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(Z)-1-[2-(Triarylstannyl)vinyl]-1-cycloheptanols: synthesis, characterization, halodemetallation and crystal structures

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Abstract

The synthesis and characterization by ^{1}H, ^{13}C, ^{119}Sn NMR and ^{119}Sn Mössbauer spectroscopy of (Z)-1-[2-(triphenylstannyl)vinyl]-1-cycloheptanol, $\overline{CH_2(CH_2)_5C}(OH)CH{=}CHSnPh_3$ (**1**), and (Z)-1-[2-(tri-p-tolylstannyl)vinyl]-1-cycloheptanol, $\overline{CH_2(CH_2)_5C}(OH)CH{=}CHSn(p\text{-}tol)_3$ (**2**), are described, together with their halodemetallation by I_2, Br_2 and ICl1 to yield derivatives of the types $\overline{CH_2(CH_2)_5C}(OH)CH{=}CHSnAr_{3-n}X_n$ (Ar = phenyl or p-tolyl, $n = 1, 2$; X = I, Br, Cl, respectively). The solid-state structures of four compounds have been determined by X-ray diffraction analysis. In the crystals of $\overline{CH_2(CH_2)_5C}(OH)CH{=}CHSnPh_3$ (**1**) and $\overline{CH_2(CH_2)_5C}(OH)CH{=}CHSn(p\text{-}tol)_3$ (**2**) the Sn atom has a tetrahedral geometry distorted towards trigonal bipyramid as a consequence of a close intramolecular contact with the hydroxyl O(1) atom of 2.742(3) Å and 2.768(3) Å, respectively. A trigonal bipyramidal geometry is found in $\overline{CH_2(CH_2)_5C}(OH)CH{=}CHSn(p\text{-}tol)Br_2$ (**12**) and $\overline{CH_2(CH_2)_5C}(OH)CH{=}CHSn(p\text{-}tol)_2Cl$ (**4**), in which significant Sn–O(1) interactions are noted [2.437(8) Å and 2.407(8) Å, respectively].

Keywords: Tin; Crystal structure; NMR

1. Introduction

Iododemetallation [1] of the products of the reactions between triphenyltin hydride and ethynyl(hydroxy)steroids [2,3] yielded diorganotin diiodides with interesting antitumour activities [4,5]. Because each of these species exhibits an intramolecular HO → Sn interaction giving rise to a five-membered tin-containing ring, we prepared several classes of model compounds [6–8]. In continuation of these studies, we describe here another class of related compounds, namely (Z)-1-[2-(triarylstannyl)vinyl]-1-cycloheptanols, as well as some of the corresponding diarylhalostannyl- and aryldihalostannyl-compounds. Their structural features, particularly the coordinative HO → Sn interactions, are compared.

2. Results and discussion

2.1. Syntheses

The (Z)-1-[2-(triarylstannyl)vinyl]-1-cycloheptanols (aryl = phenyl, p-tolyl) were synthesized by the addition of the corresponding triaryltin hydride to the triple bond of 1-ethynylcycloheptanol.

The reactions of **1** and **2** with halogens in a 1 : 1 or 1 : 2 molar ratio yield the corresponding mono- and di-halides, respectively.

The physical properties of the new products are described in the experimental details.

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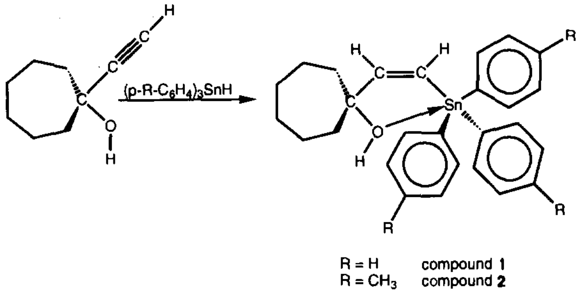
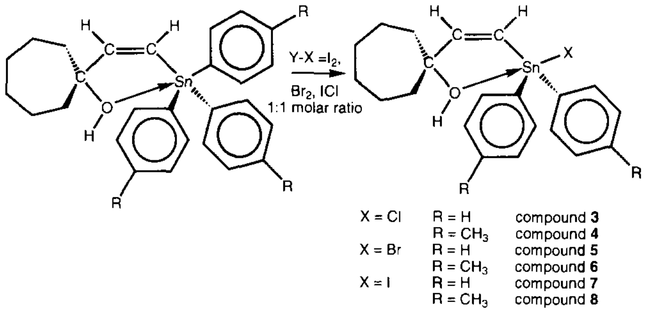


Scheme 1.



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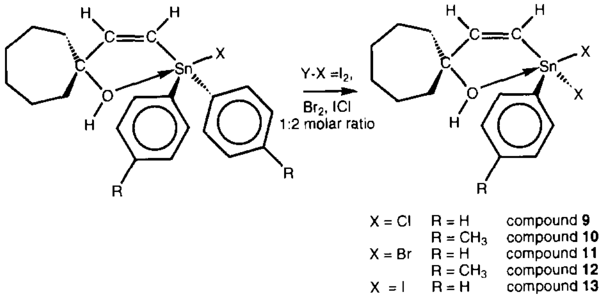

Scheme 3.

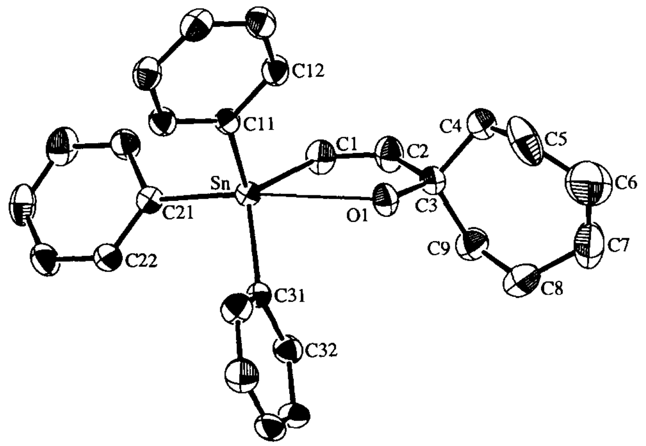

Fig. 1. Molecular structure and crystallographic numbering scheme for **1**.

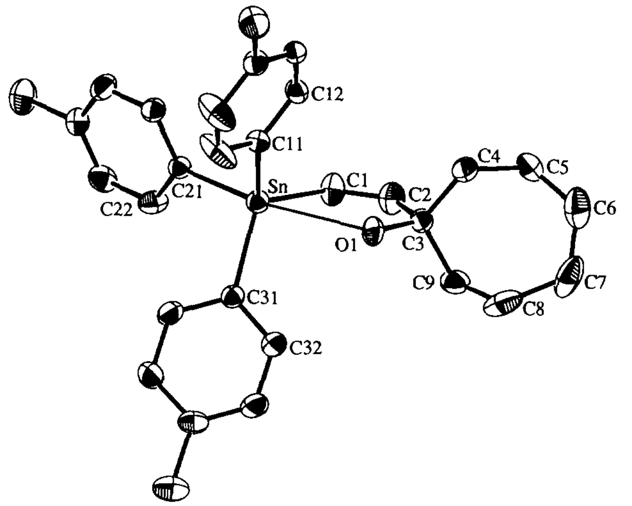

Fig. 2. Molecular structure and crystallographic numbering scheme for **2**.

