OAc)_2$, I_2, cyclohexane, room temp., 66%

spirocentre had changed and did not represent the most stable arrangement of O-1 and O-7 as predicted by the anomeric effect.[7]

The isolation of allylated spiroacetal **5a** as the only product from the addition of allylstannane **6a** to spiroacetal **1** in the presence of TMSOTf can be rationalized by axial approach of the stannane onto the oxycarbenium ion, followed by ring flipping of the disubstituted A ring in order to relieve unfavourable 1,3-diaxial interactions between the allyl group and 8-CH_2. This ring flip proceeded at the expense of a stabilizing anomeric effect at the spirocentre.

Reaction of spiroacetal **1** with more functionalized allylstannanes (entries 2–7, Table 1) also afforded spiroacetal products in which both the C-2 allyl group and the C-5 benzyloxy group occupied equatorial positions. It is also noted however, that tetrahydropyran products resulting from addition of the allylstannane to the spirocentre and C-2 (*e.g.* **9**) were not observed.

In an effort to promote selective reaction at C-2, spiroacetal **10** which bears an acetate group at C-3 was prepared with the anticipation that this additional acetate group would stabilize the incipient oxycarbenium ion formed at C-2 by neighbouring group participation. It was also of interest as to whether the C-3 acetate group had any effect on the stereochemical outcome of the reaction. We were, however, somewhat disappointed to find that using a variety of Lewis acids the successful addition of allylsilanes and allylstannanes to **10** was not realized despite extensive investigation. Spiroacetal **10** tended to decompose to a complex mixture of products and we attribute this to the increased steric hindrance by the neighbouring acetate group towards attack of the allylating agent on the C-2 oxocarbenium ion derived from **10**.

The formation of oxaspiro rings by H-abstraction promoted by hypervalent iodine reagents has been applied to the synthesis of the bis-spiroacetal moiety of the polyether antibiotic salinomycin[8] and in the synthesis of chiral spiroacetals from carbohydrates.[9] In the present work the synthetic utility of the C-2 allylated spiroacetals was demonstrated by the conversion of allylspiroacetals **5a** and **5g** to the tricyclic bis-spiroacetals **11**

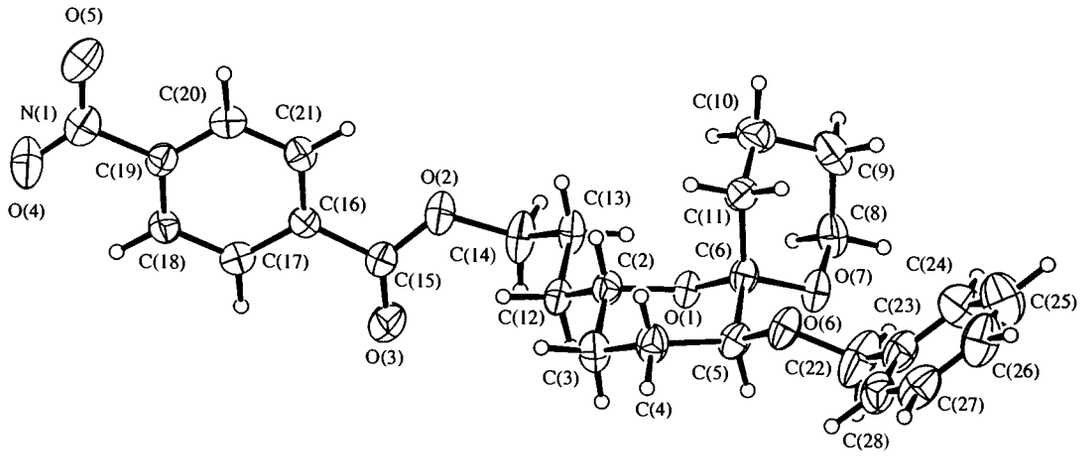
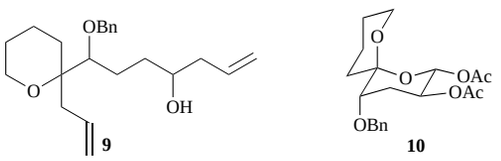
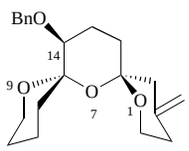


Fig. 2 A labelled ORTEP[23] projection of **8** with thermal ellipsoids depicted at the 25% level

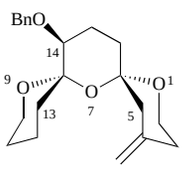


9

10



12a



12b

and **12** respectively. Thus, hydroboration of **5a** afforded alcohol **7** in 68% yield which upon treatment with iodobenzene diacetate and iodine underwent oxidative cyclization to a 1 : 1.5 mixture of bis-spiroacetals **11a** and **11b** in 66% yield (Scheme 3). The *cis* and *trans* isomers of bis-spiroacetal **11** were readily separated by flash chromatography and the stereochemistry established by NMR spectroscopy.

The ^{1}H NMR spectrum of **11a** exhibited a double doublet at δ 3.25 ppm (J = 7.5 and 4.4 Hz) indicating an equatorial disposition of the benzyloxy group at C-13. For bis-spiroacetal **11b** this same proton resonates as a double doublet at δ 3.26 ppm (J = 3.2 and 1.5 Hz) indicating an axial disposition for the benzyloxy group in this case. The major isomer **11b** exhibits three anomeric effects whilst **11a** exhibits only two anomeric effects. Further evidence for formation of bis-spiroacetals **11a** and **11b** was indicated in the IR spectra which lacked an hydroxy group absorption and by the observation of a second quaternary carbon at δ 106.2 and 107.2 ppm respectively, characteristic of the newly formed spirocentre. Similar spectral characteristics have been reported in a related system by Suarez *et al.*[9a]

Whilst cyclization of **7** led to formation of a 1,6,8-trioxadispiro[4.1.5.3]pentadecane ring system the homologous 1,7,9-trioxadispiro[5.1.5.3]hexadecane ring system was formed by oxidative cyclization of alcohol **5h**. Treatment of alcohol **5h** obtained after desilylation of allylspiroacetal **5g**, with iodobenzene diacetate and iodine afforded a 1.33 : 1 mixture of bis-spiroacetals **12a** and **12b** in 70% yield. Once again the ^{1}H NMR spectra of these isomers allowed ready assignment of stereochemistry. Thus, 14-H resonated as a double doublet at δ 3.46 ppm (J = 4.7 and 3.4 Hz) in the *cis* isomer **12b** which was significantly deshielded relative to the same proton in the *trans* isomer **12a** which resonated at δ 3.26 ppm (J = 6.8 and 4.3 Hz) due to its close proximity to O-1. The vicinal coupling constants observed for 14-H in **12b** suggest that the central ring adopts a skew-boat conformation in order to relieve unfavourable steric interactions between the methylene groups at C-5 and C-13. A similar conformation was observed for an analogous bis-spiroacetal.[10]

In summary the nucleophilic addition of allylstannanes to an oxy-stabilized carbenium ion on a 1,7-dioxaspiro[5.5]undecane ring system has been investigated. Placement of an axial benzyloxy group at C-5 on the spiroacetal ring allowed the stereochemical course of these reactions to be studied. The allylated spiroacetals thus formed can be readily transformed into tricyclic bis-spiroacetals.

Experimental

Mps were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 Fourier Transform infra-red spectrophotometer as a thin film between sodium chloride plates. Elemental analyses were performed at the Microanalytical Laboratory, University of New South Wales, Sydney, Australia. ^{1}H NMR spectra were recorded in deuteriochloroform on a Bruker AC 200 (200.13 MHz) at ambient temperature. All J values are given in Hz. ^{13}C NMR spectra were recorded on a Bruker AC 200 (50.3 MHz), spectrometer at ambient temperature with complete proton decoupling. Data are expressed in parts per million downfield shifted from tetramethylsilane as an internal standard and reported as position (δ_C). Low resolution mass spectra were recorded on a VG70-250S, a VG70-SD or a AEI model MS902 double focusing magnetic sector mass spectrometer operating with an ionization potential of 70 eV (EI, DEI, CI and DCI). High resolution mass spectra were recorded at a nominal resolution of 5000 or 10 000 as appropriate. Major fragments are given as percentages relative to the base peak and assigned where possible. Ionization methods employed were (i) electron impact (EI), (ii) desorption electron impact (DEI), (iii) chemical ionization with ammonia as reagent gas (CI) and (iv) desorption chemical ionization (DCI) with methane as reagent gas. Low resolution chemical ionization mass spectra were also recorded on a Hewlett Packard 5989A mass spectrometer using methane as reagent gas with the sample dissolved in methanol. Flash chromatography was performed using Merck Kieselgel 60 or Riedel-de Haen Kieselgel (both 230–400 mesh) with the indicated solvents. Thin layer chromatography (TLC) was performed using 0.2 mm thick precoated silica gel plates (Merck Kieselgel 60 F_{254} or Riedel-de Haen Kieselgel S F_{254}). Compounds were visualized by ultraviolet fluorescence or by staining with iodine or vanillin in methanolic sulfuric acid.

