Syntheses and structures of 3-stannylcholest-5-ene species

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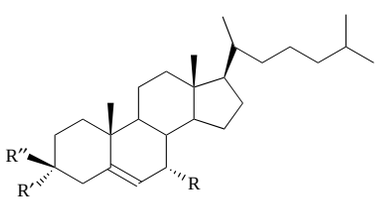
The compounds, 3α- and 3β-triphenylstannylcholest-5-ene, 1 and 2 respectively, have been prepared stereospecifically in reactions of Ph_3SnLi with cholesteryl methane- or toluene-*p*-sulfonates, and of Ph_3SnCl with the Grignard reagent from cholesteryl chloride, respectively. Complete ^1H and ^{13}C NMR spectral assignments for 1 have been obtained using HMBC and HMQC techniques: these have been used to aid the ^{13}C NMR spectral assignments for 2 and 3α- and 3β-($I_nPh_{3-n}Sn$)cholest-5-enes (n = 1–2) (9–12). Crystal structure determinations of 3α-(IPh_2Sn)cholest-5-ene 9 and 3α-(I_2PhSn)cholest-5-ene 10 indicate distorted tetrahedral geometries about the tin centres in both compounds. The Sn–I bond lengths are 2.731(5) Å in 9 and between 2.6979(12) and 2.7173(12) Å in 10. Despite the similarity in the values (*ca.* 60°) of the dihedral angles, Sn–C(3)–C(2)–C(1) [C(1) aliphatic carbon] and Sn–C(3)–C(4)–C(5) [C(5) olefinic carbon], the values of $^3J[^{119}Sn–^{13}C(1)]$ are about twice the $^3J[^{119}Sn–^{13}C(5)]$ values in each of 1, 9 and 10; in contrast, $^3J[^{119}Sn–^{13}C(1)]$ and $^3J[^{119}Sn–^{13}C(5)]$ values are essentially the same in each of 2, 11 and 12 [Sn–C(3)–C(2)–C(1) and Sn–C(3)–C(4)–C(5) *ca.* 180°].

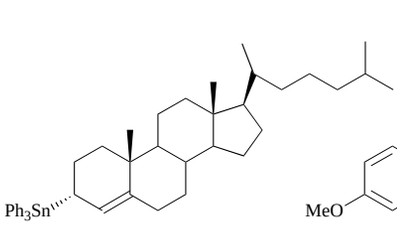
Introduction

Interest in organotin derivatives of natural products has been maintained over a long period of time for diverse reasons: biological activities (especially anti-tumour activities),[1,2] chemical reactivities[3] and structure determinations[4–6] have all featured, for example, in the publications on stannylated steroids, which date[7] from 1970. The linking of the stannyl moieties to the steroid residues has involved not only Sn–O bonds (*e.g.* in alkoxide and carboxylate derivatives)[2,8,9] but also Sn–C bonds.[3–7,10] While steroids are generally hydrophobic molecules, they can contain a variety of organic functional groups, which strongly influence their properties. Reported tin–carbon bonded triorganostannyl steroids include the non-functionalised saturated alkyl compounds, 3α- and 3β-triorganostannylcholest-5α-anes (organo group = Me or Ph),[7] and their monoene analogues, 3α- and 3β-triphenylstannylcholest-5-enes (**1** and **2**, respectively)[7] and 3α-(triphenylstannyl)cholest-4-ene **3**.[3] 7α-(Triphenylstannyl)cholest-5-en-3β-ol **4**, 7α-(triorganostannyl)cholest-5-en-3-one (**5**; organo group = Ph or Bu), 3-methoxy-19-norpregna-1,3,5,17,20-pentaen-21-yl}triphenylstannane **6**,[10] [(*Z*)-17-(2-triphenylstannyl)vinyl]estr-4-en-17β-ol **7**[4] and (20*Z*)-3-methoxy-17-[2-(triphenylstannyl)vinyl]estra-1,3,5(10)-trien-17β-ol **8**[6] illustrate well the diversity of the functionalised derivatives. Iodophenylstannyl analogues of **7** have also been reported.[4]

Structural studies of stannylated steroids are limited. Crystal structures have been determined for two compounds, **1**[5] and **7**.[4a] In addition, NMR methods (HMQC–RELAY, NOESY *etc.*) have been used to obtain solution structures and conformations of **7**[4b] and **8**.[6] Compounds **7** and **8** are two of the few tetraorganotin species to contain other than four-coordinate tin atoms, as consequences of the intramolecular coordination of hydroxy groups to the tin centres. As previously shown,[5] the tetraorganostannane **1** is more typically four-coordinate in the solid state. In this study we have carried out the complete ^{13}C NMR assignments of **1**, **2** and their iodophenyl analogues 3α- and 3β-($I_nPh_{3-n}Sn$)cholest-5-enes (**9**–**12**) and have determined the X-ray structures of 3α-(iododiphenyl)stannylcholest-5-ene **9** and 3α-(diiodophenyl)stannylcholest-5-ene **10**.



1 R′ = Ph_3Sn; R″ = R = H
2 R″ = Ph_3Sn; R′ = R = H
4 R″ = OH; R′ = H; R = Ph_3Sn
5 R′, R″ = O; R = Ph_3Sn or Bu_3Sn
9 R′ = IPh_2Sn; R″ = R = H
10 R′ = I_2PhSn; R″ = R = H
11 R″ = IPh_2Sn; R′ = R = H
12 R″ = I_2PhSn; R′ = R = H
13 R″ = *p*-$MeC_6H_4SO_3$; R′ = R = H
14 R″ = OH; R′ = R = H
15 R″ = $MeSO_3$; R′ = R = H
16 R″ = Cl; R′ = R = H



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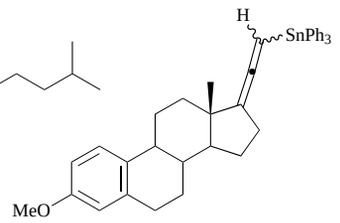

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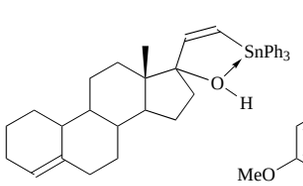

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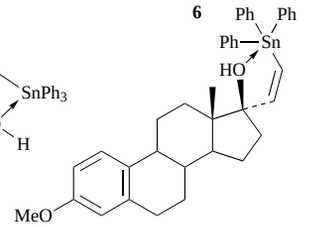