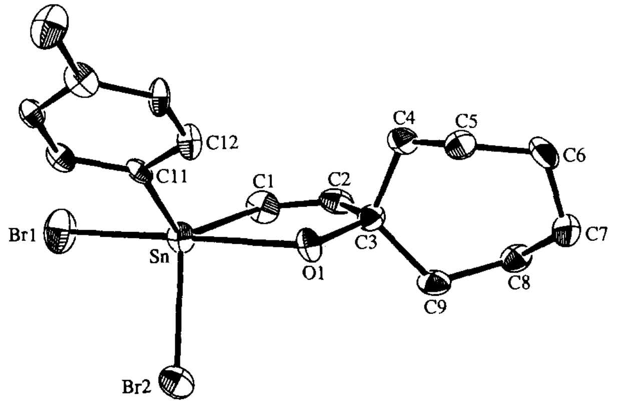

Fig. 3. Molecular structure and crystallographic numbering scheme for **12**.

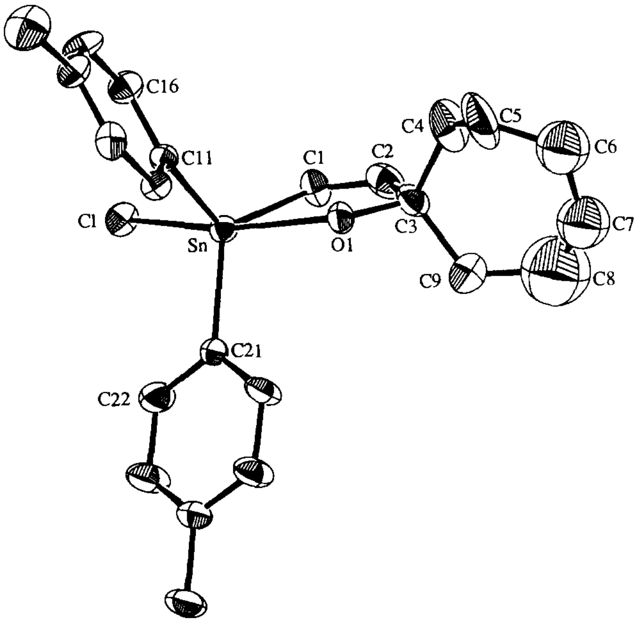

Fig. 4. Molecular structure and crystallographic numbering scheme for **4**.

2.2. Solid-state structures

The molecular structures of **1**, **2**, **12** and **4** are shown in Figs. 1–4, respectively and selected interatomic parameters are listed in Table 1. The crystal, **1**, consists of discrete molecules, with no significant intermolecular contacts; the closest non-H contact of 3.678(7) Å is between the C(14) and C(24)′ atoms (symmetry operation: $-x$, $-y$, $1-z$). The Sn atom in **1** is bound to three phenyl groups as well as to the C(1) atom of the vinyl residue (Sn–C(1), 2.089(5) Å) leading to a distorted tetrahedral geometry. The tetrahedral angles range from 103.2(2)° to 120.0(2)°, but if the C(1)–Sn–C(31) angle is excluded, the range is somewhat smaller i.e. 103.2(2)° to 112.8(2)°. The opening of the C(1)–Sn–C(31) angle may be traced to the relatively close approach of the O(1) atom of the cycloheptanol hydroxyl group at 2.742(3) Å from the tin atom. The close proximity of the O(1) atom influences the coordination geometry about the Sn atom. (The presence of the O(1) atom also influences the strength of the Sn–C(Ph) bonds.) The Sn–C(21) bond distance of 2.139(4) Å is longer than the Sn–C(11) and Sn–C(31) bond distances of 2.110(4) and 2.116(4) Å, respectively. This reflects the distortion of the tetrahedral geometry towards trigonal bipyramidal, where the Sn–C(21) bond has apical character, and the Sn–C(11) and Sn–C(31) bonds are more equatorial in nature [the O(1)–Sn–C(21) angle is 167.7(1)°]. In **1**, as in **2**, **12** and **4**, there is a Z configuration at the double bond. The structure of the tri-p-tolyl analogue, **2**, is illustrated in Fig. 2. Again the crystal consists of discrete molecules, the closest non-H contact in the lattice being that between the C(25) and C(25)′ atoms, at 3.51(1) Å (symmetry operation: 1 − X, − Y, 1 − Z). The geometry about the tin atom is essentially the same as that for **1** [Sn–C(1) 2.087(5) Å], but the range of tetrahedral angles, 102.8(2)° to 116.0(2)°, is narrower than found in **1**. The widest angle is opposite to the position occupied by the O(1) atom, which is separated by 2.768(3) Å from the Sn atom. The Sn ⋯ O(1) interaction in **2** is significantly longer (to the 5σ level) than that in **1**, reflecting the greater Lewis acidity of the Sn center in **1**. While the Sn–C(21) bond length is possibly longer than the other Sn–C(Ph) bond lengths, the differences are not statistically significant (within 3σ limits).

Table 1
Selected interatomic bond distances (Å) and angles (deg.) for **1**, **2**, **12** and **4**