(5*S,6*S**)-5-Benzyloxy-1,7-dioxaspiro[5.5]undec-2-ene 2**

To a suspension of sodium hydride (353 mg, 8.82 mmol) in dry tetrahydrofuran (15 cm^3) at 0 °C was added dropwise a solution of (5*S**,6*S**)-1,7-dioxaspiro[5,5]undec-2-en-5-ol[11] (1.25 g, 7.35

mmol) in dry tetrahydrofuran (25 cm^3) under an argon atmosphere and the resultant suspension allowed to stir at 0 °C for 1 h. Benzyl bromide (1.38 g, 8.1 mmol) was added, the reaction mixture allowed to warm to room temperature and stirred for 24 h. After quenching with sodium dihydrogen phosphate solution (15 cm^3, 10% w/v), the reaction mixture was extracted with ethyl acetate (3 × 100 cm^3), washed with water (40 cm^3) and dried over sodium sulfate. Removal of the solvent under reduced pressure gave a pale yellow oil which was purified by flash chromatography using hexane–ethyl acetate (9:1) as eluent to afford the *title compound* **2** (1.59 g, 83%) as a colourless oil (Found: C, 74.23; H, 8.08. $C_{16}H_{20}O_3$ requires C, 73.81; H, 7.75%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2946s, 2872s (CH), 1654m (C=C), 1601, 1454, 1228, 1203, 1099, 1029, 908, 792; δ_H(200 MHz; $CDCl_3$) 1.23–2.32 (8H, m, 4 × CH_2), 3.40–3.44 (1H, m, 5_{eq}-H), 3.60–3.69 (1H, m, 8_{eq}-H), 3.76–3.89 (1H, m, 8_{ax}-H), 4.50 (1H, d, $J_{A,B}$ 12.2, OC$H_A$$H_B$Ar), 4.67 (1H, d, $J_{B,A}$ 12.2, OC$H_A$$H_B$Ar), 4.70 (1H, m, 3-H), 6.27–6.32 (1H, m, 2-H), 7.25–7.38 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 17.9, 21.7, 24.9, 30.4 (CH_2, C-9, C-10, C-11 and C-4), 61.3 (CH_2, C-8), 71.1 (CH_2, O*C*H_2Ar), 74.3 (CH, C-5), 96.2 (quat., C-6), 98.7 (CH, C-3), 127.5, 127.8, 128.1, 128.6, 128.8 (CH, Ar-C), 138.1 (quat., Ar-C), 139.7 (CH, C-2); *m*/*z* 260 (M^+, 8%), 204 (38), 175 (32), 113 (100) and 91 (C_7H_7, 50).

(2*R,5*S**,6*S**)-, (2*R**,5*R**,6*S**)- and (2*S**,5*S**,6*S**)-2-Acetoxy-5-benzyloxy-1,7-dioxaspiro[5.5]undecane 1, 3 and 4**

To a solution of (5*R**,6*R**)-5-benzyloxy-1,7-dioxaspiro-[5.5]undec-2-ene **2** (680 mg, 2.62 mmol) in a mixture of THF–H_2O (4:1) (30 cm^3) was added toluene-*p*-sulfonic acid (20 mg). The mixture was stirred and heated to 35–40 °C for 48 h. Progress of the reaction was monitored by TLC. Additional amounts of toluene-*p*-sulfonic acid were added if the progress was too slow. The mixture was neutralized by the addition of a saturated solution of sodium hydrogen carbonate (10 cm^3). The aqueous layer was extracted with dichloromethane (3 × 40 cm^3). The combined organic layers were washed with brine (20 cm^3) and dried over sodium sulfate. Removal of the solvent under reduced pressure gave a colourless oil which was used directly in the next step.

To a solution of the above mixture of hemiacetals in dichloromethane (30 cm^3) at room temperature, was added dry triethylamine (398 mg, 3.93 mmol), followed by acetic anhydride (321 mg, 3.14 mmol) and 4-dimethylaminopyridine (5 mg) and the reaction mixture was stirred, gently at room temperature for 3 h or until no starting material could be detected by TLC. The reaction mixture was quenched with water (10 cm^3), extracted with dichloromethane (2 × 50 cm^3) and dried over sodium sulfate. Removal of the solvent under reduced pressure gave a colourless oil which was purified by flash chromatography using hexane–ethyl acetate (8.5:1.5) as eluent to afford:

(i) (2*R**,5*S**,6*S**)-2-Acetoxy-5-benzyloxy-1,7-dioxaspiro-[5.5]undecane **1** (400 mg, 47.8%) as colourless needles, mp 75–76 °C (from hexane) (Found: C, 67.48; H, 7.86. $C_{18}H_{24}O_5$ requires C, 67.47; H, 7.55%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2947m, 2869m (CH), 1740s (C=O, acetate), 1450, 1368, 1087, 1206; δ_H(200 MHz; $CDCl_3$) 1.23 (1H, ddd, $J_{11ax,11eq}$ 13.4, $J_{11ax,10ax}$ 13.4 and $J_{11ax,10eq}$ 4.3, 11_{ax}-H), 1.40–2.22 (9H, m, 4 × CH_2 and 11_{eq}-H), 2.09 (3H, s, Ac), 3.15 (1H, t, *J* 2.4, 5_{eq}-H), 3.59–3.71 (1H, m, 8_{eq}-H), 4.01–4.14 (1H, m, 8_{ax}-H), 4.45 (1H, d, $J_{A,B}$ 12.1, OC$H_A$$H_B$Ar), 4.66 (1H, d, $J_{B,A}$ 12.1, OC$H_A$$H_B$Ar), 5.96 (1H, dd, $J_{2ax,3ax}$ 9.7, $J_{2ax,3eq}$ 2.8, 2_{ax}-H), 7.20–7.39 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 17.9, 21.0, 23.9, 25.0, 31.5 (CH_2, C-9, C-10, C-11, C-4 and C-3), 21.3 (CH_3, Ac), 61.2 (CH_2, C-8), 71.2 (CH_2, O*C*H_2Ar), 74.7 (CH, C-5), 89.6 (CH, C-2), 99.5 (quat., C-6), 127.6, 127.9, 128.2 (CH, Ar-C), 138.2 (quat., Ar-C), 169.8 (quat., C=O); *m*/*z* (CI, CH_4) 319 (M − H, 0.1%), 261 (M − OAc, 100), 153 (M − OAc − OBn, 54) and 61 (18).

(ii) (2*R**,5*R**,6*S**)-2-Acetoxy-5-benzyloxy-1,7-dioxaspiro-[5.5]undecane **3** (265 mg, 31.6%) as a colourless oil (Found: C, 67.49; H, 7.71. $C_{18}H_{24}O_5$ requires C, 67.47; H, 7.55%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2948m, 2872m (CH), 1747s (C=O, acetate), 1454, 1371, 1236, 1071, 1045, 980; δ_H(200 MHz; $CDCl_3$) 1.20–2.12 (10H, m, 5 × CH_2), 2.10 (3H, s, Ac), 3.24 (1H, dd, $J_{5ax,4ax}$ 9.2, $J_{5ax,4eq}$ 5.8, 5_{ax}-H), 3.77–3.85 (1H, m, 8_{eq}-H), 4.01–4.14 (1H, m, 8_{ax}-H), 4.50 (1H, d, $J_{A,B}$ 12.2, OC$H_A$$H_B$Ar), 4.67 (1H, d, $J_{B,A}$ 12.2, OC$H_A$$H_B$Ar), 5.95 (1H, dd, $J_{2ax,3ax}$ 10.0, $J_{2ax,3eq}$ 2.4, 2_{ax}-H), 7.19–7.41 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 18.0, 21.8, 24.6, 29.2, 30.4 (CH_2, C-9, C-10, C-11, C-4 and C-3), 21.2 (CH_3, Ac), 61.6 (CH_2, C-8), 71.6 (CH_2, O*C*H_2Ar), 77.8 (CH, C-5), 89.0 (CH, C-2), 99.0 (quat., C-6), 127.7, 128.2, 128.3 (CH, Ar-C), 138.3 (quat., Ar-C), 169.5 (quat., C=O); *m*/*z* (CI, CH_4) 319 (M − H, 0.1%), 261 (M − OAc, 100), 153 (M − OAc − OBn, 74) and 61 (33).