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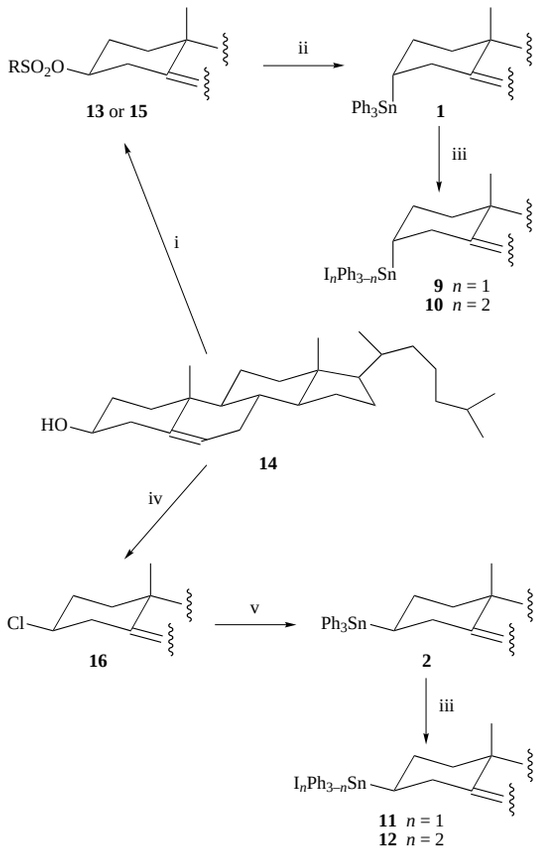


Scheme 1 *Reagents:* (i) $RS(O)_2Cl$ (R = Me or *p*-MeC_6H_4), pyridine; (ii) Ph_3SnLi; (iii) nI_2; (iv) $S(O)Cl_2$; (v) Mg, Ph_3SnCl

Results and discussion

Synthesis

The syntheses of tetraorganotin compounds from R_3SnLi and alkyl halides and tosylates have been widely studied, the mechanisms and stereochemistries of these reactions having attracted particular attention.[11–13] Reactions of R_3SnLi compounds with secondary alkyl tosylates generally occur with inversion of configuration,[11a,14,15] as further illustrated in this study by the formation of **1** from Ph_3SnLi and cholesterol sulfonates, Scheme 1.

Another stereospecific reaction, but with overall retention of configuration, occurred between Ph_3SnCl and the Grignard reagent from 3β-chlorocholest-5-ene **16** in THF with the formation of **2**, Scheme 1. The stereochemistry of reactions of alkyl-Grignard reagents with organotin halides are dependent on the alkyl halides RX, *e.g.* reactions of Me_3SnCl with (i) the 4-*tert*-butylcyclohexyl-Grignard reagent provided[15] predominantly *trans*-4-*tert*-butylcyclohexyltrimethyltin, (ii) the Grignard reagent from >95% *cis*-4-methylcyclohexyl bromide gave[14] only *trans*-4-methylcyclohexylstannanes and (iii) the Grignard reagent from *exo*-2-norbornane produced[16] an *exo–endo* mixture of 2-trimethylstannylnorbornane.

Zimmer and Bayless obtained[7] **1** from the reaction of 3β-chlorocholest-5-ene with Ph_3SnLi, while both **1** and **2** were produced from 3β-iodocholest-5-ene and Ph_3SnLi. We found in this study that the one-pot Barbieri-type reaction of **16**, Li and Ph_3SnCl in THF also produced both the α- and β-epimers, in a 1:2 ratio, based on peak heights in the ^{119}Sn NMR spectrum.

The iododephenylation products, **9**–**12**, were obtained from reactions of **1** and **2** with iodine. Attempts were made to obtain samples of **9**–**12** as well as **2** for X-ray crystallography, however, suitable crystals were only obtained for **9** and **10**.

Table 1 Selected bond lengths (Å) and angles (°) for **9**

Sn–C(28)	2.14(2)	Sn–C(34)	2.159(11)
Sn–C(3)	2.16(2)	Sn–I	2.731(5)
C(28)–Sn–C(3)	111.6(6)	C(34)–Sn–C(3)	121.7(5)
C(28)–Sn–C(34)	107.3(3)	C(34)–Sn–I	104.5(2)
C(3)–Sn–I	105.0(3)	C(28)–Sn–I	105.3(4)
C(4)–C(3)–Sn	110.9(9)	C(2)–C(3)–Sn	112.4(7)
C(29)–C(28)–Sn	119.8(4)	C(33)–C(28)–Sn	120.1(6)
C(35)–C(34)–Sn	119.4(4)	C(39)–C(34)–Sn	120.6(4)

Table 2 Selected bond lengths (Å) and angles (°) for **10**

Sn(1)–C(28)	2.149(14)	Sn(1′)–C(28′)	2.139(14)
Sn(1)–C(3)	2.187(13)	Sn(1′)–C(3′)	2.160(13)
Sn(1)–I(1)	2.709(2)	Sn(1′)–I(1′)	2.6979(12)
Sn(1)–I(2)	2.7173(12)	Sn(1′)–I(2′)	2.7072(14)
C(28)–Sn(1)–C(3)	126.0(5)	C(28′)–Sn(1′)–C(3′)	129.7(4)
C(28)–Sn(1)–I(1)	106.3(3)	C(28′)–Sn(1′)–I(1′)	106.3(3)
C(3)–Sn(1)–I(1)	107.6(4)	C(3′)–Sn(1′)–I(1′)	102.6(4)
C(28)–Sn(1)–I(2)	105.3(3)	C(28′)–Sn(1′)–I(2′)	105.5(3)
C(3)–Sn(1)–I(2)	104.2(3)	C(3′)–Sn(1′)–I(2′)	106.3(3)
I(1)–Sn(1)–I(2)	105.72(4)	I(1′)–Sn(1′)–I(2′)	107.21(4)
C(2)–C(3)–Sn(1)	110.9(10)	C(2′)–C(3′)–Sn(1′)	110.9(10)
C(4)–C(3)–Sn(1)	109.2(8)	C(4′)–C(3′)–Sn(1′)	110.8(8)
C(33)–C(28)–Sn	121.2(11)	C(33′)–C(28′)–Sn(1′)	119.9(10)
C(29)–C(28)–Sn(1)	121.4(10)	C(29′)–C(28′)–Sn(1′)	120.4(9)

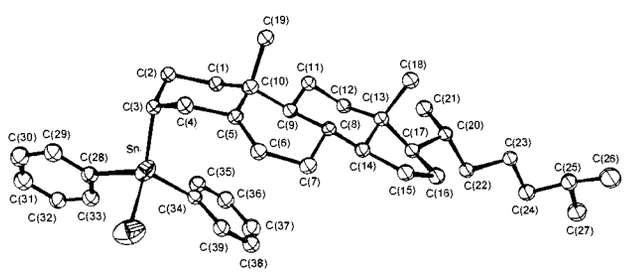


Fig. 1 Atom numbering arrangement for **9**. Thermal ellipsoids drawn at 40%.