	1	**2**	**12**	**4**
X	C(21)	C(21)	Br(1)	Cl
Y	C(31)	C(31)	Br(2)	C(21)
Sn–C(1)	2.089(5)	2.087(5)	2.08(1)	2.08(1)
Sn–O(1)	2.742(3)	2.768(3)	2.437(8)	2.407(8)
Sn–C(11)	2.110(4)	2.123(4)	2.10(1)	2.09(1)
Sn–X	2.139(4)	2.136(5)	2.528(2)	2.446(3)
Sn–Y	2.116(4)	2.119(5)	2.472(2)	2.08(1)
C(1)–C(2)	1.302(6)	1.296(7)	1.30(2)	1.27(2)
C(2)–C(3)	1.467(6)	1.492(7)	1.51(2)	1.47(2)
C(3)–O(1)	1.424(5)	1.414(5)	1.43(1)	1.44(2)
C(3)–C(4)	1.508(6)	1.518(6)	1.52(2)	1.49(2)
C(3)–C(9)	1.514(6)	1.508(7)	1.52(2)	1.53(2)
C(4)–C(5)	1.493(9)	1.496(7)	1.50(2)	1.45(3)
C(5)–C(6)	1.46(1)	1.492(9)	1.49(2)	1.44(3)
C(6)–C(7)	1.40(1)	1.47(1)	1.49(2)	1.39(3)
C(7)–C(8)	1.474(9)	1.53(1)	1.51(2)	1.42(4)
C(8)–C(9)	1.458(8)	1.512(9)	1.52(2)	1.49(4)
C(1)–Sn–O(1)	66.6(1)	66.5(2)	73.6(4)	72.6(4)
C(1)–Sn–C(11)	112.8(2)	115.2(2)	129.8(5)	123.8(5)
C(1)–Sn–X	104.8(2)	102.8(2)	97.5(4)	94.3(4)
C(1)–Sn–Y	120.0(2)	116.0(2)	112.8(4)	119.0(5)
O(1)–Sn–C(11)	87.9(1)	79.0(1)	89.0(4)	87.7(4)
O(1)–Sn–X	167.7(1)	168.4(1)	170.5(2)	166.2(2)
O(1)–Sn–Y	75.4(1)	85.9(1)	83.8(2)	91.9(4)
C(11)–Sn–X	103.9(1)	103.0(2)	99.4(4)	96.3(3)
C(11)–Sn–Y	110.1(2)	113.9(2)	111.5(3)	113.6(4)
X–Sn–Y	103.2(2)	103.4(2)	97.3(6)	98.6(4)
Sn–C(1)–C(2)	127.6(4)	128.7(4)	120(1)	119(1)
Sn–O(1)–C(3)	110.4(3)	110.2(3)	112.8(7)	113.9(8)
C(1)–C(2)–C(3)	127.4(4)	126.6(5)	126(1)	129(1)
C(2)–C(3)–O(1)	107.3(3)	108.1(4)	107(1)	105(1)

Whereas essentially a tetrahedral geometry only slightly distorted towards trigonal bipyramidal, is found in **1** and **2**, definitely five-coordinate, distorted trigonal bipyramidal geometry is found in **12** and **4**.

The structure of **12** is shown in Fig. 3. There are no significant intermolecular contacts in the lattice of **12**, the closest non-H contact, of 3.48(1) Å, being that between the O(1) and C(16)′ atoms (symmetry operation: 0.5 + X, 1.5 − Y, 0.5 + Z). The tin atom is five coordinate, being bonded to a tolyl group, two Br atoms, the vinyl C(1) atom [2.08(1) Å] and the O(1) atom of the hydroxyl group [2.437(8) Å]. The geometry about the tin atom is based on a trigonal bipyramid with the trigonal plane defined by the Br(2), C(1) and C(11) atoms with the Br(1) and O(1) atoms in the axial positions [Br(1)–Sn–O(1) = 170.5(2)°]. The Sn atom lies 0.306(1) Å out of the trigonal plane in the direction of the Br(1) atom. The Sn–Br bond distances are not equal, the Sn–Br(1) distance, 2.528(2) Å, being significantly longer than the Sn–Br(2) distance, 2.437(8) Å; this difference may be rationalized in terms of the former bond being apical (as is the O(1) atom) and the latter equatorial. The five-membered chelate ring is essentially planar, the mean deviation of the atoms from the least-square plane through the atoms being 0.04(1) Å. The coordination geometry at tin in **12** is similar to that in **4**.

In contrast to the other structures described above, in the case of **4** there is a significant intermolecular contact. The O(1) ⋯ Cl′ separation of 3.234 (9) Å (symmetry operation: −0.5 + X, 1.5 − Y, −Z) is indicative of a weak hydrogen bond. The tin atom has a distorted trigonal bipyramidal geometry, as shown in Fig. 4, and lies 0.2289(7) Å out of the trigonal plane defined by the three C atoms, in the direction of the Cl atom; the axial Cl-Sn-O(1) angle is 166.2(2) Å. The mean deviation of the atoms from the five-membered ring is 0.04(1) Å. The Sn–C(1) bond distance of 2.08(1) Å is indistinguishable from in **12**. The length of the Sn–O(1) bond, 2.407(8) Å, appears to be shorter than that of the corresponding bond in **12**, 2.437(8) Å, though the relatively high estimated standard deviations associated with these parameters should be noted. However, the presence of the weak intramolecular hydrogen-bonding contact involving the O(1) atom in **4** would be expected to lengthen the Sn–O(1) interaction; hence we conclude that the Sn–O(1) interaction in **4** is significantly stronger than that in **12**, and that the Lewis acidity of the tin atom in the $(p\text{-tol})_2SnCl$ entity is greater than in the $(p\text{-tol})SnBr_2$ entity. On the basis of the X-ray crystallographic data it is possible to place the Lewis acidities of the Sn atoms in the following order: $(p\text{-tol})_3Sn < Ph_3Sn \ll (p\text{-tol})SnBr_2 < (p\text{-tol})_2SnCl$.

Some interesting variations in some of the bond angles are apparent as the mode of coordination of the vinyl-1-cycloheptanol moieties varies in the structures. In the structures of **1** and **2**, in which the Sn ··· O(1) interactions are thought to be weak, the Sn–C(1)–C(2) angles, 127.6(4)° and 128.7(4)°, respectively, are considerably larger than the equivalent angles, 120(1)° and 119(1)°, in **12** and **4**, respectively. As the C(1)–C(2)–C(3) and C(2)–C(3)–O(1) angles are similar in the four structures, the C(1) atom can be regarded as the point about which the ligand pivots as the Sn ··· O(1) separation decreases. In the structures of **12** and **4** the Sn–O(1)–C(3) angles are approximately 3° wider as a consequence of the above effect. The other major systematic changes between the structures are those between the C(1)–Sn–C(11) and C(1)–Sn–O(1) angles. The C(1)–Sn–C(11) angles are significantly narrowed in the case of **1** and **2**, in keeping with the tetrahedral nature of the tin centers. The greater disparity between the Sn–C(1) and Sn–O(1) separations, i.e. the more asymmetric mode of coordination, in the structures of **1** and **2** also results in a contraction of the C(1)–Sn–O(1) angles and a concomitant expansion in the Sn–C(1)–C(2) angles.

Table 2
^{119}Sn Chemical shift data (in ppm) and $^1J(^{13}C-^{117/119}Sn)$ coupling data (in Hz) of the aromatic ipso and the vinylic tin-bonded ^{13}C nuclei of compounds **1** to **13**, $(CH_2CH_2CH_2)_2C(OH)-CH=CH-SnAr_{3-n}X_n$

Compound	Ar	*n*	X	$\delta(^{119}Sn)$	^1J(ipso)	^1J(vinyl)
1	Ph	0	–	−155.3	518/542	560/584
2	p-Tol	0	–	−150.7	524/549	552/577
3	Ph	1	Cl	−129.8	700/732	711/742
4	p-Tol	1	Cl	−124.8	709/742	708/741
5	Ph	1	Br	−137.7	683/715	691/723
6	p-Tol	1	Br	−131.7	691/724	687/718
7	Ph	1	I	−167.4	659/689	663/692
8	p-Tol	1	I	−161.6	668/697	657/687
9	Ph	2	Cl	−136.2	935/976	871/912
10	p-Tol	2	Cl	−129.8	hidden	866/906
11	Ph	2	Br	−186.0	874/914	811/848
12	p-Tol	2	Br	−182.5	882/928	809/847
13	Ph	2	I	−355.5	778/813	720/754

2.3. *NMR data in solution*

The solution ^{1}H and ^{13}C NMR data are consistent with the expected structures. They are given in the experimental details.

