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Tin for organic synthesis. Part 15 The use of 1,2-bis(trimethylstannyl)-1-alkenes in electrophilic destannylation reactions [1]

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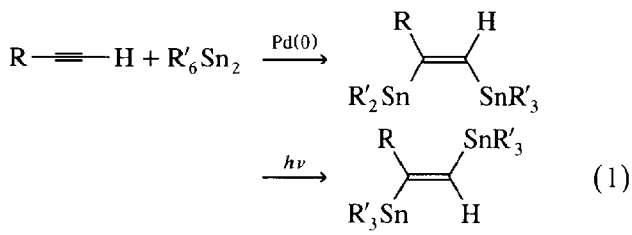
Abstract

Z-1,2-Bis(trimethylstannyl)-1-alkenes show different types of reaction behaviour towards various electrophiles. *p*-Tolysulphonylisocyanate forms five-membered tin–nitrogen-containing heterocycles. 1,1-Dichloromethylmethyl ether reacts with carbofunctionalised distannylalkenes to yield α,β-unsaturated aldehydes, which are useful tools for the synthesis of further substituted vinylstannanes. *Z*-1,2-Bis(trimethylstannyl)-1-alkenes containing heteroatoms such as O or N undergo only protodestannylation with this electrophile. The reaction of *Z*-1,2-bis(trimethylstannyl)-1-alkenes with trimethylsilyl chlorosulphonate followed by hydrolysis with aqueous $NaHCO_3$ provides the corresponding sodium sulphonates. SO_2 and SO_3 undergo insertion into both tin–carbon bonds in an ipso- and stereospecific manner to form bis-sulphinic- or bis-sulphonic bis(trialkylstannyl) esters.

Keywords: Silicon; Tin; Alkenes; Electrophilic destannylation

1. Introduction

Z-1,2-Bis(trimethylstannyl)-1-alkenes are available by palladium-catalysed addition of hexaalkylditin to terminal alkynes [2] (Eq. (1)). This method can be extended to non-terminal alkynes [3]. The *Z*-1,2-bis(trimethylstannyl)-1-alkenes can be converted into the corresponding *E*-isomers via a photochemical isomerisation [2].



(1)

e.g.

R = Bu, Ph, $MeOCH_2$, Me_2NCH_2, $CH_2=CH-CH_2$

R′ = Me, Bu

Pd(0) = $Pd(PPh_3)_4$, $Pd(dba)_2$

The *Z*-1,2-bis(trimethylstannyl)-1-alkenes are of considerable interest not only in the field of organotin chemistry but also in organic synthesis. This has, for example, been demonstrated by their use in [2,3]-Wittig-rearrangements [4], epoxidations with *m*-chloroperbenzoic acid (MCPBA) [5] or hydrogenation of the double bond [6]. Tin–lithium exchange is another important reaction of vinyltins [7], as it facilitates the synthesis of vinyllithiums not accessible by other means.

The weakness of the carbon–tin bond makes possible the use of vinyltins in electrophilic substitution reactions. These lead to α,β-unsaturated compounds, as has been demonstrated for example by nitrations [8], acylations [9], amidations with various isocyanates [10], sulphonations [11] and formylations [1].

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[1] For part 14, see Ref. [1].

[2] Deceased.

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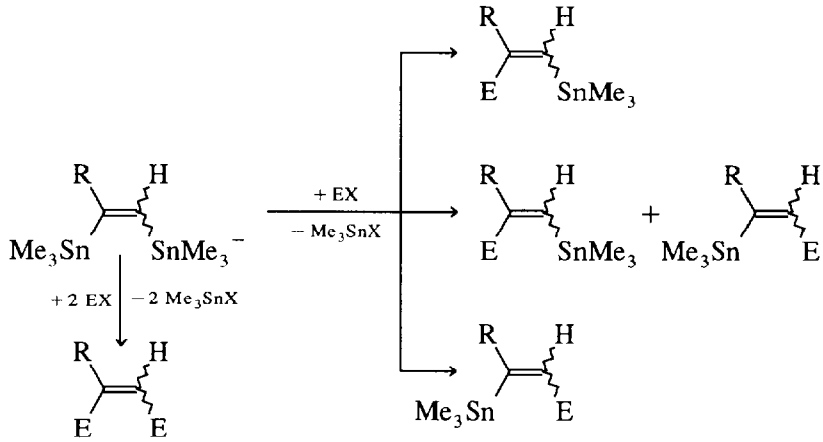
Electrophilic substitution reactions should also be possible for Z-1,2-bis(trimethylstannyl)-1-alkenes. The products obtained from these compounds will depend on the quantity of the electrophile used and on the reactivity of the two trialkylstannyl groups (Eq. (2)).