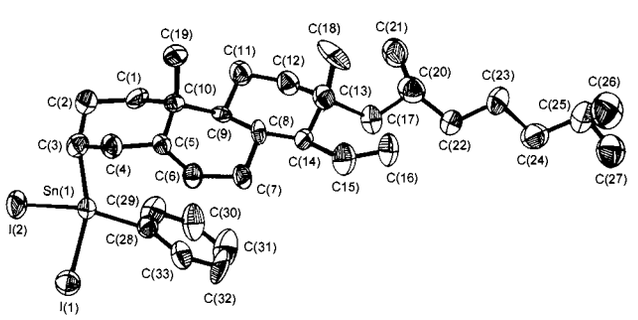


Fig. 2 Atom numbering arrangement for **10** (molecule 1). Thermal ellipsoids drawn at 40%.

Crystal structure of 9

Selected bond lengths are listed in Table 1. Fig. 1 shows the atom arrangements. The tin atom in **9** has a distorted tetrahedral geometry, with bond angles at tin ranging from 104.5(2) to 121.7(5)°; the largest angle is for C(34)–Sn–C(3), while the three smallest angles [104.5(2) to 105.3(4)] are C–Sn–I angles. The Sn–C bond lengths are in the range 2.14(2) to 2.159(11) Å and are unexceptional. The Sn–I bond length is 2.731(5) Å and is at the higher end of the range (2.69–2.73 Å) found for Sn–I bond lengths in tetrahedral, tetracoordinate R_3SnI molecules.[17] There are no intermolecular Sn · · · I or I · · · I interactions close to the appropriate sums of the van der Waals radii.

Crystal structure of 10

Selected bond lengths are listed in Table 2. Fig. 2 shows the atom arrangements. There are two independent molecules in

Table 3 Torsion angles (°) involving carbon atoms in ring A of **9**, **10** and **1** in the solid state

		10			
Torsion angle	**9**	molecule 1	molecule 2	**1**[a]	
C(1)–C(2)–C(3)–Sn	−67.7(11)	−64.9(12)	−62.6(12)	−67(2)	−72(2)
Sn–C(3)–C(4)–C(5)	66.6(11)	66.9(12)	65.8(10)	69(2)	70(2)
C(1)–C(2)–C(3)–C(4)	55.5(12)	57(2)	57.6(14)	59(2)	58(2)
C(2)–C(3)–C(4)–C(5)	−57.5(12)	−55.6(14)	−55.7(14)	−55(2)	−59(2)
C(3)–C(4)–C(5)–C(10)	53.9(13)	52.1(13)	51.9(13)	50(2)	52(2)
C(4)–C(5)–C(10)–C(1)	−42.8(12)	−45.8(13)	−44.9(13)	−43(2)	−44(2)
C(5)–C(10)–C(1)–C(2)	39.4(12)	44.7(13)	43.4(12)	45(2)	47(2)
C(10)–C(1)–C(2)–C(3)	−48.3(13)	−52.1(14)	−52.5(13)	−55(2)	−54(2)

[a] Ref. 5.

the unit cell. These are arranged about a pseudo inversion centre at 0.185, 0.027, 0.033: approximately 75% of the atoms in **10** are related by this feature. One of the molecules, molecule 2, shows disorder in the C(17) side chain with two positions for each of the atoms, C(25), C(26) and C(27); in contrast, no disorder is found in molecule 1. The tin atoms in **10** have distorted tetrahedral geometries, the largest angle in each molecule being the C–Sn–C angle: C(3)–Sn(1)–C(28) = 126.0(5) and C(3′)–Sn(1′)–C(28′) = 129.7(4), in molecules 1 and 2, respectively. The other angles at tin occur in the narrow ranges, 104.2(3) to 107.6(4) and 102.6(4) to 107.21(4)°. The Sn–C bond lengths are within the expected range. The Sn–I bond lengths are shorter than that found in **9**, being 2.709(2) and 2.7173(12) Å in molecule 1, and 2.6979(12) and 2.7072(14) in molecule 2. These are very similar to the values, 2.6980(9) and 2.7106(10) Å, determined in $I_2PhSn(CH_2)_4SnPhI_2$, another distorted tetrahedral, tetracoordinate alkylaryltin diiodide.[18] As with **9**, there are no intermolecular Sn · · · I or I · · · I interactions close to the appropriate sums of the van der Waals radii.

Comparison of crystal structures. As shown by the similar dihedral angles for the A rings in **1**, **9** and **10**, no significant structural change occurs on iodide substitution of phenyl groups in **1**, see Table 3: the ring conformations in the cholestene moiety of **9** and **10** are generally very similar to those determined previously[5] for **1** and for **13**.[19] In each of **1**, **9** and **10**, a phenyl ring lies under the A ring of the cholestene moiety.

NMR Spectra

In order to identify unambiguously $\delta^{13}C$ and J(Sn–C) values with particular carbon atoms in **1**, **2** and **9**–**12**, a complete assignment of the NMR spectra of **1** was carried out using HMQC[16] and HMBC[17] NMR spectra, obtained at 150.8 MHz and the known ^{13}C NMR shifts for cholesterol (Table 4).[18] The major deviations from the cholesterol chemical shifts occurred in the A ring due to the effect of the triphenylstannyl moiety. That C(3) in **1** was at δ 31.93 ppm [*cf.* the value δ 71.3 ppm for C(3) of cholesterol] was certain because of the large $J(^{119}Sn–^{13}C)$ and $J(^{117}Sn–^{13}C)$ values (435, 416 Hz, respectively) associated with this resonance. The three remaining A ring methylene carbon atoms had $\delta^{13}C$ = 38.52, 36.67 and 26.58 ppm with values of $J(^{119,117}Sn–^{3}C)$ = 15, 11, 13 Hz, respectively. As these methylene carbons could neither be assigned simply from the values of the carbon–tin coupling constants nor by analogy with the $\delta^{13}C$ values of cholesterol, HMBC was used. The double bond proton, H(6) ($\delta^{1}H$ = 5.14), was used as the starting point for this analysis. An HMBC correlation was observed between the signal, $\delta^{13}C$ at 36.67 and that for H(6); thus C(4) was considered to have $\delta^{13}C$ at 36.67. Similarly, a correlation was observed between the signal $\delta^{13}C$ at 38.52 and that for H(19), thus δ 38.52 was considered to arise from C(1), and by a process of elimination δ 26.58 was due to C(2). Other correlations confirming these assignments are given in Table 5. The assignments for **2** and **9**–**12** were then obtained using the assignments for **1** and the ^{13}C NMR spectra of **2** and **9**–**12**, obtained at 62.9 MHz, see Table 4.