Table 2 presents a summary of the ^{119}Sn chemical shift data and the $^1J(^{13}C-^{117/119}Sn)$ coupling constants for all the compounds. The ^{119}Sn chemical shifts for the phenyl derivatives are in agreement with those previously reported for species of similar structure [2,3,6,7,9]. Noteworthy is the systematic high-frequency shift of the observed ^{119}Sn resonance for all p-tolyl compounds with relative to that for the corresponding phenyl compounds. We ascribe this effect to the electron release by the p-tolyl group, which results in the decrease of the Lewis acidity of the tin atom and so, in a weakening of the HO → Sn coordination. In the case of compounds **1** and **2**, this interpretation is consistent with the fact that the HO → Sn bond in **2** [2.768(3) Å] is longer than that in **1** [2.742(3) Å].

There is a slight but significant tendency towards higher values of the $^1J(^{13}C-^{117/119}Sn)$ coupling constants for the ipso coordination and lower values for the tin-bonded vinyl carbon atom in the p-tolyl compared with the phenyl compounds. We suggest that this reflects a slight increase in the s-character [10] in the p-tolyl–Sn than in phenyl–Sn bonds, this again being related to the higher electron release by the p-tolyl than by the phenyl group.

The $^1J(^{13}C-^{119}Sn)$ coupling constant of 584 Hz found for the tin-bonded vinylic carbon atom of compound **1** confirms that the slight trigonal bipyramidal distortion found in the crystalline state is maintained in solution. This value lies in the range 580–600 Hz found for similar compounds [6,7,8] and thus is significantly larger than that for triphenylvinyltin (511 Hz) [8], in which the geometry is tetrahedral.

Finally the $^1J(^{13}C-^{117/119}Sn)$ coupling constants decrease to comparable extents for the ipso, and vinylic carbon atoms fall to comparable extents in the sequence Cl > Br > I for both mono- and di-halides. This sequence reflects decreasing the apicophilicity on going from chlorine to iodine, resulting in a decrease in the s-character of the equatorial aryl–Sn and vinyl–Sn bonds, and thus in the ^1J couplings [10].

3. Experimental details

3.1. Chemicals

1-Ethynylcycloheptanol was synthesized by the procedure of Vercruijsse et al. [11] in 70% yield, b.p. 80–81°C/10 torr, $n_D^{25} = 1.4868$.

Triphenyltin hydride [12] and tri-p-tolyltin hydride [13] were prepared by published methods.

3.2. Instruments

Elemental analyses were carried out with a Perkin-Elmer PE 2400 CHN instrument. The infrared spectra were recorded with an Alpha Centacr FT-IR instrument. The ^{1}H, ^{13}C and ^{119}Sn spectra were recorded in $CDCl_3$ on a Bruker AC250 and/or on a Bruker AMX500 spectrometer. Chemical shifts were referenced to the solvent peak and converted to the standard scales by adding 7.24 ppm and 77.0 ppm for ^{1}H and ^{13}C nuclei, respectively. The ^{119}Sn chemical shift is given in parts per million with respect to neat external tetramethyltin ($\Xi(^{119}Sn) = 37.290665$). The Mössbauer spectra were recorded as described previously [14]

3.3. Syntheses and Characterizations

3.3.1. Syntheses of compounds 1 and 2

1-Ethynylcycloheptanol (6 ml, 37.6 mmol) and dibenzoyl peroxide (300 mg) were added to an ether solution of triphenyltin hydride prepared from 2.05 g (54 mmol) of $LiAlH_4$ and 20.8 g (54 mmol) of triphenyltin chloride. The mixture was stirred for 25 h at room temperature under nitrogen, the ether was evaporated off, and the residue recrystallized three times from ethanol to yield 11.7 g of compound **1**, and 3.5 g of hexaphenylditin, m.p. 233–234°C [1] as a by-product.

The same procedure was used for the reaction of 1-ethynylcycloheptanol with tri-p-tolyltin hydride.

3.3.2. Reaction of compounds 1 and 2 with halogens

A solution of bromine (0.316 g, 1.98 mmol) in 10 ml of CCl_4 was added dropwise with stirring to an ice-cooled solution of 0.968 g (1.98 mmol) of **1** in 12 ml of CCl_4. The colour disappeared immediately. The mixture was allowed to warm to room temperature and was set aside for 5 h. The solvent was evaporated off, and the residue recrystallized three times from cyclohexane to yield 0.7 g of compound **5**.

The other vinylphenyltin halides were prepared analogously by use of ICl (chlorides) or I_2 (iodides).

Abbreviations: ^{1}H NMR data: s = singlet; d = doublet; dd = doublet of doublets; m = complex pattern; b = broad; $^nJ(^1H-^1H)$ between parentheses; $^nJ(^1H-^{117/119}Sn)$ between brackets; ^{13}C NMR; $^nJ(^{13}C-^{117/119}Sn)$ between parentheses. All coupling constants are in hertz.

(Z)-1[2-(triphenylstannyl)vinyl]-1-cycloheptanol, *1*. Yield: 63%; m.p. (recrystallized from ethanol): 90–91°C. Elemental analysis: Found (Calc.): C: 66.5 (66.29); H: 6.2 (6.18); Sn: 24.6 (24.26)%. IR: ν(O–H): 3599, ν(C–O): 1075 cm^{-1}. Mössbauer parameters: QS: 0.61; IS (with respect to $Ca^{119}SnO_3$): 1.21; Γ: 0.96 mm s^{-1}. ^{1}H NMR: 1.24, s, OH; 1.3–1.9, m, C_7H_{12}; 6.213, d (12.4) [93/97], CH–Sn; 7.042, d (12.4) [178/186], CH; 7.2–7.5, m, *meta* + *para*; 7.5–7.7, m [≈ 55, unresolved], *ortho*. ^{13}C NMR: 22.3 and 29.4, $\beta + \gamma$-CH_2; 42.1 (8), α-CH_2; 78.1 (28), C–OH; 120.3 (560/584), CH–Sn; 128.3 (49/51), *meta*; 128.4 (11), *para*; 137.0 (36/38), *ortho*; 142.6 (518/542), *ipso*; 156.5 (4), CH.