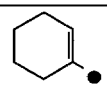
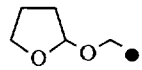
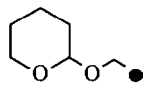
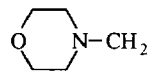
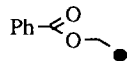
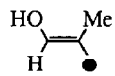
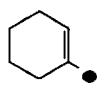
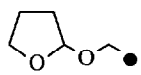
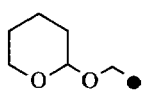


(2)

Treatment of a Z-1,2-bis(trimethylstannyl)-1-alkene with 2 molar equivalents of an electrophile should lead to bis-functionalised olefins if both of the trialkylstannyl groups are reactive enough to be cleaved. If the reaction is carried out with equimolar quantities of the electrophile and distannylalkene, either the 1- or the 2-stannyl groups can, in principle, be attacked. A mixture of the isomeric destannylation products will be formed if the reactivity of both trialkylstannyl groups is similar.

Whereas the destannylation of vinyltins has been

Table 1
Palladium-catalysed addition of $Me_3SnSnMe_3$ to alkynes RC≡CH (yielding Z-isomers) and photochemical isomerisation to the E-isomers (marked with *)

	R	Temperature (°C)	Time (h)	Yield (%)	B.p. (°C/Torr)
2c		60	8	52	100/0.01
2l	Me_3SiOCH_2	RT	1	91	100/0.02
2f		RT	1	90	120/0.01
2g		RT	1	93	120/0.03
2i		RT	1	96	110/0.02
2k		RT	1	94	160/0.01
1e		RT	1	49	130/0.02
3b*		RT	72	69	110/0.02
3c*	Me_3SiOCH_2	RT	168	86	95/0.01
3d*		RT	96	76	120/0.01
3e*		RT	168	75	115/0.04

examined using various electrophiles, few investigations on the electrophilic substitution of 1,2-bis(trialkylstannyl)-1-alkenes have been carried out. Halodestannylation with bromine yields mixtures of mono-and bis-destannylation products, while NBS attacks only the trialkylstannyl group [12]. Tin–mercury exchange with $HgCl_2$ or organomercury chlorides takes place at both stannyl moieties to yield 1,2-bismercurialkenes [13].

In this paper we present further investigations in the field of electrophilic substitution using 1,2-bis(trialkylstannyl)-1-alkenes. Electrophiles, such as *p*-tolylsulphonylisocyanate (TSI), 1,1-dichloromethylmethyl ether (DCME), trimethylsilyl chlorosulphonate, SO_2 and SO_3, which have been shown to react readily with monostannylalkenes, will be used to examine the reaction behaviour of different distannylalkenes.

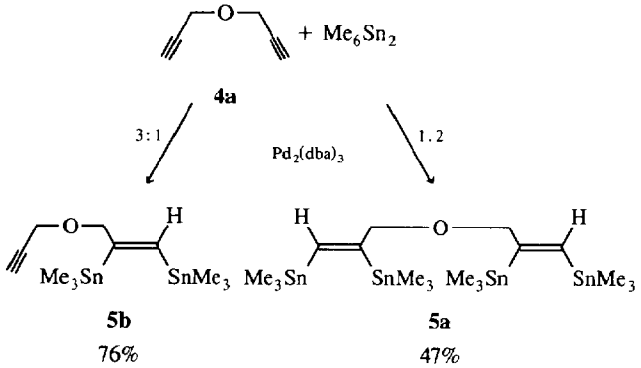
2. Results and discussion

2.1. Preparation of new 1,2-bis(trialkylstannyl)-1-alkenes

Most of the 1,2-bis(trialkylstannyl)-1-alkenes which have so far been prepared contain OH functions. Since these are able to react with the electrophile to be introduced, 1,2-bis(trialkylstannyl)-1-alkenes bearing no OH-moiety must be synthesised. Two different routes are feasible for the production of appropriate distannylalkenes. The first is the reaction of hexamethylditin with terminal alkynes (analogue to Eq. (1)) that do not carry an OH-function, or which bear protected OH groups such as acetals, esters, or ethers. The addition reaction proceeds in good to excellent yields if the alkynes contain heteroatoms (Table 1).