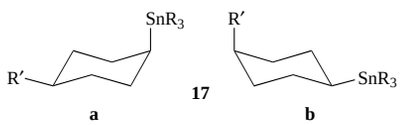


Fig. 3

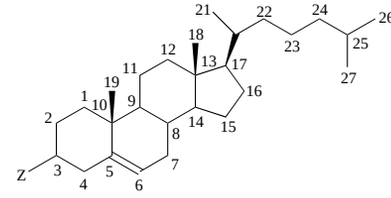
The two phenyl groups in solid **9**, as shown by the crystal structure determination, have quite different locations, with one of the phenyl groups being placed under the A ring of the cholestene moiety. The phenyl ring diastereotopy is maintained in $CDCl_3$ solution up to 44 °C; coalescence of the aryl signals in the ^{13}C NMR spectra occurs at that temperature.

The very much favoured conformation in solution of a cyclohexyl-SnR_3 derivative (*e.g.* **17**: R = Me or Ph; R′ = H, see Fig. 3), has the organostannyl substituent in an equatorial site of a chair-shaped cyclohexane ring, *i.e.* conformation **b**, Fig. 3.[11a,20,21] It is only at −69 °C that the chair-chair conformation interconversion for (**17**: R = Me; R′ = H) is frozen out: the $^{3}J(^{119}Sn–^{13}C)$ at −69 °C for conformer **b** (with the equatorially sited Me_3Sn group) has a value of 65 Hz, in comparison to the average value of 57.7 Hz recorded at equilibrium[21] at 35 °C. No simple stannylated cyclohexane derivative has yet been reported to exist in solution in a fixed conformation with the organostannyl substituent in an axial position. The extents of the conformations **a** and **b** of *cis*-4-R′-cyclohexyl-SnR_3[11] (Fig. 3), at equilibrium can be calculated from the appropriate A factors: values of the A factors for Me_3Sn, Ph_3Sn and Me groups have been found to be 1.06,[21] 1.44[22] and 1.74[23] kcal mol^{-1}, respectively.

The fused ring molecules, **1**, **2** and **9**–**12**, are considered to be rigid molecules in solution. It is anticipated that the conformations of the cholestene rings in solution are similar to those in the solid state. Thus the two $^{3}J(^{119,117}Sn–^{13}C)$ values in the ^{13}C NMR spectra for each of the fused-ring 3α- and 3β-stannylcholest-5-ene compounds can be related to well-defined Sn–C–C–C dihedral angles. The Sn–C(3)–C(4)–C(5) and Sn–C(3)–C(2)–C(1) dihedral angles were found to be essentially the same in each of the α-derivatives (see Table 2); a similar result is expected for the β-compounds with the Sn–C(3)–C(4)–C(5) and Sn–C(3)–C(2)–C(1) dihedral angles near 180°. As shown in Table 4, both the $^{3}J(^{119}Sn–^{13}C)$ values, associated with C(5) and C(1), are practically the same in each of the β-stannyl derivatives being 69 ± 1 Hz for **2**, 83 ± 1 Hz for **11** and 111 ± 3 Hz for **12**. In contrast for the α-derivatives, $^{3}J(^{119}Sn–^{13}C)$ values associated with the C(1) atoms (alkyl carbon atoms) are generally *ca.* twice the values for the C(5) (olefinic) carbon atoms, being 15 and 8 in **1**, 20 and 11 in **9**, and 28 and 16 Hz in **10**. The Sn–C(3) σ-bonds in the α-derivatives (but not in the β-derivatives) are almost ideally situated to interact with the C(5)–C(6) π-orbitals; this σ–π interaction must result in the reduced coupling constants.

Karplus type equations, relating coupling constants, $^{3}J(^{119}Sn–^{13}C)$, with Sn–C–C–C dihedral angles, have been established for organostannanes.[24] The original correlations were

Table 4 ^{13}C and ^{119}Sn NMR data measured in $CDCl_3$ solution. ^{13}C NMR data for **1** at 150.8 MHz, all others at 62.9 MHz; $\delta^{119}Sn$ values measured at 93.3 MHz.



	C atom $\delta^{13}C$/ppm [J(Sn–C)]/Hz																
Comp. (Z)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
14 (β-OH)	37.5	31.6	71.3	42.4	141.2	121.3	32.0	32.0	50.5	36.5	21.2	28.3	42.4	56.9	24.3	40.0	56.5
1 (α-$SnPh_3$)	38.52 [15][a]	26.58 [13][a]	31.93 [435, 416][b]	36.67 [11][a]	141.83 [8][a]	121.26	31.51	31.38	48.80	37.15	20.44	28.16	42.15	56.82	24.14	39.71	56.10
2 (β-$SnPh_3$)	42.3 [70][a]	27.6 [18][a]	29.3 [424, 405][b]	37.5 [16][a]	142.1 [68, 65][b]	119.0	31.8	31.6	50.6	37.5	20.6	28.2	42.2	56.8	24.2	39.7	56.1
9 (α-$SnPh_2I$)	38.5 [20][a]	26.1 [14][a]	40.2 [445, 427][b]	36.1 [nd]	141.0 [11][a]	122.4	31.5	31.2	48.8	37.2	20.4	28.1	42.1	56.7	24.1	39.6	56.0
11 (β-$SnPh_2I$)	41.6 [83][a]	27.2 [22][a]	33.7 [422, 403][b]	37.4 [19][a]	143.0 [84, 80][b]	120.0	31.7	31.6	50.5	37.0	20.6	28.1	42.2	56.7	24.1	39.6	56.0
10 (α-$SnPhI_2$)	38.9 [28][a]	25.7 [12][a]	51.5 [461, 440][b]	35.5 [nd]	140.1 [16][a]	123.7	31.3	31.1	49.0	37.3	20.4	28.1	42.0	56.6	24.1	39.5	56.0
12 (β-$SnPhI_2$)	41.0 [114, 109][b]	26.9 [28][a]	41.0 [428, 409][b]	36.5 [25][a]	141.7 [108, 103][b]	121.2	31.8	31.6	50.3 [11][a]	37.3 [11][a]	20.6	28.1	42.2	56.6	24.1	39.6	56.0
13 (β-OSO_2Tol)	38.7	27.9	82.3	36.2	138.7	123.4	31.7	31.6	49.8	36.7	20.9	28.4	42.1	56.5	24.1	39.5	56.0
15 (β-OSO_2Me)	38.6	27.9	81.9	36.2	138.5	123.7	31.7	31.6	49.2	36.8	20.9	28.8	42.2	56.5	24.1	39.5	56.0
16 (β-Cl)	39.0	33.3	60.2	43.3	140.7	122.4	31.7	31.6	49.9	36.2	20.8	28.1	42.2	56.6	24.1	39.6	56.0