(Z)-1-[2-(tri-p-tolylstannyl)vinyl]-1-cycloheptanol, *2*. Yield: 63%; m.p. (recrystallized from ethanol): 98–99°C. Elemental analysis: C: 67.6 (67.82); H: 6.7 (6.83); Sn: 22.6 (22.34)%. IR: ν(O–H): 3566, ν(C-O): 1069 cm^{-1}. Mössbauer: QS: 0.56; IS: 1.25; Γ: 0.89 mm s^{-1}. ^{1}H NMR: 1.25, s, OH; 1.4–1.9, m, C_7H_{12}; 2.421, s, CH_3; 6.233, d (12.4) [90/95], CH–Sn; 7.053, d (12.4) [175/183], CH; 7.245, d (7.8), *meta*; 7.604, d (7.8) [47], *ortho*. ^{13}C NMR: 21.6, CH_3; 22.4 and 29.5, $\beta + \gamma$-CH_2; 42.2 (8), α-CH_2; 77.9 (28), C–OH; 120.8 (552/577), CH–Sn; 129.8 (52), *meta*; 137.0 (39), *ortho*; 138.0 (11), *para*; 138.8 (524/549), *ipso*; 156.4 (4), CH.

(Z)-1-[2-(chlorodiphenylstannyl)vinyl]-1-cycloheptanol, *3*. Prepared from **1** and ICl in a 1:1 molar ratio at −10°C, yield: 86%; m.p. (recrystallized from cyclohexane): 147–148°C. Elemental analysis: C: 55.7 (56.35); H: 5.4 (5.63); Sn: 27.0 (26.50)%. IR: ν(O–H): 3401, ν(C–O): 1073 cm^{-1}. Mössbauer: QS: 3.55; IS: 1.37; Γ_1: 0.87; Γ_2: 0.91 mm s^{-1}. ^{1}H NMR: 1.3–1.9, m, C_7H_{12}; 2.42, b, OH; 6.244, d (11.3) [113/118], CH–Sn; 6.902, d (11.3) [239/249], CH; 7.2–7.5, m, *meta* + *para*; 7.6–7.8, m [≈ 65, unresolved], *ortho*. ^{13}C NMR: 22.3 and 29.2, $\beta + \gamma$-CH_2; 41.7 (11), α-CH_2; 80.7 (36), C–OH; 125.0 (711/742), CH–Sn; 128.7 (65/70), *meta*; 129.4 (14), *para*; 135.7 (50), *ortho*; 142.1 (700/732), *ipso*; 153.0 (4), CH.

(Z)-1-[2-(chlorodi-p-tolylstannyl)vinyl]-1-cycloheptanol, *4*. Prepared from **2** and ICl in a 1:1 molar ratio at −10°C, yield: 43%; m.p. (recrystallized from cyclohexane/CCl_4 1:1): 153–154°C. Elemental analysis: C: 57.5 (58.08); H: 6.0 (6.15); Sn: 24.5 (24.95)%. IR: ν(O–H): 3412, ν(C–O): 1067 Mössbauer: QS: 3.38; IS: 1.33; Γ_1: 0.85; Γ_2: 0.88 mm s^{-1}. ^{1}H NMR: 1.4–1.9, m, C_7H_{12}; 2.354, s, CH_3; 2.54, bs, OH; 6.234, d (11.3) [112/117], CH–Sn; 6.893, d (11.3) [236/247], CH; 7.211, d (8) [18], *meta*; 7.628, d (8) [≈ 63, unresolved], *ortho*. ^{13}C NMR: 21.5, CH_3; 22.3 and 29.3, $\beta + \gamma$-CH_2; 41.8 (11), α-CH_2; 80.7 (36), C–OH; 125.4 (708/741), CH–Sn; 129.5 (68/72), *meta*; 135.7 (52), *ortho*; 138.5 [709/742], *ipso*; 139.2 (14), *para*; 152.9 (4), CH.

(Z)-1-[2-(bromodiphenylstannyl)vinyl]-1-cycloheptanol, ***5***. Prepared from **1** and Br_2 in a 1:1 molar ratio at −10°C, yield: 72%; m.p. (recrystallized from cyclohexane): 139–140°C. Elemental analysis: C: 50.3 (51.26); H: 5.1 (5.12); Sn: 24.0 (24.12)%. IR: ν(O–H): 3409, ν(C–O): 1072 cm^{-1} Mössbauer: QS: 3.50; IS: 1.39; Γ_1: 0.91; Γ_2: 0.95 mm s^{-1}. ^{1}H NMR: 1.3–1.9, m, C_7H_{12}; 2.38, bs, OH; 6.295, d (11.3) [117/122], CH–Sn; 6.871, d (11.2) [238/250], CH; 7.2–7.5, m, *meta* + *para*; 7.6–7.8, m [≈ 70, unresolved], *ortho*. ^{13}C NMR: 22.2 and 29.2, $\beta + \gamma$-CH_2; 41.7 (11), α-CH_2; 80.8 (36), C–OH; 125.7 (690/722), CH–Sn; 128.7 (66/69), *meta*; 129.4 (14), *para*; 135.8 (48/51), *ortho*; 141.9 (683/715), *ipso*; 152.8 (4), CH.

(Z)-1-[2-(bromodi-p-tolylstannyl)vinyl]-1-cycloheptanol, ***6***. Prepared from **2** and Br_2 in a 1:1 molar ratio at room temperature, yield: 55%; m.p. (recrystallized from cyclohexane): 135–136°C. Elemental analysis: C: 52.8 (53.12); H: 5.6 (5.62); Sn: 23.0 (22.84)%. IR: ν(O–H): 3533, ν(C–O): 1075 cm^{-1}. Mössbauer: QS: 3.11; IS: 1.36; Γ_1: 0.87; Γ_2: 0.85 mm s^{-1}. ^{1}H NMR: 1.4–1.9, m, C_7H_{12}; 2.35 and 2.36, overlapping singlets, CH_3 and OH; 6.296, d (11.3) [115/120], CH–Sn; 6.866, d (11.3) [231/253], CH; 7.216, d (8) [≈ 20], *meta*; 7.634, d (8) [62/65], *ortho*. ^{13}C NMR: 21.5, CH_3; 22.3 and 29.3, $\beta + \gamma$-CH_2; 41.7 (11), α-CH_2; 80.7 (35), C–OH; 126.0 (687/719), CH–Sn; 129.5 (68/71), *meta*; 135.6 (50/53), *ortho*; 138.2, (691/724), *ipso*; 139.3 (14), *para*; 152.6 (4), CH.