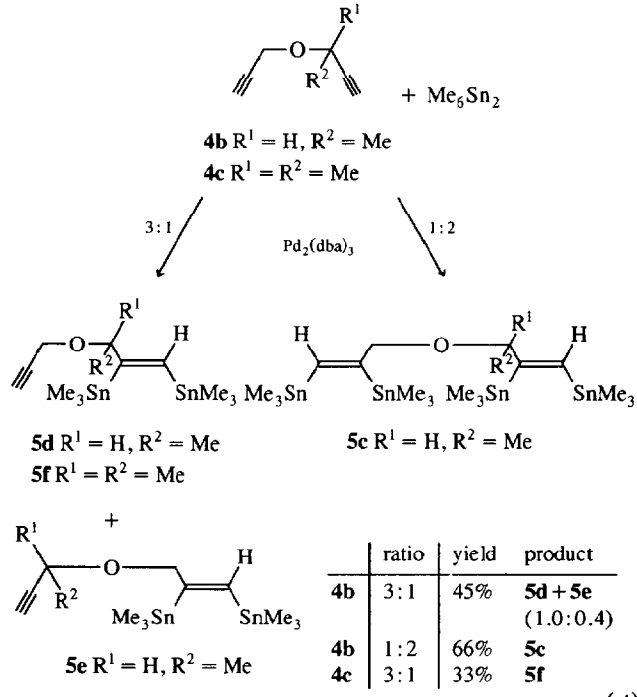
Hexamethylditin can also be added to bisalkinyl ethers. A reaction between hexamethylditin and the bispropargylic ether **4a** in the ratio 1:2 yields the tetrastannylated product **5a**.

The pure mono-addition product **5b** results if the ether is used in a threefold excess. A reaction using an equimolar ratio leads to a mixture of **5a** and **5b** (Eq. (3)) with a total yield of 60%.



(3)

If the alkyne contains a methyl group in one of the α-positions (**4b**), the reaction with an excess of the ether yields a mixture of both possible isomeric monoaddition products (**5d** and **5e**). However, the product of addition at the unsubstituted triple bond is the main one. If hexamethylditin is used in excess, the tetrastannylated alkene **5c** is formed. Twofold methylation of the α-position of the ether (**4c**) results in the formation of only compound **5f**. A compound with a structure analogous to **5e** or derived from the addition of Me_6Sn_2 to both C=C bonds cannot be observed in this case.



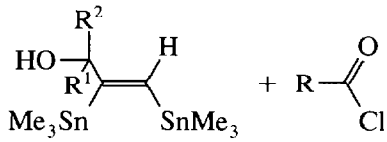
	ratio	yield	product
4b	3:1	45%	5d+5e (1.0:0.4)
4b	1:2	66%	5c
4c	3:1	33%	5f

(4)

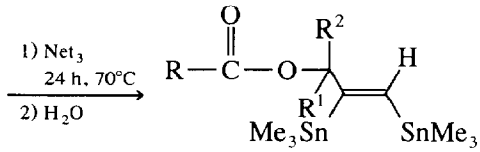
The OH functions of *Z*-1,2-bis(trimethylstannyl)-1-alkenols (**1a–e**) can be protected using standard methods.