	C atom $\delta^{13}C$/ppm [J(Sn–C)]/Hz															
Comp. (Z)	18	19	20	21	22	23	24	25	26	27	C_i	C_o	C_m	C_p	Me	Sn atom $\delta^{119}Sn$/ppm
14 (β-OH)	12.0	19.4	35.8	18.8	36.4	24.1	39.6	28.0	22.6	22.9						
1 (α-$SnPh_3$)	11.73	19.79	35.72	18.60	36.13	23.82	39.44	27.91	22.47	22.74	140.13 [450, 430][b]	137.29 [34][a]	128.15 [46][a]	128.36 [5][a]		
2 (β-$SnPh_3$)	11.8	19.4	35.7	18.7	36.1	23.8	39.5	28.0	22.5	22.8	138.5 [459, 439][b]	137.3 [33][a]	128.4 [46][a]	128.7 [*ca.* 5][a]		−114.8 −117.1
9 (α-$SnPh_2I$)	11.7	19.6	35.7	18.6	36.2	23.8	39.4	27.9	22.4	22.7	138.8, 138.7 [nd]	136.4, 136.3 [46][a]	128.6 [54][a]	129.5, 129.4 [nd]		−52.4
11 (β-$SnPh_2I$)	11.8	19.2	35.7	18.6	36.1	23.7	39.4	27.9	22.5	22.7	136.9 [458, 438][b]	136.3 [44][a]	128.8 [55, 53][b]	129.8 [12][a]		−50.9
10 (α-$SnPhI_2$)	11.7	19.4	35.7	18.6	36.1	23.8	39.4	27.9	22.4	22.7	140.2 [nd]	134.8 [63, 60][b]	128.6 [69, 67][b]	130.3 [15][a]		−101.9
12 (β-$SnPhI_2$)	11.7	19.2	35.7	18.6	36.1	23.7	39.4	27.9	22.5	22.7	136.9 [nd]	135.0 [58, 56][b]	129.0 [66, 63][b]	130.8 [14][a]		−116.6
13 (β-OSO_2Tol)	11.7	19.0	35.6	18.6	36.0	23.7	39.4	28.1	22.4	22.7	134.5	129.6	127.5	144.3	21.5	
15 (β-OSO_2Me)	11.7	19.1	35.6	18.6	36.0	23.7	39.4	28.1	22.4	22.7					39.0	
16 (β-Cl)	11.7	19.1	35.6	18.6	36.1	23.7	39.4	28.1	22.4	22.7						

[a] J ($^{119-117}Sn$–^{13}C) (Hz); [b] J(^{119}Sn–^{13}C) (Hz, J(^{117}Sn–^{13}C) (Hz)); nd = not detected.

Table 5 HMQC and HMBC NMR Spectra for **1**

C	δ^{13}C (150.8 MHz)	mult	J_{C-Sn} (Hz)	δ^{1}H (599.6 MHz)	mult (*J* in Hz)	HMBC
1	38.52	t	15	1.70	ddm *J* 13.4, 1.6	H2, H19
				1.23	dd *J* 13.3, 3.3	
2	26.58	t	13	2.18	dddd *J* 14.0, 14.0, 3.9, 3.9	H1′, H4′
				2.09	dm *J* 13.2	
3	31.93	d	435	2.76	dddd *J* 3.9, 3.9, 2.1, 2.1	H1/1′, H4′
			416			
4	36.67	t	11	2.90	dq *J* 14.1, 2.9	H2, H6
				2.45	dt *J* 14.4, 1.7	
5	141.83	s	8			H4′
6	121.26	d		5.14	dd *J* 3.4, 1.8	H4′
7	31.51	t		1.86	m	H6, H9, H14
				1.30	m	
8	31.38	d		1.35	dd *J* 10.9, 5.0	H6, H9, H11, H14
9	48.80	d		0.49	ddd *J* 10.9, 10.9, 7.5	H1′, H8, H11, H12, H19
10	37.15	s				H1′, H4′, H6, H9, H19
11	20.44	t		1.32	m	
12	28.16	t		1.88	m	H17
				1.56	m	
13	42.15	s				H14, H15′, H16, H17, H18
14	56.82	d		0.80	ddd *J* 12.7, 10.7, 7.2	H8, H15′, H16, H18
15	24.14	t		1.56	m	
				1.04	m	
16	39.71	t		1.94	dt *J* 12.4, 3.5	H15
				0.98	m	
17	56.10	d		1.08	bq *J* 9.5	H16, H21, H22
18	11.73	q		0.65	s	H14, H17
19	19.79	q		1.00	s	H1′, H9
20	35.72	d		1.39	m	H17, H21
21	18.60	q		0.94	d *J* 6.5	H17, H20, H22/22′
22	36.13	t		1.39	m	
				1.04	m	
23	23.82	t		1.39	m	H24
				1.18	m	
24	39.44	t		1.18	m	H26, H27
25	27.91	d		1.28	m	H26, H27
26	22.47	q		0.91	d *J* 6.5	H24, H27
27	22.74	q		0.92	d *J* 6.6	H24, H26
C_i	140.13	s	450, 43			
			0			
C_o	137.29	d	34	7.58	m	
C_m	128.15	d	46	7.36	m	
C_p	128.36	d	5	7.36	m	