(iii) (2*S**,5*S**,6*S**)-2-Acetoxy-5-benzyloxy-1,7-dioxaspiro-[5.5]undecane **4** (35 mg, 4.2%) as a colourless oil (Found: C, 67.50; H, 7.82. $C_{18}H_{24}O_5$ requires C, 67.47; H, 7.55%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2947m, 2870m (CH), 1730s (C=O, acetate), 1453, 1255, 1364, 1064, 1182, 1228; δ_H(200 MHz; $CDCl_3$) 1.20–2.21 (10H, m, 5 × CH_2), 2.09 (3H, s, Ac), 3.32 (1H, dd, *J* 3.0 and 1.1, 5_{eq}-H), 3.57–3.65 (1H, m, 8_{eq}-H), 3.72–3.85 (1H, m, 8_{ax}-H), 4.48 (1H, d, $J_{A,B}$ 12.0, OC$H_A$$H_B$Ar), 4.66 (1H, d, $J_{B,A}$ 12.0, OC$H_A$$H_B$Ar), 6.15 (1H, d, $J_{2eq,3ax}$ 2.43, 2_{eq}-H), 7.18–7.39 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 17.7, 18.0, 23.2, 25.0, 32.6 (CH_2, C-9, C-10, C-11, C-4 and C-3), 21.2 (CH_3, Ac), 62.0 (CH_2, C-8), 71.8 (CH_2, O*C*H_2Ar), 76.8 (CH, C-5), 92.1 (CH, C-2), 97.5 (quat., C-6), 127.7, 128.2, 128.3 (CH, Ar-C), 138.2 (quat., Ar-C), 171.3 (quat., C=O); *m*/*z* (CI, CH_4) 319 (M − H, 0.1%), 261 (M − OAc, 64), 153 (M − OAc − OBn, 100), 107 (17) and 91 (C_7H_7, 26).

General procedure for the preparation of the stannanes (6b–e)

The appropriate allyl chloride (6 mmol) was added to a mixture of tributyltin chloride (1.36 cm^3, 1.63 g, 5 mmol), a crystal of iodine and magnesium turnings (156 mg, 6.5 mmol) in THF (10 cm^3) using the procedure reported by Naruta *et al.*[12] The ^{1}H NMR data were in agreement with those reported in the literature.[12,13,14]

1-(*tert*-Butyldimethylsilyloxy)-3-(tributylstannyl)propene 6f

The title compound was prepared from *tert*-butyldimethylsilylallyl ether (2.58 g, 15 mmol) and tributyltin chloride (4.47 cm^3, 16.6 mmol) following the procedure by Keck *et al.*[15] as a colourless oil (3.9 g, 60%). The ^{1}H and ^{13}C NMR spectra were in agreement with those reported in the literature.[15]

4-(*tert*-Butyldiphenylsilyloxy)-2-[(tributylstannyl)methyl]but-1-ene 6g

The title compound was prepared in 70% yield as a colourless oil according to the method reported by Weigand *et al.*[13] The spectroscopic data were in agreement with those reported in the literature.[13]

General procedure for allylation

The lactol acetate **1**, the appropriate stannane (2.5–3 equiv.) and powdered molecular sieves (200 mg, 4 Å) in dichloromethane (8 cm^3) were placed under an atmosphere of dry argon. The solution was cooled to −78 °C, a catalytic quantity of trimethylsilyl trifluoromethanesulfonate was added and the reaction mixture was stirred whilst warming to room temperature. Progress of the reaction was monitored by TLC. After the reaction was complete, the solvent was removed *in vacuo*, the residue taken up in diethyl ether and washed once with pH 7 phosphate buffer (10 cm^3). The ether layer was added to a saturated aqueous solution of potassium fluoride and the mixture was stirred vigorously for 30 min, whereupon tributyltin(IV) fluoride precipitated. After removal of the salts by filtration, the organic phase was dried over anhydrous sodium sulfate and concentrated to give an oil which was purified by flash chromatography using hexane–ethyl acetate as eluent to give the allylated products:

(2*R,5*S**,6*S**)-2-(Prop-2′-enyl)-5-benzyloxy-1,7-dioxaspiro-[5.5]undecane 5a**

The *title compound* **5a** was prepared from (2*R**,5*S**,6*S**)-2-acetoxy-5-benzyloxy-1,7-dioxaspiro[5.5]undecane **1** (183 mg, 0.57 mmol) and allyltributyltin **6a** as a colourless oil (124 mg, 72%) (Found: C, 75.65; H, 9.04. $C_{19}H_{26}O_3$ requires C, 75.45; H, 8.67%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3066w (=CH), 2947s, 2876m (CH), 1641w (C=C), 1454, 1357, 1224, 1081; δ_H(200 MHz; $CDCl_3$) 0.90–2.12 (10H, m, 5 × CH_2), 2.14–2.42 (2H, m, CH_2CH=CH_2), 3.26 (1H, dd, $J_{5ax,4ax}$ 11.1, $J_{5ax,4eq}$ 4.9, 5_{ax}-H), 3.36–3.49 (1H, m, 2_{ax}-H), 3.64–3.78 (1H, m, 8_{eq}-H), 3.96–4.18 (1H, m, 8_{ax}-H), 4.60 (1H, d, $J_{A,B}$ 12.1, OCH_AH$_B$Ar), 4.85 (1H, d, $J_{B,A}$ 12.1, OCH$_A$$H_B$Ar), 5.02–5.12 (2H, m, CH=CH_2), 5.79–6.00 (1H, m, CH=CH$_2$), 7.15–7.45 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 17.5, 22.4, 25.5, 26.6, 30.5 (CH_2, C-9, C-10, C-11, C-4 and C-3), 40.4 (CH, CH_2CH=CH_2), 61.4 (CH_2, C-8), 71.6 (CH, C-2), 72.6 (CH_2, OCH_2Ar), 79.8 (CH, C-5), 99.9 (quat., C-6), 116.5 (CH_2, CH=CH_2), 127.3, 127.7, 128.2 (CH, Ar-C), 135.3 (CH, CH=CH_2), 139.2 (quat., Ar-C); *m*/*z* (CI, CH_4) 303 (MH^+, 14%), 285 (M − OH, 16), 261 (M − C_3H_5, 16), 195 (M − OBn, 100) and 91 (C_7H_7, 24).

(2*R,5*S**,6*S**)-2-(2′-Methylprop-2′-enyl)-5-benzyloxy-1,7-dioxaspiro[5.5]undecane 5b**

The *title compound* **5b** was prepared from (2*R**,5*S**,6*S**)-2-acetoxy-5-benzyloxy-1,7-dioxaspiro[5.5]undecane **1** (85 mg, 0.27 mmol) and 2-methyl-3-(tributylstannyl)prop-1-ene **6b** as a colourless oil (57 mg, 67%) (Found: C, 75.47; H, 9.26. $C_{20}H_{28}O_3$ requires C, 75.90; H, 8.92%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2997w, 2946s, 2876m (CH), 1602w (C=C), 1454, 1357, 1290, 1115, 1090, 1004; δ_H(200 MHz; $CDCl_3$) 1.30–2.05 (10H, m, 5 × CH_2), 1.79 (3H, s, CH_3), 2.12 [1H, dd, $J_{1'a,1'b}$ 13.8, $J_{1'a,2ax}$ 4.9, CH_aH$_b$C(CH$_3$)=CH$_2$], 2.31 [1H, dd, $J_{1'b,1'a}$ 13.8, $J_{1'b,2ax}$ 7.6, CH$_a$$H_b$C(CH$_3$)=CH$_2$], 3.26 (1H, dd, $J_{5ax,4ax}$ 11.1, $J_{5ax,4eq}$ 4.9, 5_{ax}-H), 3.48–3.61 (1H, m, 2_{ax}-H), 3.63–3.76 (1H, m, 8_{eq}-H), 4.03–4.14 (1H, m, 8_{ax}-H), 4.60 (1H, d, $J_{A,B}$ 12.0, OCH_AH$_B$Ar), 4.85 (1H, d, $J_{B,A}$ 12.0, OCH$_A$-H_BAr), 4.74–4.80 (2H, m, =CH_2), 7.18–7.42 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 17.5, 22.3, 25.5, 26.7, 30.9 (CH_2, C-9, C-10, C-11, C-4 and C-3), 23.1 [CH_3, C(CH_3)=CH_2)], 44.2 [CH_2, CH_2C(CH$_3$)=CH$_2$], 61.4 (CH_2, C-8), 70.7 (CH, C-2), 72.7 (CH_2, OCH_2Ar), 79.9 (CH, C-5), 96.9 (quat., C-6), 112.4 [CH_2, C(CH$_3$)=CH_2], 127.3, 127.7, 128.2 (CH, Ar-C), 139.2 (quat., Ar-C), 142.9 [quat., C(CH$_3$)=CH$_2$]; *m*/*z* 316 (M^+, 4%), 261 (M − C_4H_7, 26), 225 (M − $C_6H_5CH_2$, 16) and 91 (C_7H_7, 100).