Thus, reaction of **1** with acid chlorides in the presence of triethylamine leads to the corresponding esters (Eq. (5)). The yield decreases with increasing substitution at the α-position of **1**, so that a distannylalkenol bearing two methyl groups in α-position (**1c**) shows no reaction towards either acetyl or benzoyl chloride. The yield of the ester is generally higher when acetyl chloride is used. A further increase of the yield of the acetate derived from **1a** is obtained if acetic anhydride is employed. This method for the synthesis of esters of bis(trimethylstannyl)-1-alkenols is especially useful if the terminal acetylenic ester is not easily available, or if direct addition of hexamethylditin to the alkyne is not possible, as in the case of the two cyclohexyl-substituted distannylalkenes **6 c** and **6d**. Other acid chlorides, such as those derived from cinnamic or camphanic acid, can also be used. Electrophilic destannylation by the acid chloride is not observed.

The use of benzenesulphonic acid chloride makes sulphonic acid esters of 1,2-bis(trimethylstannyl)-1-alkenes accessible, a class of distannylalkenes not available via the addition of hexaalkylditins to the corresponding alkynes, as this reaction proceeds with decomposition of the starting materials.

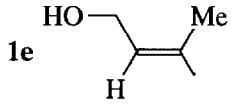


1

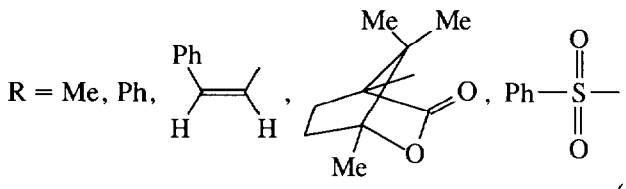


40–95%

1a $R^1 = R^2 = H$
1b $R^1 = Me$, $R^2 = H$
1c $R^1 = R^2 = Me$
1d $R^1 - R^2 = -[CH_2]_5-$

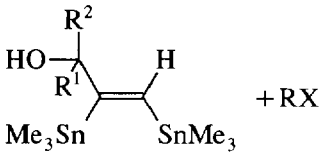


1e

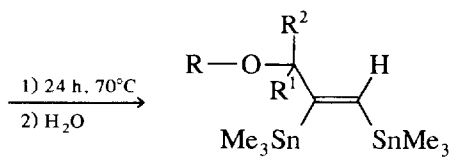


(5)

A further method for the conversion of Z-1,2-bis(trimethylstannyl)-1-alkenols involves their reaction with organic halides in the presence of potassium hydroxide to form bisstannylated allylic ethers (Eq. (6)).



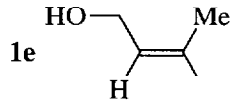
1



30–100%

(6)

1a $R^1 = R^2 = H$
1b $R^1 = Me$, $R^2 = H$
1c $R^1 = R^2 = Me$
1d $R^1 - R^2 = -[CH_2]_5-$



1e

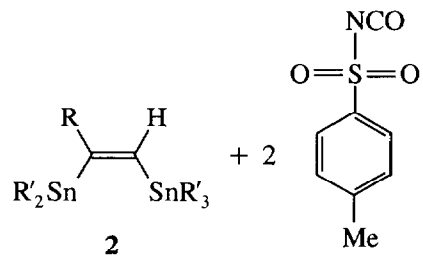
RX = MeI, $H_2C{=}CHCH_2Br$, Me_3SiCl

Trimethylsilyl ethers are formed if Me_3SiCl is used as the electrophile. In the case of **1a** and **1b** the yields are quantitative, whereas compound **1c** shows no reaction (Table 2).

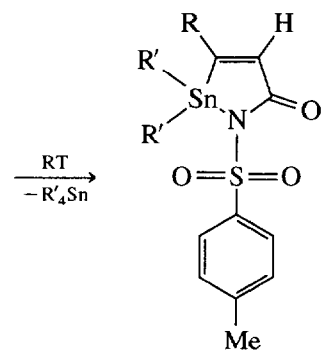
2.2. Reaction of 1,2-bis(trialkylstannyl)-1-alkenes with electrophiles

2.2.1. Reaction of 1,2-bis(trialkylstannyl)-1-alkenes with TSI

Isocyanates are powerful electrophiles and react with aryl-[14,15] or vinylstannanes [10] to form aryl- or α,β-unsaturated carboxamides. TSI **7** is particularly reactive and the yields of the resulting carboxamides are high. The reaction of a twofold excess of **7** with various Z-1,2-bis(trimethylstannyl)-1-alkenes surprisingly leads not to the expected olefinic mono-or bis-*N*-tosylcarboxamides but to five-membered tin–nitrogen heterocycles formed by elimination of tetramethylstannane (Eq. (7)).