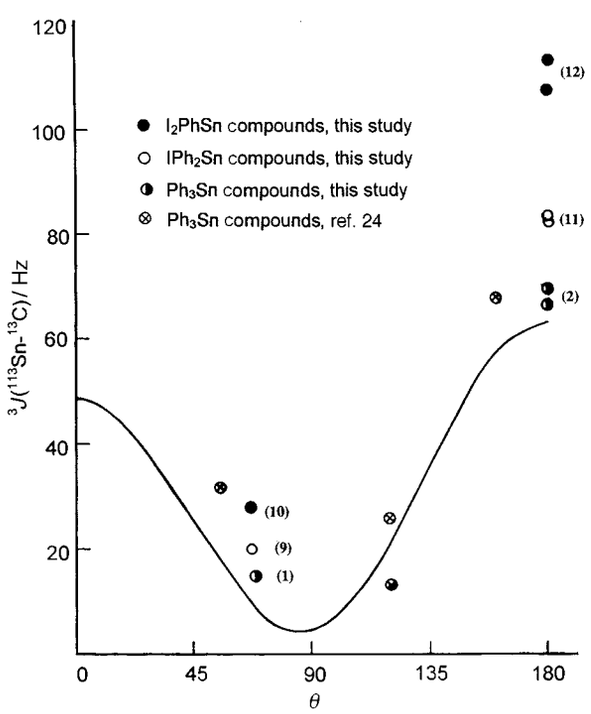


Fig. 4 Plot of torsion angle, C–C–C–Sn θ against $^3J(^{119}Sn–^{13}C)$/Hz. Continuous plot is for Me_3Sn derivatives.[24]

developed by Kuivila and co-workers using data for Me_3Sn derivatives of bi- and poly-*cyclo*alkanes, Fig. 4. As the tin–carbon coupling constants depend on the substituents on tin, *e.g.* see the differences in the ^3J(Sn–C) values for **1**, **9** and **10**, there is a need to establish Karplus type correlations for other stannyl systems, in particular the widely studied phenylstannyl derivatives. However, ^3J(Sn–C) data, linked with precise values for dihedral angles, remain limited for Ph_3Sn derivatives: apart from the data obtained in this study, Rahm *et al.* have obtained ^3J(Sn–C) data for 2-*exo*- and 2-*endo*-triphenylstannylnorbornanes.[25] These values are assembled in Fig. 4. The ^3J(Sn–C) data used for the α-derivatives in Fig. 4 relate only to C(1) since the data for C(5) are affected by the C(5)–C(6) π-bond. Modified Karplus equations, with terms involving the electronegativities of substituents, have been successfully developed for proton–proton couplings;[26] a modified Karplus equation, taking into account additional factors such as interactions of Sn–C bonds with π-bonds, may be required for tin–carbon couplings in organostannanes.

Experimental

Melting points were measured using a Kofler hot-plate microscope and are uncorrected. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were generally recorded on a Bruker 250 MHz instrument: the ^{1}H and ^{13}C NMR spectra for **1** were also obtained on a 600 MHz instrument by the EPSRC NMR service, based at the University of Edinburgh. *J* Values are given in Hz. IR spectra

were recorded on a Nicolet 205 Fourier-transform instrument. Ether refers to diethyl ether. X-Ray data for **9** and **10** were collected at 120 K and 150 K, respectively, by the EPSRC service, based at the University of Wales, Cardiff.

3β-Tosyloxycholest-5-ene (cholesteryl toluene-*p*-sulfonate) 13
Toluene-*p*-sulfonyl chloride (14.6 g, 0.076 mol) was added to a solution of cholesterol **14** (14.6 g, 0.038 mol) in dry pyridine (17 cm^3). The solution was left standing overnight at room temperature after which time needles were produced. Ether was added to dissolve the solid, and the resulting solution was washed with water, dried and evaporated *in vacuo*. Recrystallisation of the residue from acetone yielded the product (15.4 g, 75.6%), mp 132–134 °C (lit.,[27] mp 131.5–132.5 °C); $\delta_H(CDCl_3)$ 0.67 (s, 3H, Me-18), 0.87 (d, 6H, *J* 6.6, Me-26 and Me-27), 0.91 (d, 3H, *J* 6.5, Me-21), 0.98 (s, 3H, Me-19), 1.05–2.80 (m, 26H), 2.46 (s, 3H, C_6H_4*Me-p*), 4.3–4.4 (m, 1H, *J* 5.6, H-3), 5.31 (d, 1H, *J* 5.2, H-6), 7.34 (d, 2H, *J* 8.0, aryl-H), 7.8 (d, 2H, *J* 8.0, aryl-H). ^{13}C NMR data are displayed in Table 4.

3β-Mesyloxycholest-5-ene (cholesteryl methanesulfonate) 15
Methanesulfonyl chloride (5.4 cm^3) was added to a solution of **14** (16.4 g, 0.42 mol) in dry pyridine. The solution was left overnight at −5 °C before being allowed to return to room temperature and extracted with ether. The ether extract was washed with water and evaporated *in vacuo*. The resulting solid was further washed with water. Ether and methanol were added and the solution cooled to −5 °C to yield the product (15.1 g, 81.6%), mp 120–122 °C (lit.,[28] mp 121–123 °C); $\delta_H(CDCl_3)$ 0.68 (s, 3H, Me-18), 0.86 (d, 3H, *J* 6.6, Me-26), 0.87 (d, 3H, *J* 6.6, Me-27), 0.91 (d, 3H, *J* 6.5, Me-21), 1.02 (s, 3H, Me-19), 1.06–2.73 (m, 26H), 3.00 (s, 3H, $MeSO_2$), 4.46–4.59 (m, 1H, *J* 6.3, H-3), 5.42 (d, 1H, *J* 5.1, H-6). ^{13}C NMR data are displayed in Table 4.

3β-Chlorocholest-5-ene (cholesteryl chloride) 16[29,30]
A mixture of **14** (12.5 g, 32 mmol) and thionyl chloride (15 ml, 0.2 mol) was stirred for 24 h at 0 °C. The reaction mixture was dissolved in ether and water was added until gas evolution ceased. The ether layer was collected, washed, dried over magnesium sulfate and evacuated under reduced pressure. The residue was recrystallised from acetone to yield 8.9 g (67.9%) of a yellow solid, mp 93–95 °C; $\delta_H(CDCl_3)$ 0.68 (s, 3H, Me-18), 0.86 (d, 3H, *J* 6.6, Me-26), 0.87 (d, 3H, *J* 6.6, Me-27), 0.91 (d, 3H, *J* 6.5, Me-21), 1.03 (s, 3H, Me-19), 1.06–2.62 (m, 26H), 3.7–3.8 (m, 1H, H-3), 5.36 (d, 1H, *J* 5.2, H-6). ^{13}C NMR data are displayed in Table 4.