(2*R,5*S**,6*S**)-2-(1′,1′-Dimethylprop-2′-enyl)-5-benzyloxy-1,7-dioxaspiro[5.5]undecane 5c**

The *title compound* **5c** was prepared from (2*R**,5*S**,6*S**)-2-acetoxy-5-benzyloxy-1,7-dioxaspiro[5.5]undecane **1** (120 mg, 0.375 mmol) and 2-methyl-4-(tributylstannyl)but-2-ene **6c** as a colourless oil (64 mg, 52%) (Found: C, 76.67; H, 9.29. $C_{21}H_{30}O_3$ requires C, 76.31; H, 9.16%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3085w (=CH), 2948m, 2869s (CH), 1637w (C=C), 1495, 1454, 1356, 1113, 1082, 1012; δ_H(200 MHz; $CDCl_3$) 1.20–2.05 (10H, m, 5 × CH_2), 1.05 (3H, s, Me), 1.07 (3H, s, Me), 3.10 (1H, dd, $J_{2ax,3eq}$ 1.9, $J_{2ax,3ax}$ 11.0, 2_{ax}-H), 3.19 (1H, dd, J 5.1, 7.0, 5_{ax}-H), 3.68–3.76 (1H, m, 8_{eq}-H), 4.05–4.19 (1H, m, 8_{ax}-H), 4.58 (1H, d, $J_{A,B}$ 12.0, OCH_AH$_B$Ar), 4.86 (1H, d, $J_{B,A}$ 12.0, OCH$_A$$H_B$Ar), 4.95 (1H, dd, $J_{3'a,2'}$ 5.9, $J_{3'a,3'b}$ 1.4, CH=CH$_a$$H_b$), 5.02 (1H, br s, CH=C$H_aH_b$), 5.88–6.03 (1H, m, C$H$=CH$_2$), 7.19–7.40 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 17.4, 21.9, 25.3, 25.6, 27.0 (CH_2, C-9, C-10, C-11, C-4 and C-3), 23.3, 23.7 (CH_3, 2 × Me), 40.4 (quat., CMe$_2$), 61.4 (CH_2, C-8), 72.7 (CH_2, OCH_2Ar), 78.3 (CH, C-2), 80.3 (CH, C-5), 100.0 (quat., C-6), 111.7 (CH_2, CH=CH_2), 127.2, 127.6, 128.2 (CH, Ar-C), 139.3 (quat., Ar-C), 145.4 (CH, CH=CH$_2$); *m*/*z* (CI, CH_4) 331 (MH^+, 37%), 316 (M − CH_3, 25), 261 (M − C_5H_4, 27), 223 (M − OBn, 100) and 91 (C_7H_7, 20).

(2*R,5*S**,6*S**,1′*R**)- and (2*R**,5*S**,6*S**,1′*S**)-2-(1′-Phenylprop-2′-enyl)-5-benzyloxy-1,7-dioxaspiro[5.5]undecane 5d**

The *title compound* **5d** was prepared from (2*R**,5*S**,6*S**)-2-acetoxy-5-benzyloxy-1,7-dioxaspiro[5.5]undecane **1** (120 mg, 0.375 mmol) and (*E*)-1-phenyl-3-(tributylstannyl)prop-1-ene **6d** as a colourless oil (53 mg, 37%) (Found: C, 79.06; H, 7.99. $C_{25}H_{30}O_3$ requires C, 79.33; H, 7.99%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3006m, 2928s, 2855m (CH), 1601w (C=C), 1454, 1099, 1001; δ_H(200 MHz; $CDCl_3$) 0.84–1.95 (10H, m, 5 × CH_2), 2.05–2.19 (1H, m, CHPh), 3.12 (1H, t, J 2.6, 5_{eq}-H), 3.36 (1H, t, J 8.0, 2_{ax}-H), 3.48–3.54 (1H, m, 8_{eq}-H), 3.75–3.86 (1H, m, 8_{ax}-H), 4.41 (1H, d, $J_{A,B}$ 12.2, OCH_AH$_B$Ar), 4.63 (1H, d, $J_{B,A}$ 12.2, OCH$_A$-H_BAr), 5.00 (1H, dt, $J_{3'b,2'}$ 17.0, $J_{3'b,3'a}$ 1.5, $3'_b$-H), 5.11 (1H, dt, $J_{3'a,2'}$ 10.4, $J_{3'a,3'b}$ 1.5, $3'_a$-H), 6.33 (1H, ddd, $J_{2',3'b}$ 17.1, $J_{2',3'a}$ 10.1 and $J_{2',1'}$ 7.5, 2′-H), 7.10–7.39 (10H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 18.2, 22.2, 23.6, 25.4, 32.2 (CH_2, C-9, C-10, C-11, C-4 and C-3), 55.5 (CH, CHPh), 60.4 (CH_2, C-8), 70.9 (CH_2, OCH_2Ar), 72.2 (CH, C-2), 75.3 (CH, C-5), 96.9 (quat., C-6), 116.1 (CH_2, CH=CH_2), 126.4, 127.5, 128.0, 128.2, 128.3, 128.6 (CH, Ar-C), 139.0 (quat., Ar-C), 139.2 (CH, CH=CH$_2$); *m*/*z* (CI, CH_4) 379 (MH^+, 9%), 271 (M − OBn, 18), 261 (M − C_9H_9, 18), 107 (BnO, 25) and 91 (C_7H_7, 11).

(2*R,5*S**,6*S**,1′*R**)- and (2*R**,5*S**,6*S**,1′*S**)-2-(1′-Methylprop-2′-enyl)-5-benzyloxy-1,7-dioxaspiro[5.5]undecane 5e**

The *title compound* **5e** was prepared from (2*R**,5*S**,6*S**)-2-acetoxy-5-benzyloxy-1,7-dioxaspiro[5.5]undecane **1** (100 mg, 0.31 mmol) and (*E*)-4-(tributylstannyl)but-2-ene **6e** as a colourless oil (64 mg, 65%) (Found: M^+, 316.2044. $C_{20}H_{28}O_3$ requires *M*, 316.2038); $\nu_{max}(CHCl_3)/cm^{-1}$ 3006m, 2947s, 2856m (CH), 1680m (C=C), 1454, 1356, 1098, 1009, 919; δ_H(200 MHz; $CDCl_3$) 0.85–2.08 (10H, m, 5 × CH_2), 1.14 (3H, d, J 6.7, Me), 2.13–2.31 (1H, m, CHMe), 3.11 (1H, ddd, $J_{2ax,1'}$ 8.4, $J_{2ax,3ax}$ 11.0 and $J_{2ax,3eq}$ 2.3, 2_{ax}-H), 3.24 (1H, dd, $J_{5ax,4eq}$ 5.1, $J_{5ax,4ax}$ 11.5, 5_{ax}-H), 3.65–3.79 (1H, m, 8_{eq}-H), 4.04–4.19 (1H, m, 8_{ax}-H), 4.59 (1H, d, $J_{A,B}$ 12.1, OCH_AH$_B$Ar), 4.85 (1H, d, $J_{B,A}$ 12.1, OCH$_A$-H_BAr), 4.95–5.08 (2H, m, CH=CH_2), 5.70 (1H, ddd, $J_{2',3'b}$ 17.1, $J_{2',3a}$ 10.0 and $J_{2',1'}$ 8.1, 2′-H), 7.20–7.45 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 16.9 (CH_3, Me), 17.5, 22.0, 25.6, 26.9, 29.2 (CH_2, C-9, C-10, C-11, C-4 and C-3), 44.0 (CH, CHMe), 61.5 (CH_2, C-8), 72.7 (CH_2, OCH_2Ar), 75.1 (CH, C-2), 80.1 (CH, C-5), 100.0 (quat., C-6), 114.7 (CH_2, CH=CH_2), 127.3, 127.7, 128.2 (CH, Ar-C), 139.3 (quat., Ar-C), 140.8 (CH, CH=CH$_2$); *m*/*z* (CI, CH_4) 317 (MH^+, 22%), 302 (M − CH_3, 16), 261 (M − C_4H_7, 32), 209 (M − OBn, 100) and 91 (C_7H_7, 21).