2 **7**



8

(7)

Table 2
Yields of the reaction of Z-1,2-bis(trimethylstannyl)-1-alkenols with acid chlorides, organic halides and Me_3SiCl (Eqs. (5) and (6))

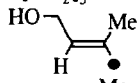
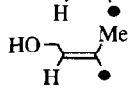
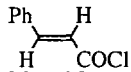
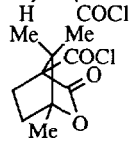
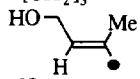
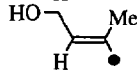
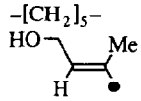
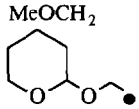
	R^1	R^2	Electrophile	Yield (%)	Product
1a	H	H	MeCOCl	70	**2j**
1a	H	H	$Me_2(CO)_2O$	90	**2j**
1a	H	H	PhCOCl	95	**2k**
1b	H	Me	MeCOCl	50	**6a**
1b	H	Me	PhCOCl	40	**6b**
1c	Me	Me	MeCOCl	0	
1c	Me	Me	PhCOCl	0	
1d	$-[CH_2]_5-$		MeCOCl	70	**6c**
1d	$-[CH_2]_5-$		PhCOCl	70	**6d**
1e			MeCOCl	80	**6e**
1e			PhCOCl	70	**6f**
1a	H	H		70	**6g**
1a	H	H		70	**6h**
1a	H	H	$PhSO_2Cl$	70	**6i**
1a	H	H	MeI	60	**2d**
1a	H	H	$H_2C{=}CHCH_2Br$	50	**6j**
1b	H	Me	MeI	30	**6k**
1b	H	Me	$H_2C{=}CHCH_2Br$	35	**6l**
1c	Me	Me	MeI	0	
1c	Me	Me	$H_2C{=}CHCH_2Br$	0	
1d	$-[CH_2]_5-$		MeI	65	**6m**
1d	$-[CH_2]_5-$		$H_2C{=}CHCH_2Br$	70	**6n**
1e			MeI	60	**6o**
1e			$H_2C{=}CHCH_2Br$	65	**6p**
1a	H	H	Me_3SiCl	100	**2l**
1b	H	Me	Me_3SiCl	100	**6q**
1c	Me	Me	Me_3SiCl	0	
1d	$-[CH_2]_5-$		Me_3SiCl	40	**6r**
1e			Me_3SiCl	90	**6s**

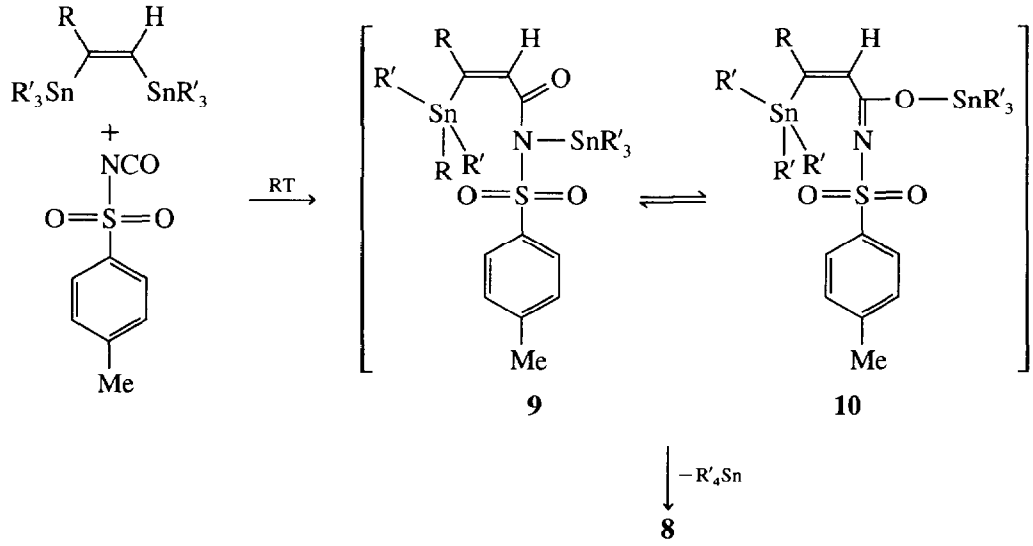
Table 3
Products **8** of the reaction of Z-1,2-bis(trialkylstannyl)-1-alkenols **2** with TSI **7**