(Z)-1-[2-(iododiphenylstannyl)vinyl]-1-cycloheptanol, ***7***. Prepared from **1** and I_2 in a 1:1 molar ratio at room temperature, yield: 85%; m.p. (recrystallized from cyclohexane): 127–128°C. Elemental analysis: C: 46.8 (46.79); H: 4.6 (4.67); Sn: 22.2 (22.02)%. IR: ν(O–H): 3536, ν(C–O): 1074 cm^{-1} Mössbauer: QS: 2.98; IS: 1.38; Γ_1: 0.81; Γ_2: 0.85 mm s^{-1}. ^{1}H NMR: 2.27, s, OH; 1.3–1.9, m, C_7H_{12}; 6.377, d (11.2) [121/127], CH–Sn; 6.799, d (11.2) [238/249], CH; 7.2–7.5, m, *meta* + *para*; 7.6–7.8, m [≈ 65, unresolved], *ortho*. ^{13}C NMR: 22.3 and 29.2, $\beta + \gamma$-CH_2; 41.5 (11), α-CH_2; 80.7 (36), C–OH; 126.9 (663/692), CH–Sn; 128.7 (65/68), *meta*; 129.4 (15), *para*; 135.9 (48/51), *ortho*; 141.5 (659/689), *ipso*; 152.6 (4), CH.

(Z)-1-[2-(iododi-p-tolylstannyl)vinyl]-1-cycloheptanol, ***8***. Prepared from **2** and I_2 in a 1:1 molar ratio at room temperature, yield: 88%; m.p. (recrystallized from cyclohexane): 142–143°C. Elemental analysis: C: 48.7 (48.72); H: 5.1 (5.15); Sn: 20.9 (20.93)%. IR: ν(O–H): 3529, ν(C–O): 1074 cm^{-1} Mössbauer: QS: 3.11; IS: 1.40; Γ_1: 0.82; Γ_2: 0.82 mm s^{-1}. ^{1}H NMR: 1.3–1.9, m, C_7H_{12}; 2.23 (s), OH; 6.382, d (11.4) [120/126], CH–Sn; 6.792, d (11.3) [246/254], CH; 7.214, d (8) [≈ 36], *meta*; 7.635 (8) [62/65], *ortho* ^{13}C NMR: 21.5, CH_3; 22.2 and 29.3, $\beta + \gamma$-CH_2; 41.7 (11), α-CH_2; 80.7 (35), C–OH; 127.1 (657/687), CH–Sn; 129.5 (67/70), *meta*; 135.7 (50/53), *ortho*; 137.8 (668/697), *ipso*; 139.2 (14), *para*; 152.4 (5), CH.

(Z)-1-[2-(dichlorophenylstannyl)vinyl]-1-cycloheptanol, ***9***. Prepared from **1** and ICl in a 1:2 molar ratio at −10°C, then allowed to warm to room temperature, yield: 62%; m.p. (recrystallized from $CHCl_3$/petroleum ether 30/60°C, 1/1): 97–98°C. Elemental analysis: C: 43.5 (44.38); H: 4.8 (4.96); Sn: 29.0 (29.24)%. IR: ν(O–H): 3525, ν(C–O): 1066 cm^{-1}. ^{1}H NMR: 1.3–2.0, m, C_7H_{12}; 3.324, s, OH; 6.199, d (10.4) [186/194], CH–Sn; 6.956, d (10.4) [326/340], CH; 7.3–7.5, m, *meta* + *para*; 7.7–7.9, m [≈ 88, unresolved], *ortho*. ^{13}C NMR: 22.2 and 29.2, $\beta + \gamma$-CH_2; 41.4 (11), α-CH_2; 80.7 (52/54), C–OH; 124.3 (871/912), CH–Sn; 129.2 (93/95), *meta*; 130.8 (19), *para*; 135.0 (64/67), *ortho*; 141.2 (935/976), *ipso*; 154.5 (4), CH.

(Z)-1-[2-(dichloro-p-tolylstannyl)vinyl]-1-cycloheptanol, ***10***. Prepared from **2** and ICl in a 1:2 molar ratio at −10°C, then allowed to warm to room temperature, yield: 24%; m.p. (recrystallized from $CHCl_3$/petroleum ether 30/60°C, 1/1): 118–119°C. Elemental analysis: C: 45.6 (45.76); H: 5.2 (5.29); Sn: 27.9 (28.26)%. IR: ν(O–H): 3523, v(C–O): 1066 cm^{-1} ^{1}H NMR: 1.3–2.0, m, C_7H_{12}; 2.358, s, CH_3; 3.172, s, OH; 6.234, d (10.4) [182/190], CH–Sn; 6.958, d (10.4) [322/336], CH; 7.258, d (8) [30], *meta*; 7.665, d [86/90], *ortho*. ^{13}C NMR: 21.5, CH_3; 22.2 and 29.3, $\beta + \gamma$-CH_2; 41.4 (11), α-CH_2; 80.5 (52/53), C–OH; 124.6 (866/906), CH–Sn; 129.9 (94/99), *meta*; 134.8 (67/70), *ortho*; 141.0 (19), *para*; 137.6 (^1J hidden), *ipso*; 154.3 (5), CH.

(Z)-1-[2-(dibromophenylstannyl)vinyl]-1-cycloheptanol, ***11***. Prepared from **1** and Br_2 in a 1:2 molar ratio at −10°C, then allowed to warm to room temperature, yield: 50%; m.p. (recrystallized from cyclohexane/CCl_4): 75–76°C Elemental analysis: C: 36.4 (36.41); H: 3.9 (4.07); Sn: 23.8 (23.99)%, IR: ν(O–H): 3529, v(O–O): 1064 cm^{-1}. Mössbauer: QS: 2.94; IS: 1.38; Γ_1: 1.00; Γ_2: 1.01 mm s^{-1}. ^{1}H NMR: 1.5–1.9, m, C_7H_{12}; 3.03, s, OH; 6.304, d (10.4) [186/195], CH–Sn; 6.873, d (10.4) [323/338], CH; 7.3–7.5, m, *meta* + *para*; 7.7–7.8, m [≈ 85, unresolved], *ortho*. ^{13}C NMR: 22.3 and 29.2, $\beta + \gamma$-CH_2; 41.4 (11), α-CH_2; 80.6 (50), C–OH; 125.9 (811/848), CH–Sn; 129.0 (90/94), *meta*; 130.6 (19), *para*; 134.7 (65/68), *ortho*; 141.6 (874/914), *ipso*; 153.9 (4), CH.