Modified procedure for 5f–g

The following modifications were made to the above general allylation procedure: the potassium fluoride was omitted and the reaction was quenched by the addition of a saturated solution of sodium hydrogen carbonate. The aqueous layer was extracted with dichloromethane and the combined organic layers were washed with water and dried over sodium sulfate.

(2*R,5*S**,6*S**,1′*R**)- and (2*R**,5*S**,6*S**,1′*S**)-2-(1′-tert-Butyldimethylsilyloxyprop-2′-enyl)-5-benzyloxy-1,7-dioxaspiro[5.5]-undecane 5f**

The *title compound* **5f** was prepared from (2*R**,5*S**,6*S**)-2-acetoxy-5-benzyloxy-1,7-dioxaspiro[5.5]undecane **1** (160 mg, 0.5 mmol) and the stannane **6f** as a colourless oil (62 mg, 28%) (Found: M^+, 432.2701. $C_{25}H_{40}O_4Si$ requires *M*, 432.2695); $\nu_{max}(CHCl_3)/cm^{-1}$ 3006w, 2954s, 2857m (CH), 1602w (C=C), 1462, 1360, 1257, 1206, 1094, 1006, 837; δ_H(200 MHz; $CDCl_3$) 0.11 (6H, m, $SiMe_2$), 0.9 (9H, m, Bu^t), 1.18–2.07 (10H, m, 5 × CH_2), 3.15–3.40 (2H, m, 5_{ax}-H and 2_{ax}-H), 3.62–3.80 (1H, m, 8_{eq}-H), 4.05–4.22 (2H, m, 8_{ax}-H and CHOSi), 4.60 (1H, d, $J_{A,B}$ 12.0, OCH_AH$_B$Ar), 4.83 (1H, d, $J_{B,A}$ 12.0, OCH$_A$$H_B$Ar), 5.05–5.25 (2H, m, CH=CH_2), 5.72–5.91 (1H, m, CH=CH$_2$), 7.15–7.36 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) −4.7, −4.4 (CH_3, Me_2Si), 17.1, 22.2, 25.5, 26.7, 27.4 (CH_2, C-9, C-10, C-11,

C-4 and C-3), 18.2 (quat., *C*Me$_3$), 25.8 (CH$_3$, CMe$_3$), 61.3 (CH$_2$, C-8), 72.7 (CH$_2$, O*C*H$_2$Ar), 75.4 (CH, C-2), 76.4 (CH, CHOSi), 80.2 (CH, C-5), 100.1 (quat., C-6), 116.0 (CH$_2$, CH=*C*H$_2$), 127.3, 127.6, 128.2 (CH, Ar-C), 137.3 (CH, *C*H=CH$_2$), 139.3 (quat., Ar-C); *m*/*z* 432 (M$^+$, 6%), 341 (M − C$_6$H$_5$CH$_2$, 70), 241 (20), 91 (C$_6$H$_5$CH$_2$, 100) and 73 (45).

(2*R,5*S**,6*S**)-2-[2′-(2″-*tert*-Butyldiphenylsilyloxyethyl)prop-2′-enyl]-5-benzyloxy-1,7-dioxaspiro[5.5]undecane 5g**

The *title compound* **5g** was prepared from (2*R**,5*S**,6*S**)-2-acetoxy-5-benzyloxy-1,7-dioxaspiro[5.5]undecane **1** (50 mg, 0.156 mmol) and the stannane **6g** as a colourless oil (53 mg, 58%) (Found: M$^+$, 584.3328. C$_{37}$H$_{48}$O$_4$Si requires *M*, 584.3322); ν_{max}(CHCl$_3$)/cm^{-1} 3028w (=CH), 2946s, 2858m (CH), 1602w (C=C), 1455, 1428, 1360, 1226, 1111, 1008, 899, 822; δ_H(200 MHz; CDCl$_3$) 1.05 (9H, s, Bu^t), 1.25–2.28 (12H, m, 6 × CH$_2$), 2.36 (2H, t, *J* 6.9, C*H*$_2$CH$_2$OSi), 3.25 (1H, dd, $J_{5ax,4ax}$ 11.1 and $J_{5ax,4eq}$ 4.9, 5$_{ax}$-H), 3.39–3.53 (1H, m, 2$_{ax}$-H), 3.67–3.75 (1H, m, 8$_{eq}$-H), 3.78 (2H, t, *J* 6.9, C*H*$_2$OSi), 3.99–4.10 (1H, m, 8$_{ax}$-H), 4.60 (1H, d, $J_{A,B}$ 12.0, OC*H*$_A$H$_B$Ar), 4.85 (1H, d, $J_{B,A}$ 12.0, OCH$_A$*H*$_B$Ar), 4.79–4.86 (2H, m, =C*H*$_2$), 7.28–7.44 (10H, m, Ar-H) and 7.66–7.70 (5H, m, Ar-H); δ_C(50 MHz; CDCl$_3$) 17.5, 22.3, 25.5, 26.7, 30.9 (CH$_2$, C-9, C-10, C-11, C-4 and C-3), 19.2 (quat., *C*Me$_3$), 26.8 (CH$_3$, CMe$_3$), 39.3, 42.8 (CH$_2$, C-1′ and C-1″), 61.4 (CH$_2$, C-8), 62.9 (CH$_2$, *C*H$_2$OSi), 70.8 (CH, C-2), 72.7 (CH$_2$, O*C*H$_2$Ar), 79.9 (CH, C-5), 99.9 (quat., C-6), 113.4 (CH$_2$, =*C*H$_2$), 127.3, 127.6, 127.7, 128.2, 129.6, 135.6 (CH, Ar-C), 133.9, 139.2 (quat., Ar-C), 143.6 (quat., *C*=CH$_2$); *m*/*z* (CI, CH$_4$) 585 (MH$^+$, 9%), 477 (M − OBn, 22), 399 (M − OBn − C$_6$H$_5$, 20), 329 (M − C$_{16}$H$_{19}$OSi − OBn, 34), 261 (M − C$_{21}$H$_{27}$OSi, 57), 91 (C$_6$H$_5$CH$_2$, 24) and 153 (C$_9$H$_{13}$O$_2$, 100).

(2*R,5*S**,6*S**)-2-[2′-(2″-Hydroxyethyl)prop-2′-enyl]-5-benzyloxy-1,7-dioxaspiro[5.5]undecane 5h**

Tetra-*n*-butylammonium fluoride (0.31 cm^3 of a 1.0 M solution in tetrahydrofuran, 0.31 mmol) was added to a solution of **5g** (163 mg, 0.28 mmol) in dry tetrahydrofuran (10 cm^3) at room temperature under argon. After stirring for 30 min, the solvent was evaporated and the oily residue purified by flash chromatography, using hexane–ethyl acetate (7:3) as eluent to afford the *title compound* **5h** (87 mg, 90%) as a colourless oil (Found: M$^+$, 346.2150. C$_{21}$H$_{30}$O$_4$ requires *M*, 346.2144); ν_{max}(CHCl$_3$)/cm^{-1} 3450 (br s, OH), 3032w (=CH), 2946s, 2881s (CH), 1642w (C=C), 1454, 1357, 1262, 1080, 1047, 1009, 908; δ_H(200 MHz; CDCl$_3$) 1.27–2.28 (13H, m, 6 × CH$_2$ and OH), 2.35 (2H, t, *J* 6.3, C*H*$_2$CH$_2$OH), 3.23 (1H, dd, $J_{5ax,4ax}$ 11.1 and $J_{5ax,4eq}$ 4.9, 5$_{ax}$-H), 3.48–3.61 (1H, m, 2$_{ax}$-H), 3.70 (2H, t, *J* 6.3, C*H*$_2$OH), 3.67–3.73 (1H, m, 8$_{eq}$-H), 3.97–4.07 (1H, m, 8$_{ax}$-H), 4.57 (1H, d, $J_{A,B}$ 12.0, OC*H*$_A$H$_B$Ar), 4.82 (1H, d, $J_{B,A}$ 12.0, OCH$_A$*H*$_B$Ar), 4.90 (1H, br s, =C*H*$_A$H$_B$), 4.94 (1H, br s, =CH$_A$*H*$_B$), 7.16–7.39 (5H, m, Ar-H); δ_C(50 MHz; CDCl$_3$) 17.4, 22.2, 25.4, 26.6, 30.8 (CH$_2$, C-9, C-10, C-11, C-4 and C-3), 39.6, 41.9 (CH$_2$, C-1′ and C-1″), 60.4 (CH$_2$, C-8), 61.5 (CH$_2$, *C*H$_2$OH), 71.2 (CH, C-2), 72.7 (CH$_2$, O*C*H$_2$Ar), 79.8 (CH, C-5), 100.0 (quat., C-6), 114.0 (CH$_2$, =*C*H$_2$), 127.2, 127.6, 128.1 (CH, Ar-C), 139.1 (quat., Ar-C), 143.4 (quat., *C*=CH$_2$); *m*/*z* 346 (M$^+$, 0.15%), 261 (M − C$_5$H$_9$O, 7), 155 (M − C$_9$H$_{13}$O$_2$, 35), 96 (100), 107 (60) and 55 (82).