3α-Triphenylstannylcholest-5-ene 1
Triphenylstannyllithium was prepared[31] from Li (1.6 g, 0.23 mol) and triphenyltin chloride (10.0 g, 0.023 mol) in anhydrous THF (30 cm^3) in an ultrasonic bath with a typical reaction time of 18 h. The olive-green solution of triphenylstannyllithium was filtered through glass-wool, cooled to −68 °C (acetone–ice slush bath) and **13** (5.0 g, 0.007 mol) in dry THF (25 cm^3) added. The reaction mixture was stirred under nitrogen and allowed to reach room temperature overnight, hydrolysed with saturated aqueous ammonium chloride and extracted with ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate and evaporated *in vacuo* to give an oil. The oil was dissolved in ether, filtered to remove the insoluble hexaphenylditin by-product, and the filtrate evaporated. The resultant oil was chromatographed on silica preparatory plates [eluent 5–10% ethyl acetate–light petroleum (bp 60–80 °C)]. The top band on the plates was collected as an oil and was crystallised from chloroform and ethanol (1 : 5) as colourless plates (1.46 g, 29%), mp 88–90 °C (lit.,[29] mp 85–91 °C) (Found: C, 75.3; H, 8.7%. $C_{45}H_{60}Sn$ requires C, 75.1; H, 8.4%).

A similar reaction of **15** with Ph_3SnLi also produced **1**. The ^{1}H and ^{13}C NMR spectra of compound **1** were assigned (see Table 2) using HMQC[32] and HMBC[33] NMR spectra, as well as by analogy to the ^{13}C NMR shifts of cholesterol.[34] ^{119}Sn NMR data are displayed in Table 4.

3β-Triphenylstannylcholest-5-ene 2 (Method 1)
(*a*) *Preparation of cholesterylmagnesium chloride.* A concentrated solution of cholesteryl chloride **16** (2.0 g) in anhydrous THF (2 cm^3) was added to magnesium ribbon (1.2 g, 0.049 mol), activated by iodine. The reaction mixture was gently heated and the remaining cholesteryl chloride (in total 10.0 g, 0.025 mol) in anhydrous THF added. The solution was refluxed for 4 h and used immediately.

(*b*) *Reaction of the Grignard reagent.* To the cholesterylmagnesium chloride solution was added triphenyltin chloride (9.52 g, 0.025 mol) in anhydrous THF. The reaction mixture was refluxed for 24 h, and hydrolysed with saturated aqueous ammonium chloride. The ether layer was collected, washed with saturated aqueous sodium hydrogen carbonate, dried over magnesium sulfate and evaporated *in vacuo* to leave an oil. The oil was purified by column chromatography (eluent $CHCl_3$), followed by recrystallisation from dichloromethane–ethanol or acetone to yield colourless needles, mp 151–152 °C.

3β-Triphenylstannylcholest-5-ene 2 (Method 2)
A reaction mixture containing **15** (3.8 g, 0.0098 mol), triphenyltin chloride (4 g, 0.0098 mol) and magnesium ribbon (0.61 g, 0.025 mol), activated by iodine, in anhydrous THF was refluxed until TLC [eluent: 10% ethyl acetate–light petroleum (bp 60–80 °C)] indicated consumption of the cholesteryl chloride. The solution was hydrolysed with saturated aqueous ammonium chloride and extracted with ether. The ether layer was washed with saturated aqueous sodium hydrogen carbonate and dried over magnesium sulfate. Evaporation of the solvent *in vacuo* left a yellow coloured oil. The oil was redissolved in ether and the solution was left to allow the remaining hexaphenylditin by-product to precipitate out. The ether solution was filtered and evacuated *in vacuo* to leave a glassy oil, which was crystallised from dichloromethane–ethanol (1 : 5) to give needles, mp 147–148 °C (lit.,[29] mp 151–153 °C) (Found: C, 75.3; H, 8.7%. $C_{45}H_{60}Sn$ requires C, 75.1; H, 8.4%); $\delta_H(CDCl_3)$ 0.66 (s, 3H, Me-18), 0.85 (d, 3H, *J* 6.5, Me-26), 0.86 (d, 3H, *J* 6.6, Me-27), 0.90 (d, 3H, *J* 6.5, Me-21), 0.96 (s, 3H, Me-19), 0.98–2.72 (m, 26H), 5.24 (d, 1H, *J* 5.2, H-6), 7.34–7.39 (m, 10H, *p*- + *m*-aryl H), 7.40–7.62 (m, 5H, *o*-aryl H). ^{13}C and ^{119}Sn NMR data are displayed in Table 4.

Preparation of 3-(iodophenyl)stannylcholest-5-ene derivatives
3α- or 3β-Triphenylstannylcholest-5-ene (**1** or **2**) was dissolved in chloroform and a solution containing a calculated quantity of iodine (1 or 2 mol equiv.) in chloroform was then added dropwise with stirring. The reaction was stirred until all the iodine had reacted. All volatiles were removed under vacuum to leave oily solid residues.

3α-(Iododiphenyl)stannylcholest-5-ene 9. From **1** (0.5 g, 0.70 mmol) and I_2 (0.176 g, was recrystallised from chloroform–methanol as needles, 0.24 g, 44.9%, mp 120–121 °C; $\delta_H(CDCl_3)$ 0.60 (s, 3H Me-18), 0.87 (d, 3H, *J* 6.5, Me-26), 0.87 (d, 3H, *J* 6.5, Me-27), 0.88 (d, 3H, *J* 6.4, Me-21), 0.96 (s, 3H, Me-19), 1.00–2.90 (m, 26H), 5.25 (d, 1H, *J* 5.0, H-6), 7.26–7.41 (m, 10H, *p*- + *m*-aryl H), 7.51–7.73 (m, 5H, *o*-aryl H). ^{13}C and ^{119}Sn NMR data are displayed in Table 4.