(Z)-1-[2-(dibromo-p-tolylstannyl)vinyl]-1-cycloheptanol, ***12***. Prepared from **2** and Br_2 in a 1:2 molar ratio at −10°C, then allowed to warm to room temperature, yield: 72%; m.p. (recrystallized from cyclohexane/CCl_4 1/1): 99–101°C. Elemental analysis: C: 37.4 (37.77); H:

Table 3
Crystallographic data

Compound	1	2	12	4
Formula	$C_{27}H_{30}OSn$	$C_{30}H_{36}OSn$	$C_{16}H_{22}Br_2OSn$	$C_{23}H_{29}ClOSn$
Formula wt.	489.2	531.3	508.9	475.6
Cryst size, mm	0.11 × 0.24 × 0.32	0.13 × 0.23 × 0.39	0.03 × 0.10 × 0.15	0.08 × 0.08 × 0.24
Cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
a, Å	14.765(3)	11.227(4)	8.660(2)	13.772(4)
b, Å	9.901(7)	11.818(4)	17.354(6)	15.376(3)
c, Å	15.774(2)	11.031(4)	12.187(4)	10.402(3)
α, deg	90	92.44(3)	90	90
β, deg	90.69(1)	91.38(3)	105.43(2)	90
γ, deg	90	115.47(2)	90	90
V, Å^3	2305(1)	1318.7(9)	1765.5(9)	2203(1)
Z	4	2	4	4
ρ_{calcd}, g cm^{-3}	1.409	1.338	1.914	1.434
$F(000)$	1000	548	984	968
μ, cm^{-1}	11.23	9.87	59.81	12.89
Transm coeffs	0.933–1.042	0.951–1.045	0.961–1.079	0.952–1.019
Data collcd	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$
No. of data collcd	4656	5101	3601	2313
No. of unique data	4477	4835	3370	2313
No. of unique data with $I \geq 3.0\sigma(I)$	2858	3712	1109	1375
R	0.030	0.038	0.041	0.043
R_w	0.028	0.040	0.032	0.039
Residual density, e Å^{-3}	0.34	0.54	0.58	0.49

Table 4
Fractional atomic coordinates and their estimated standard deviations for **1**

Atom	x	y	z
Sn	0.05786(2)	0.01170(3)	0.78488(2)
O(1)	0.2040(2)	0.1104(3)	0.8740(2)
C(1)	0.1105(3)	−0.1248(5)	0.8736(3)
C(2)	0.1784(4)	−0.1062(5)	0.9258(3)
C(3)	0.2303(3)	0.0184(5)	0.9392(3)
C(4)	0.3303(3)	−0.0095(6)	0.9316(3)
C(5)	0.3918(4)	0.1100(9)	0.9359(5)
C(6)	0.4114(6)	0.1610(10)	1.0211(8)
C(7)	0.3452(6)	0.1869(8)	1.0819(5)
C(8)	0.2485(5)	0.1940(7)	1.0579(4)
C(9)	0.2048(4)	0.0721(6)	1.0255(3)
C(11)	0.1366(3)	0.0244(4)	0.6745(2)
C(12)	0.2275(3)	−0.0029(5)	0.6731(3)
C(13)	0.2760(3)	0.0035(6)	0.6008(3)
C(14)	0.2341(4)	0.0388(5)	0.5272(3)
C(15)	0.1444(4)	0.0652(5)	0.5249(3)
C(16)	0.0955(3)	0.0576(5)	0.5983(3)
C(21)	−0.0662(3)	−0.0779(4)	0.7417(2)
C(22)	−0.1454(3)	−0.0068(5)	0.7371(3)
C(23)	−0.2233(3)	−0.0654(6)	0.7087(3)
C(24)	−0.2241(4)	−0.1956(6)	0.6841(3)
C(25)	−0.1474(4)	−0.2685(5)	0.6870(4)
C(26)	−0.0691(3)	−0.2092(5)	0.7158(3)
C(31)	0.0176(3)	0.2070(4)	0.8237(3)
C(32)	−0.0158(3)	0.2319(5)	0.9033(3)
C(33)	−0.0423(3)	0.3599(6)	0.9267(3)
C(34)	−0.0368(4)	0.4626(5)	0.8707(4)
C(35)	−0.0044(4)	0.4398(5)	0.7930(4)
C(36)	0.0236(3)	0.3124(5)	0.7696(3)

4.3 (4.36); Sn: 23.4 (23.33) %. IR: ν(O–H): 3530, v(C–O): 1062 cm^{-1}. Mössbauer: QS: 2.99; IS: 1.38; Γ_1: 0.85; Γ_2: 0.88 mm s^{-1}. ^{1}H NMR: 1.5–1.9, m, C_7H_{12}; 2.363, s, CH_3; 2.93, bs, OH; 6.300, d (10.1) [185/194], CH–Sn; 6.867, dd (10.2, 3.0) [322/336], CH; 7.254, d (8) [30], *meta*; 7.652, d (8) [86/91], *ortho*. ^{13}C NMR: 21.5, CH_3; 22.2 and 29.2, $\beta + \gamma$-CH_2; 41.4 (11), α-CH_2; 80.5 (50), C–OH; 126.2 (809/847), CH–Sn; 129.7 (93/97), *meta*; 134.5 (67/70), *ortho*; 140.8 (18), *para*; 138.0 (882/928), *ipso*; 153.8 (4), CH.

(Z)-1-[2-(diiodophenylstannyl)vinyl]-1-cycloheptanol, 13. Prepared from **1** and I_2 in a 1 : 2 molar ratio at room temperature, yield: 69%; m.p. (recrystallized from cyclohexane): 75–76°C. Elemental analysis: C: 31.0 (30.60); H: 3.4 (3.27); Sn: 19.7 (20.16) %. IR: ν(O–H): 3445, v(C–O): 1067 cm^{-1}. ^{1}H NMR: 1.4–2.0, m, C_7H_{12}; 2.614, s [38], OH; 6.400, d (10.3) [190/198], CH–Sn; 6.627, d (10.3) [313/327], CH; 7.2–7.6, m, *meta* + *para*; 7.7–7.8, m [≈ 85, unresolved], *ortho*. ^{13}C NMR: 22.3 and 29.2, $\beta + \gamma$-CH_2; 41.5 (11), α-CH_2; 80.9 (45/47), C–OH; 126.9 (720/754), CH–Sn; 128.8 (86/90), *meta*; 130.4 (19), *para*; 134.2 (64/67), *ortho*; 140.1 (778/813), *ipso*; 153.2 (5), CH.

3.4. X-ray diffraction studies

Crystals of **1** and **2** were grown from ethanol. Crystals of **12** and **4** were grown from cyclohexane/CCl_4.