(6*R,8*S**,14*S**)- and (6*S**,8*S**,14*S**)-14-Benzyloxy-4-methylidene-1,7,9-trioxadispiro[5.1.5.3]hexadecane 12a and 12b**

A solution of the alcohol **5h** (70 mg, 0.20 mmol), iodine (102 mg, 0.40 mmol), and iodobenzene diacetate (129 mg, 0.40 mmol) in cyclohexane (20 cm^3) was purged with Ar and irradiated with a 500 W tungsten filament lamp. After 4 h, during which time the temperature was maintained at about 23 °C, the solution was diluted with diethyl ether (25 cm^3), washed with 10% aqueous sodium thiosulfate (20 cm^3), water (20 cm^3), brine (20 cm^3) and dried over potassium carbonate. The solvent was evaporated under reduced pressure and the resultant oil purified by flash chromatography using hexane–ethyl acetate (9:1 containing 1% of triethylamine) as eluent to afford:

(i) The less polar product identified as the (6*R**,8*S**,14*S**)-diastereomer **12a** as a colourless oil (28.0 mg, 40%) (Found: M$^+$, 344.1992. C$_{21}$H$_{28}$O$_4$ requires *M*, 344.1987); ν_{max}(CHCl$_3$)/cm^{-1} 3013m, 2949s, 2889m (CH), 1657w (C=C), 1361, 1260, 1095, 1050, 980, 911; δ_H(200 MHz; CDCl$_3$) 1.26–2.44 (13H, m, 6 × CH$_2$ and 5$_{eq}$-H), 2.65 (1H, d, $J_{5ax,5eq}$ 13.7, 5$_{ax}$-H), 3.24 (1H, dd, $J_{14ax,15ax}$ 6.8, $J_{14ax,15eq}$ 4.3, 14$_{ax}$-H), 3.58–3.79 (2H, m, 2$_{eq}$-H and 10$_{eq}$-H), 3.99–4.15 (2H, m, 2$_{ax}$-H and 10$_{ax}$-H), 4.63 (2H, s, OC*H*$_2$Ar), 4.83 (1H, br s, =C*H*$_A$H$_B$), 4.77 (1H, br s, =CH$_A$*H*$_B$), 7.19–7.39 (5H, m, Ar-H); δ_C(50 MHz; CDCl$_3$) 19.0, 21.0, 25.4, 29.9, 32.6, 34.0 (CH$_2$, C-3, C-11, C-12, C-13, C-15 and C-16), 44.7 (CH$_2$, C-5), 61.7 (CH$_2$, C-10), 62.0 (CH$_2$, C-2), 71.8 (CH$_2$, O*C*H$_2$Ar), 78.4 (CH, C-14), 98.4, 99.7 (quat., C-6 and C-8), 110.3 (CH$_2$, =*C*H$_2$), 127.4, 127.8, 128.2 (CH, Ar-C), 138.8 (quat., Ar-C), 142.1 (quat., *C*=CH$_2$).

(ii) The more polar product identified as the (6*S**,8*S**,14*S**)-diastereomer **12b** as a colourless oil (21.0 mg, 30%) (Found: M$^+$, 344.1991. C$_{21}$H$_{28}$O$_4$ requires *M*, 344.1987); ν_{max}(CHCl$_3$)/cm^{-1} 3015m, 2952s, 2893m (CH), 1653w (C=C), 1365, 1264, 1100, 1039, 983, 908; δ_H(200 MHz; CDCl$_3$) 1.26–2.36 (13H, m, 6 × CH$_2$ and 5$_{eq}$-H), 2.41 (1H, d, $J_{5ax,5eq}$ 13.4, 5$_{ax}$-H), 3.46 (1H, dd, $J_{14,15eq}$ 3.4, $J_{14,15ax}$ 4.7, 14 pseudoaxial-H), 3.55–3.78 (2H, m, 2$_{eq}$-H and 10$_{eq}$-H), 3.97–4.11 (2H, m, 2$_{ax}$-H and 10$_{ax}$-H), 4.50 (1H, d, $J_{A,B}$ 11.9, OC*H*$_A$H$_B$Ar), 4.63 (1H, d, $J_{B,A}$ 11.9, OCH$_A$-*H*$_B$Ar), 4.78 (1H, br s, =C*H*$_A$H$_B$), 4.74 (1H, br s, =CH$_A$*H*$_B$), 7.22–7.39 (5H, m, Ar-H); δ_C(50 MHz; CDCl$_3$) 18.3, 18.6, 25.5, 28.2, 32.4, 34.1 (CH$_2$, C-3, C-11, C-12, C-13, C-15 and C-16), 46.4 (CH$_2$, C-5), 61.7 (CH$_2$, C-10), 62.6 (CH$_2$, C-2), 71.1 (CH$_2$, O*C*H$_2$Ar), 76.1 (CH, C-14), 97.9, 98.1 (quat., C-6 and C-8), 109.6 (CH$_2$, =*C*H$_2$), 127.4, 127.6, 128.3 (CH, Ar-C), 138.8 (quat., Ar-C), 142.1 (quat., *C*=CH$_2$).

(2*S,5*S**,6*S**)-2-(3′-Hydroxypropyl)-5-benzyloxy-1,7-dioxaspiro[5.5]undecane 7**

To a solution of **5a** (169 mg, 0.56 mmol) in dry THF (20 cm^3) at 0 °C and under Ar was added dropwise a 1 M solution of BH$_3$–THF complex (3.08 cm^3, 3.08 mmol) and stirred at room temperature for 5 h. The mixture was then cooled to 0 °C and treated with a 3 M aqueous solution of sodium hydroxide (18 cm^3). Oxidation was then carried out by slow dropwise addition of 30% H$_2$O$_2$ (18 cm^3) with the temperature being maintained below 40 °C. After stirring for an additional 0.5 h, the reaction mixture was poured into water and extracted with dichloromethane (3 × 30 cm^3). The combined extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure to give a colourless oil which was purified by flash chromatography using hexane–ethyl acetate (1:1) as eluent to afford the *title compound* **7** (120 mg, 68%) as a colourless oil (Found: M$^+$, 320.1992. C$_{19}$H$_{28}$O$_4$ requires *M*, 320.1987); ν_{max}(CHCl$_3$)/cm^{-1} 3206 (br s, OH), 3024m (=CH), 2947s, 2876s (CH), 1454, 1357, 1262, 1090, 1009, 908; δ_H(200 MHz; CDCl$_3$) 1.20–2.09 (14H, m, 7 × CH$_2$), 2.21 (1H, br s, OH), 3.25 (1H, dd, $J_{5ax,4ax}$ 11.0, $J_{5ax,4eq}$ 4.9, 5$_{ax}$-H), 3.32–3.48 (1H, m, 2$_{ax}$-H), 3.64 (2H, t, *J* 5.9, C*H*$_2$OH), 3.70–3.79 (1H, m, 8$_{eq}$-H), 3.97–4.14 (1H, m, 8$_{ax}$-H), 4.60 (1H, d, $J_{A,B}$ 12.0, OC*H*$_A$H$_B$Ar), 4.84 (1H, d, $J_{B,A}$ 12.0, OCH$_A$*H*$_B$Ar), 7.19–7.39 (5H, m, Ar-H); δ_C(50 MHz; CDCl$_3$) 17.4, 22.0, 25.3, 26.7, 29.2, 31.0, 32.1 (CH$_2$, C-9, C-10, C-11, C-4, C-3, C-1′, C-2′), 61.4 (CH$_2$, C-8), 62.6 (CH$_2$, *C*H$_2$OH), 71.6 (CH, C-2), 72.6 (CH$_2$, O*C*H$_2$Ar), 79.9 (CH, C-5), 99.9 (quat., C-6), 127.2, 127.6, 128.1 (CH, Ar-C), 139.0 (quat., Ar-C); *m*/*z* (CI, CH$_4$) 321 (MH$^+$, 17%), 303 (M − OH, 26), 214 (M − OBn, 81) and 195 (M − H$_2$O − OBn, 100).