3α-(Diiodophenyl)stannylcholest-5-ene (10). From **1** (0.204 g, 0.283 mmol) and I_2 (0.144 g, 0.567 mmol), was crystallised from chloroform–methanol as platelets, 0.14 g, 60%, mp 120.5–121.5 °C; $\delta_H(CDCl_3)$ 0.60 (3H, s, Me-18), 0.87 (d, 3H, *J* 6.5, Me-26), 0.87 (d, 3H, *J* 6.6, Me-27), 0.88 (3H, d, Me-21, *J* 6.3 Hz), 0.96 (s, 3H, Me-19), 1.02–3.7 (m, 26H), 5.40 (d, 1H, *J* 5.0, H-6), 7.33–7.47 (m, 10H, *p*- + *m*-aryl H), 7.61–7.78 (m, 5H, *o*-aryl H). ^{13}C and ^{119}Sn NMR data are displayed in Table 4.

3β-(Iododiphenyl)stannylcholest-5-ene (11). From **2** (0.101 g, 0.14 mmol) and I_2 (0.0389 g, 0.15 mmol), was recrystallised

Table 6 Crystal data and structure refinement for **9** and **10**

	9	**10**
Empirical formula	$C_{39}H_{55}ISn$	$C_{33}H_{50}I_2Sn$
Formula weight	769.42	819.22
Temperature (K)	120(2)	150(2)
Wavelength (Å)	0.710 69	0.710 69
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$
Unit cell dimensions		
a/Å	14.51(16)	10.141(2)
b/Å	7.620(13)	10.830(3)
c/Å	16.25(8)	15.518(5)
α/°	90	88.62(3)
β/°	99.0(3)	89.30(2)
γ/°	90	63.08(2)
Volume/Å^3	1775(21)	1691.4(8)
Z	2	2
Density (calc) (mg m^{-3})	1.440	1.609
Absorption coeff./mm^{-1}	1.641	2.599
F(000)	784	808
Crystal size (mm)	0.18 × 0.18 × 0.35	0.41 × 0.28 × 0.28
Theta range/°	1.75 to 24.93	1.89 to 24.89
Index ranges		
	$-16 \leqslant h \leqslant 15$	$-11 \leqslant h \leqslant 11$
	$-8 \leqslant k \leqslant 5$	$-12 \leqslant k \leqslant 12$
	$0 \leqslant l \leqslant 17$	$-17 \leqslant l \leqslant 13$
Reflections collected	4565	7363
Independent reflections	4565	6133
	[R(int) = 0.0748]	[R(int) = 0.0548]
Observed reflections [$I > 2\sigma(I)$]	4314	6133
Refinement method	Full-matrix l.s. on F^2	Full-matrix l.s. on F^2
Number of parameters	334	693
Goodness-of-fit on F^2 (S)	1.182	1.142
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0473	$R1$ = 0.0459
	$wR2$ = 0.1367	$wR2$ = 0.1170
R indices (all data)	$R1$ = 0.0488,	$R1$ = 0.0472
	$wR2$ = 0.1372	$wR2$ = 0.1190
Final weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2]$	$w = 1/[\sigma^2(F_o^2) + (0.0758P)^2]$
	where $P = (F_o^2 + 2F_c^2)/3$	where $P = (F_o^2 2F_c + ^2)/3$
Flack x parameter	0.01(5)	−0.04(4)
Residual diffraction max/min (e Å^{-3})	1.342/−0.841	1.398/−0.750

from ethanol as needles, 0.08 g, 74%, mp 148–149 °C; $\delta_H(CDCl_3)$ 0.67 (s, 3H, Me-18), 0.86 (d, 3H, J 6.7, Me-26), 0.86 (d, 3H, J 6.6, Me-27), 0.91 (d, 3H, J 6.5, Me-21), 1.00 (s, 3H, Me-19), 1.03–2.71 (m, 26H), 5.29 (d, 1H, J 3.7, H-6), 7.37–7.50 (m, 10H, p- + m-aryl H), 7.58–7.76 (m, 5H, o-aryl H). ^{13}C and ^{119}Sn NMR data are displayed in Table 4.

3β-(Diiodophenyl)stannylcholest-5-ene (12). From **2** (0.102 g, 0.14 mmol) and I_2 (0.0071 g, 0.28 mmol), was recrystallised from ethanol as platelets, 0.07 g, 61%, mp 152–153 °C; $\delta_H(CDCl_3)$ 0.67 (s, 3H, Me-18), 0.86 (d, 3H, J 6.6, Me-26), 0.87 (d, 3H, J 6.5, Me-27), 0.91 (d, 3H, J 6.5, Me-21), 1.03 (s, 3H, Me-19), 1.06–2.64 (m, 26H), 5.34 (d, 1H, J 5.2, H-6), 7.36–7.56 (m, 10H, p- + m-aryl H), 7.57–7.71 (m, 5H, o-aryl H). ^{13}C and ^{119}Sn NMR data are displayed in Table 4.

Crystal structure determinations of 9 and 10 †

The colourless crystals used in the analyses were grown from $CHCl_3$–MeOH. The unit cell and intensity data were collected on a Delft Instruments FAST diffractometer with monochromated Mo-Kα radiation using the routines ENDEX, REFINE and MADONL in the MADNES[35] software and processed using ABSMAD;[36] detailed procedures have been described.[37]

Compound 9. Corrections were made for Lorentz and polarisation effects. Corrections were made for absorptions effects using the empirical absorption correction program, XABS2;[38] (correction range 0.84–1.00). The positions of the tin and iodine were located from a Patterson vector map using SHELXS86.[22] The positions of the remaining non-hydrogen atoms were located on successive difference Fourier maps using SHELXL93.[39] The positions of the hydrogen atoms were calculated from geometrical calculations. During refinement hydrogens were allowed to ride on their attached carbon atoms. Full-matrix least-squares calculations with anisotropic displacement parameters for non-hydrogen atoms and common isotropic displacement parameters according to type (methyl, aromatic, *etc.*) for hydrogen atoms were calculated. Molecular diagrams were obtained by the program ZORTEP.[40] Crystal data and structure refinement details are listed in Table 6.

Compound 10. The structure was solved with SIR92[41] and refined with SHELXL93.[39] Corrections were made for absorptions effects using the absorption correction program, DIFABS;[42] (correction range 0.82–1.01). The tin, carbon and iodine atoms were refined with anisotropic displacement parameters and the hydrogen atoms were allowed to ride on their attached atoms with common isotropic displacement parameters for the methyl and non-methyl hydrogens. Molecular diagrams were obtained by the program ZORTEP.[40] Crystal data and structure refinement details are listed in Table 6.

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† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web pages (http://chemistry.rsc.org/rsc/p1pifa.htm). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/162.

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