Intensity data for the colorless crystals were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å; the $\omega:2\theta$ scan technique was employed to measure data up to a maximum Bragg angle of 25.0° in each case. The data sets were corrected for Lorentz and polarization effects [15] and an empirical absorption correction was applied [16]. The net intensities of three standards (measured after every 400 measurements) decreased to approximately 93% of their original values during the data collection on **4** and the reflection data were scaled accordingly. Relevant crystal data and refinement details are given in Table 3. The structures were solved by direct-methods [17] and refined by a full-matrix least-squares procedure based on F[15]. Non-H atoms were refined with anisotropic thermal parameters except for the C(6)–C(8) atoms in **4**, for which high thermal motion was noted, indicating some disorder in their positions. The H atoms attached to carbon were included in their calculated positions (C–H, 0.97 Å). In no case was the hydrogen of the OH group located, and hence these atoms were not included. The refinements were continued until convergence, employing sigma weights; the analysis of variance showed no special features, indicating that an appropriate weighting scheme had been applied in all cases. The absolute configuration of **4** was determined on the basis of reversing the signs of

Table 5
Fractional atomic coordinates and their estimated standard deviations for **2**

Atom	*x*	*y*	*z*
Sn	0.51885(3)	0.26793(3)	0.18989(3)
O(1)	0.3803(3)	0.2846(3)	−0.0143(3)
C(1)	0.4353(5)	0.1023(5)	0.0797(5)
C(2)	0.3639(6)	0.0791(5)	−0.0204(5)
C(3)	0.3241(4)	0.1682(5)	−0.0824(4)
C(4)	0.1748(5)	0.1190(5)	−0.0871(5)
C(5)	0.0994(5)	0.0242(6)	−0.1877(6)
C(6)	0.0798(7)	0.0782(7)	−0.3023(7)
C(7)	0.1992(10)	0.1454(7)	−0.3699(6)
C(8)	0.3210(8)	0.2421(6)	−0.2981(6)
C(9)	0.3797(5)	0.1862(5)	−0.2069(5)
C(11)	0.3817(4)	0.3248(4)	0.2700(4)
C(12)	0.2506(5)	0.2511(4)	0.2694(4)
C(13)	0.1654(4)	0.2903(5)	0.3244(4)
C(14)	0.2077(5)	0.4045(5)	0.3799(5)
C(14′)	0.1155(6)	0.4497(6)	0.4368(6)
C(15)	0.3371(6)	0.4771(5)	0.3819(7)
C(16)	0.4230(5)	0.4386(5)	0.3273(7)
C(21)	0.6013(4)	0.2153(4)	0.3418(4)
C(22)	0.7168(5)	0.1992(5)	0.3363(5)
C(23)	0.7674(5)	0.1648(5)	0.4358(6)
C(24)	0.7077(5)	0.1440(5)	0.5421(5)
C(24′)	0.7629(6)	0.1066(7)	0.6485(6)
C(25)	0.5942(5)	0.1584(6)	0.5479(5)
C(26)	0.5425(5)	0.1937(5)	0.4504(5)
C(31)	0.6844(4)	0.4171(4)	0.1217(4)
C(32)	0.6950(5)	0.4529(5)	0.0056(5)
C(33)	0.8092(6)	0.5448(5)	−0.0337(5)
C(34)	0.9183(5)	0.6055(5)	0.0416(5)
C(34′)	1.0453(6)	0.7045(5)	0.0003(6)
C(35)	0.9105(5)	0.5738(5)	0.1600(5)
C(36)	0.7948(5)	0.4813(5)	0.1988(5)

Table 6
Fractional atomic coordinates and their estimated standard deviations for **12**

Atom	*x*	*y*	*z*
Sn	0.0614(1)	0.8470(1)	0.4402(1)
Br(1)	−0.0713(2)	0.8971(1)	0.2429(1)
Br(2)	0.3183(2)	0.9160(1)	0.4666(1)
O(1)	0.1669(9)	0.8162(5)	0.6414(6)
C(1)	−0.0902(15)	0.8996(8)	0.5242(11)
C(2)	−0.0682(15)	0.8885(8)	0.6325(12)
C(3)	0.0652(16)	0.8418(9)	0.7088(10)
C(4)	−0.0072(16)	0.7718(9)	0.7508(12)
C(5)	0.0912(17)	0.7297(8)	0.8525(12)
C(6)	0.0757(17)	0.7619(10)	0.9622(11)
C(7)	0.1470(16)	0.8397(11)	0.9946(11)
C(8)	0.0970(16)	0.9034(8)	0.9074(11)
C(9)	0.1634(16)	0.8908(8)	0.8054(12)
C(11)	0.0829(14)	0.7300(8)	0.4013(11)
C(12)	0.1158(17)	0.6735(9)	0.4846(11)
C(13)	0.1228(16)	0.5986(9)	0.4533(10)
C(14)	0.0992(16)	0.5750(9)	0.3437(13)
C(14′)	0.0978(19)	0.4911(9)	0.3101(12)
C(15)	0.0747(16)	0.6321(9)	0.2629(11)
C(16)	0.0662(15)	0.7077(9)	0.2914(11)

Table 7
Fractional atomic coordinates and their estimated standard deviations for **4**

Atom	*x*	*y*	*z*
Sn	0.14033(5)	0.69086(5)	0.01537(7)
Cl	−0.0334(2)	0.6969(2)	0.0638(3)
O(1)	0.2998(5)	0.6551(5)	−0.0629(8)
C(1)	0.1361(10)	0.5628(8)	−0.0480(13)
C(2)	0.2138(14)	0.5273(10)	−0.0877(16)
C(3)	0.3121(11)	0.5646(11)	−0.0944(15)
C(4)	0.3445(12)	0.5582(13)	−0.2303(22)
C(5)	0.4376(18)	0.5914(14)	−0.2745(24)
C(6)	0.5161(20)	0.5308(19)	−0.2583(31)
C(7)	0.5295(19)	0.4929(18)	−0.1378(30)
C(8)	0.4685(29)	0.4693(25)	−0.0328(44)
C(9)	0.3842(15)	0.5258(12)	0.0017(20)
C(11)	0.1426(9)	0.7982(8)	−0.1072(10)
C(12)	0.2130(9)	0.8606(8)	−0.0899(13)
C(13)	0.2109(10)	0.9365(9)	−0.1653(14)
C(14)	0.1406(12)	0.9496(9)	−0.2555(13)
C(14′)	0.1442(14)	1.0313(11)	−0.3306(17)
C(15)	0.0745(10)	0.8883(11)	−0.2708(13)
C(16)	0.0733(9)	0.8141(11)	−0.1990(13)
C(21)	0.1937(9)	0.7172(7)	0.1988(12)
C(22)	0.1351(11)	0.7394(10)	0.2969(15)
C(23)	0.1698(11)	0.7603(12)	0.4183(14)
C(24)	0.3032(11)	0.7834(13)	0.5776(14)
C(24′)	0.2640(12)	0.7611(9)	0.4445(13)
C(25)	0.3238(10)	0.7361(11)	0.3515(15)
C(26)	0.2893(9)	0.7145(11)	0.2287(13)

the reflections. Fractional atomic coordinates are listed in Tables 4–7, and the numbering schemes employed are shown in Figs. 1–4, which were drawn with ORTEP [18] at 25% probability ellipsoids (20% for **4**). Selected bond distances and angles are given in Table 1. The teXsan [15] package, installed on an Iris Indigo workstation, was employed for all calculations. Full lists of bond lengths and angles, and tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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