(2*S,5*S**,6*S**)-3-(5-Benzyloxy-1,7-dioxaspiro[5.5]undec-2-yl)-propyl *p*-nitrobenzoate 8**

To a solution of the alcohol **7** (58 mg, 0.18 mmol) in dichloromethane (9 cm^3) was added triethylamine (0.05 cm^3, 0.36 mmol) followed by 4-nitrobenzoyl chloride (40 mg, 0.216 mmol) and

4-dimethylaminopyridine (3 mg). The mixture was stirred at room temperature for 30 min. Saturated sodium hydrogen carbonate solution (5 cm^3) was added and the mixture extracted with dichloromethane (3 × 20 cm^3), washed with brine (10 cm^3) and dried over potassium carbonate. The solvent was then evaporated to give a yellow oil which was purified by flash chromatography using hexane–ethyl acetate (4:1) to afford the *title compound* **8** (75.6 mg, 89%) as colourless needles, mp 75–76 °C (from MeOH); δ_H(200 MHz; $CDCl_3$) 1.30–2.20 (14H, m, 7 × CH_2), 3.26 (1H, dd, $J_{5ax,4ax}$ 11.2, $J_{5ax,4eq}$ 5.0, 5_{ax}-H), 3.39–3.53 (1H, m, 2_{ax}-H), 3.70–3.81 (1H, m, 8_{eq}-H), 4.07–4.20 (1H, m, 8_{ax}-H), 4.38–4.46 (2H, m, CH_2OC=O), 4.60 (1H, d, $J_{A,B}$ 12.0, OC$H_A$$H_B$Ar), 4.85 (1H, d, $J_{B,A}$ 12.0, OC$H_A$$H_B$Ar), 7.28–7.40 (5H, m, Ar-H), 8.20–8.45 (4H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 17.6, 22.1, 25.4, 25.6, 26.7, 31.2, 32.5 (CH_2, C-9, C-10, C-11, C-4, C-3, C-3′, C-2′), 60.4 (CH_2, C-8), 66.0 (CH_2, CH_2OC=O), 71.4 (CH, C-2), 72.7 (CH_2, OCH_2Ar), 79.9 (CH, C-5), 100.0 (quat., C-6), 123.5, 127.3, 127.7, 128.2, 130.7 (CH, Ar-C), 135.7, 139.1, 150.5 (quat., Ar-C), 164.7 (quat., C=O).

(5*S,7*S**,13*S**)- and (5*R**,7*S**,13*S**)-13-Benzyloxy-1,6,8-trioxadispiro[4.1.5.3]pentadecane 11a and 11b**

A solution of the alcohol **7** (94 mg, 0.30 mmol), iodine (153 mg, 0.60 mmol), and iodobenzene diacetate (192 mg, 0.60 mmol) in cyclohexane (25 cm^3) was purged with Ar and irradiated with a 500 W tungsten filament lamp. After 1 h, during which time the temperature was maintained at about 23 °C, the solution was diluted with diethyl ether (75 cm^3), washed with 10% aqueous sodium thiosulfate (30 cm^3), water (30 cm^3), brine (30 cm^3) and dried over potassium carbonate. The solvent was evaporated under reduced pressure and the resultant oil purified by flash chromatography using hexane–ethyl acetate (4:1 containing 1% of triethylamine) as eluent to afford:

(i) The less polar product identified as the (5*S**,7*S**,13*S**)-diastereomer **11a** (25.2 mg, 26.4%) as a colourless oil (Found: M^+, 318.1836. $C_{19}H_{26}O_4$ requires *M*, 318.1831); ν_{max}($CHCl_3$)/cm^{-1} 3004m, 2947s, 2881m (CH), 1585, 1453, 1359, 1148, 1097, 1046, 979, 947; δ_H(200 MHz; $CDCl_3$) 1.49–2.31 (14H, m, 7 × CH_2), 3.25 (1H, dd, $J_{13ax,14ax}$ 7.5, $J_{13ax,14eq}$ 4.4, 13_{ax}-H), 3.62–3.75 (1H, m, 9_{eq}-H), 3.82–3.95 (2H, m, 2-CH_2), 4.00–4.14 (1H, m, 9_{ax}-H), 4.61 (1H, d, $J_{A,B}$ 12.0, OC$H_A$$H_B$Ar), 4.70 (1H, d, $J_{B,A}$ 12.0, OC$H_A$$H_B$Ar), 7.24–7.42 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 18.5, 23.0, 24.4, 25.6, 29.4, 31.5, 37.8 (CH_2, C-3, C-4, C-10, C-11, C-12, C-14, C-15), 61.6 (CH_2, C-9), 68.1 (CH_2, C-2), 71.9 (CH_2, OCH_2Ar), 78.7 (CH, C-13), 100.0 (quat., C-7), 107.2 (quat., C-5), 127.3, 127.6, 128.2 (CH, Ar-C), 138.9 (quat., Ar-C); *m*/*z* (CI, CH_4) 319 (MH^+, 0.7%), 317 (M − H, 16), 301 (M − OH, 100), 211 (M − OBn, 87) and 193 (M − OBn − H_2O, 37).

(ii) The more polar product identified as the (5*R**,7*S**,13*S**)-diastereomer **11b** (37.4 mg, 39%) as a colourless oil (Found: M^+, 318.1837. $C_{19}H_{26}O_4$ requires *M*, 318.1831); ν_{max}($CHCl_3$)/cm^{-1} 3004m, 2946s, 2885m (CH), 1453, 1442, 1379, 1216, 1181, 1069, 982; δ_H(200 MHz; $CDCl_3$) 1.17–2.21 (14H, m, 7 × CH_2), 3.26 (1H, dd, *J* 3.3 and 1.5, 13_{eq}-H), 3.56–3.66 (1H, m, 9_{eq}-H), 3.80–3.97 (2H, m, 2-CH_2), 4.04–4.13 (1H, m, 9_{ax}-H), 4.44 (1H, d, $J_{A,B}$ 12.0, OC$H_A$$H_B$Ar), 4.65 (1H, d, $J_{B,A}$ 12.0, OC$H_A$$H_B$Ar), 7.20–7.42 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 18.4, 19.0, 24.4, 25.6, 27.9, 33.0, 39.8 (CH_2, C-3, C-4, C-10, C-11, C-12, C-14, C-15), 61.0 (CH_2, C-9), 69.3 (CH_2, C-2), 70.9 (CH_2, OCH_2Ar), 78.2 (CH, C-13), 97.0 (quat., C-7), 106.2 (quat., C-5), 127.5, 127.8, 128.2 (CH, Ar-C), 138.9 (quat., Ar-C); *m*/*z* (CI, CH_4) 319 (MH^+, 0.6%), 317 (M − H, 19), 301 (M − OH, 93), 211 (M − OBn, 100) and 193 (M − OBn − H_2O, 46).

(2*R,3*S**,5*S**,6*S**)-5-Benzyloxy-2,3-diacetoxy-1,7-dioxaspiro-[5.5]undecane 10**

To a solution of (5*S**,6*S**)-5-benzyloxy-1,7-dioxaspiro[5.5]-undec-2-ene **2** (1.00 g, 3.85 mmol) in dry dichloromethane (20 cm^3) was added a solution of dimethyldioxirane in acetone (50 cm^3, 5.5 mmol as a 0.1 mmol cm^{-3} solution in acetone) and the reaction mixture allowed to stir for 1 h at room temperature. Removal of solvent under reduced pressure gave an oil which was dissolved in dichloromethane (50 ml) and dried over sodium sulfate. To the filtered solution was added dry triethylamine (1.17 g, 11.5 mmol), acetic anhydride (845 mg, 8.28 mmol) and 4-(dimethylamino)pyridine (3 mg) and the reaction mixture was stirred gently at room temperature for 3 h. The reaction was quenched with water (30 cm^3), extracted with dichloromethane (2 × 50 cm^3) and dried over sodium sulfate. Removal of the solvent under reduced pressure gave a yellow oil which was purified by flash chromatography using hexane–ethyl acetate (4:1) as eluent to afford the *title compound* **10** (810 mg, 56%) as a colourless solid, mp 91–92 °C (Found: C, 63.42; H, 7.00. $C_{20}H_{26}O_7$ requires C, 63.46; H, 6.93%); ν_{max}($CHCl_3$)/cm^{-1} 3042w (=CH), 2948w (CH), 1740s (C=O, acetate), 1228s (C–O), 1454, 1370, 1217, 1093, 1053, 983, 796; δ_H(200 MHz; $CDCl_3$) 1.16–1.32 (1H, ddd, $J_{11ax,11eq}$ 13.3, $J_{11ax,10ax}$ 13.3, $J_{11ax,10eq}$ 4.5, 11_{ax}-H), 1.50–1.98 (6H, m, 9-CH_2, 10-CH_2, 11_{eq}-H and 4_{eq}-H), 2.40 (1H, m, 4_{ax}-H), 2.11 and 2.18 (2 × 3H, 2s, 2 × Ac), 3.34 (1H, t, *J* 2.8, 5_{eq}-H), 3.70–3.80 (1H, m, 8_{eq}-H), 4.1–4.2 (1H, m, 8_{ax}-H), 4.55 (1H, d, $J_{A,B}$ 11.9, OC$H_A$$H_B$Ar), 4.79 (1H, d, $J_{B,A}$ 11.9, OC$H_A$$H_B$Ar), 5.18 (1H, ddd, $J_{3ax,4ax}$11.6, $J_{3ax,2ax}$ 8.5 and $J_{3ax,4eq}$ 5.2, 3_{ax}-H), 6.0 (1H, d, $J_{2ax,3ax}$ 8.5, 2_{ax}-H), 7.38–7.41 (5H, m, Ar-H); δ_C(50 MHz; $CDCl_3$) 18.4, 25.2, 27.6, 31.0 (CH_2, C-9, C-10, C-11 and C-4), 21.4 (CH_3, 2 × Ac), 61.9 (CH_2, C-8), 67.5 (CH, C-3), 71.1 (CH_2, OCH_2Ar), 76.9 (CH, C-5), 89.7 (CH, C-2), 99.7 (quat., C-6), 127.5, 128.0, 128.4, 128.6 (CH, Ar-C), 138.0 (quat., Ar-C), 170.2 (quat., 2 × C=O); *m*/*z* (CI, CH_4) 379 (MH^+, 0%), 319 (MH − Ac, 73), 259 (MH − 2Ac, 45) and 211 (MH − OAc − OBn, 100).

Crystal data and structure refinement for 1 and 8

1: $C_{18}H_{24}O_5$, $M = 320.38$, orthorhombic, space group *Pbca* (#61), $a = 26.882(4)$, $b = 14.808(6)$, $c = 8.632(5)$ Å, $V = 3436(1)$ $Å^3$, $Z = 8$, $D_c = 1.239$ g cm^{-3}, $F(000) = 1376.00$, μ(Cu-Kα) = 7.36 cm^{-1}, crystal size 0.55 × 0.05 × 0.03 mm, $T_{min,max}$ 0.87, 0.99, $N = 2945$, $N_o = 1099$ [$I > 3.0\sigma(I)$], *hkl* 0 30, 0 16, 0 9, $2\theta_{max}$ = 120.1°, $R^* = 0.041$, $R_w^* = 0.041$, residual extrema −0.19 0.15 e $Å^{-3}$.

8: $C_{26}H_{31}NO_7$, $M = 469.53$, monoclinic, space group $P2_1/a$ (#14), $a = 11.352(4)$, $b = 11.775(2)$, $c = 18.602(2)$ Å, $\beta = 100.65(2)°$, $V = 2443.7(8)$ $Å^3$. $Z = 4$, $D_c = 1.276$ g cm^{-3}, $F(000) = 1000.00$, μ(Cu-Kα) = 7.64 cm^{-1}, crystal size 0.30 × 0.10 × 0.08 mm, $T_{min,max}$ 0.87, 0.99, $N = 4623$, $N_{ind} = 4286$ ($R_{merge} = 0.024$), $N_o = 1386$ [$I > 3.0\sigma(I)$], *hkl* 0 13, 0 13, −21 21, $2\theta_{max} = 130.2°$, $R^* = 0.054$, $R_w^* = 0.051$, residual extrema −0.20 0.17 e $Å^{-3}$.

* $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

$R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$; $w = 1/\sigma^2(F_o)$

Atomic coordinates, thermal parameters and bond lengths have been deposited at the Cambridge Crystallographic Data Centre (CCDC).‡

A colourless acicular crystal of **1** was attached to a thin glass fibre and mounted on a Rigaku AFC7R diffractometer employing graphite monochromated Cu-Kα radiation ($\lambda = 1.541\,78$ Å) from a rotating anode generator. A colourless blade like crystal of **8** cut from a cluster was similarly mounted on the AFC7R diffractometer. Diffraction data were collected at a temperature of 21 ± 1 °C using $\omega - 2\theta$ scans to a maximum 2θ value of 120.1° for **1** and 130.2° for **8**. In both cases, the intensities of three representative reflections measured every 150 reflections, did not change significantly during the data collection. An

‡ For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/177.

empirical absorption correction based on azimuthal scans of three reflections was applied and the data were also corrected for Lorentz and polarization effects.

All calculations were undertaken with the TEXSAN[16] crystallographic software package. Neutral atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_{calc}[18] and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[19] The values for the mass attenuation coefficients were those of Creagh and Hubbell.[20] The structures were solved by direct methods[21] and expanded using Fourier techniques.[22] Non-hydrogen atoms were modelled with anisotropic thermal parameters and hydrogen atoms were included in the model at calculated positions with group thermal parameters. ORTEP[23] projections of the molecule are provided in Figs. 1 and 2.

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References

1 For reviews on the synthesis of spiroacetals see: (*a*) F. Perron and K. F. Albizati, *Chem. Rev.*, 1989, **89**, 1617; (*b*) T. L. B. Boivin, *Tetrahedron*, 1987, **43**, 3309; (*c*) A. F. Kluge, *Heterocycles*, 1986, **24**, 1699.
2 (*a*) G. R. Pettit, Z. A. Cichacz, F. Gao, C. L. Herald, M. R. Boyd, J. M. Schmidt and J. N. A. Hooper, *J. Org. Chem.*, 1993, **58**, 1302; (*b*) G. R. Pettit, Z. A. Cichacz, F. Gao, C. L. Herald and M. R. Boyd, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1166.
3 T. Hu, J. M. Curtis, Y. Oshima, M. A. Quillam, J. A. Walter, W. Watson-Wright and J. L. C. Wright, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2159.
4 K. T. Mead and R. Zemribo, *Synlett*, 1996, 1063.
5 G. D. Hartman and T. G. Traylor, *Tetrahedron Lett.*, 1975, 939.
6 R. E. Ireland and D. Haebich, *Chem. Ber.*, 1981, **114**, 1418.
7 (*a*) A. J. Kirby, in *The Anomeric and Related Stereoelectronic Effects at Oxygen*, Springer-Verlag, New York, 1983; (*b*) *The Anomeric Effect and Associated Stereoelectronic Effects*, ed. G. R. J. Thatcher, American Chemical Society Symposium Series, 539, American Chemical Society, Washington DC, 1993; (*c*) P. P. Graczyk and M. Mikolajczyk, *Top. Stereochem.*, 1994, **21**, 159; (*d*) E. Juaristi and G. Cuevas, *Tetrahedron*, 1992, **48**, 5019.
8 M. A. Brimble and G. M. Williams, *J. Org. Chem.*, 1992, **57**, 5818.
9 (*a*) R. L. Dorta, A. Martin, E. Suarez and T. Prange, *Tetrahedron: Asymmetry*, 1996, **7**, 1907; (*b*) A. Martin, J. A. Salazar and E. Suarez, *J. Org. Chem.*, 1996, **61**, 3999.
10 M. A. Brimble and C. J. Rush, *J. Chem. Soc.*, *Perkin Trans. 1*, 1994, 497.
11 (*a*) M. A. Brimble and A. D. Johnston, *J. Org. Chem.*, in the press; (*b*) M. A. Brimble, A. D. Johnston and R. Furneaux, *Tetrahedron Lett.*, 1997, **38**, 3591.
12 Y. Naruta, Y. Nishigaichi and K. Maruyama, *Chem. Lett.*, 1986, 1857.
13 S. Weigand and R. Bruckener, *Synthesis*, 1995, 475.
14 A. Barbero, P. Cuadrado, I. Fleming, A. M. Gonzalez and F. J. Pulido, *J. Chem. Soc.*, *Perkin Trans. 1*, 1992, 327.
15 G. E. Keck, D. E. Abbott and M. R. Wiley, *Tetrahedron Lett.*, 1987, **28**, 139.
16 TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).
17 D. T. Cromer and J. T. Waber, in *International Tables for X-ray Crystallography*, The Kynoch Press, Birmingham, England, 1974, vol. IV, Table 2.2 A.
18 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.
19 D. C. Creagh and W. J. McAuley, in *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, vol. C, Table 4.2.6.8, pp. 219–222.
20 D. C. Creagh and J. H. Hubbell, in *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, vol. C, Table 4.2.4.3, pp. 200–206.
21 SIR92: A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
22 DIRDIF94: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, 1994, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
23 ORTEP: C. K. Johnson, ORTEPII. Report ORNL-5138, 1976, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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