R′	R	Yield (%)	M.p. (°C)	Time (h)	**8**
Me	Ph	78	196–198 (dec.)	22	**a**
Bu	Ph	72	210 (dec.)	22	**b**
Me	Bu	87 [a]	180–182 (dec.)	96	**c**
Me		70	104–105 (dec.)	48	**d**
Me	$MeOCH_2$	92	200–201 (dec.)	48	**d**
Me		82	99–100	12	**f**
Me	$PhCH_2OCH_2$	86 [b]	120/0.01 Torr [c]	24	**g**
Me	$Me(CO)OCH_2$	90	123 (dec.)	24	**h**

[a] Contaminated with 10% of an unknown by-product. [b] Contaminated with 20% of an unknown by-procuct. [c] Boiling point.

This reaction proceeds in good yields (48–95%) at room temperature. Even the corresponding *Z*-1,2-bis(tributylstannyl)-1-alkenes undergo this reaction, as has been demonstrated for the phenyl-substituted compound. Yields and reaction conditions are given in Table 3.

In the case of the butyl- and benzoyloxy-substituted compounds a by-product is formed which cannot be clearly characterised by NMR spectroscopy. The formation of the cyclic products is presumably initiated by an attack of TSI at the 1-trialkylstannyl group; the intermediate product will exist as a mixture of tautomers **9**, **10** (Eq. (8)). In the next step the nitrogen can coordinate to the remaining trialkylstannyl group, thus encouraging cyclisation and elimination of a molecule of tetraalkylstannane.



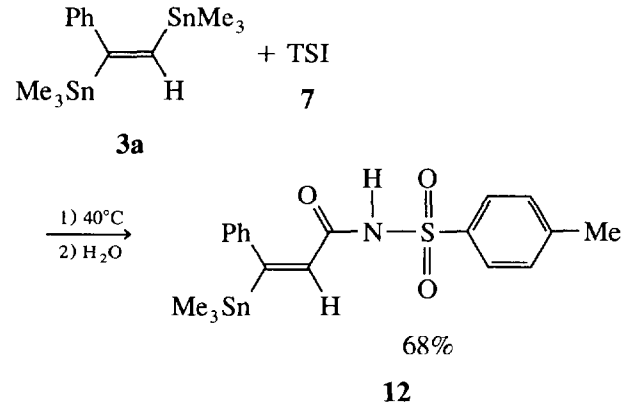
(8)

However, no evidence for the existence of the intermediates **9** or **10** could be obtained from IR- or NMR-spectroscopy; it appears that any intermediate formed is very short-lived.

The definite identification of the heterocycles **8** can be carried out via NMR spectroscopy. Both values of $^1J_{SnC}$ are close to 500 Hz, indicating that the tin is bonded to an electronegative element. The magnitudes of the couplings to the olefinic carbons define the position of the dimethylstannyl moiety, while that of the coupling to the carbonyl carbon suggests the presence of a multipath interaction.

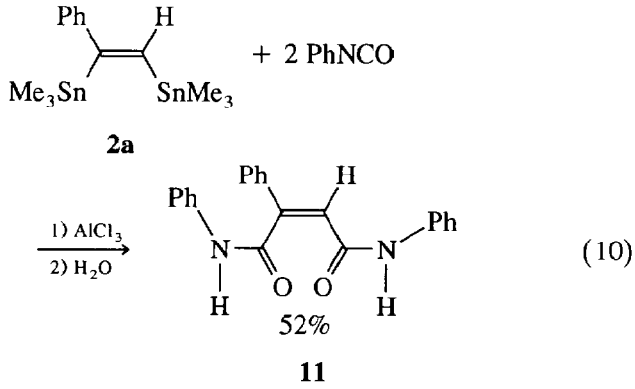
The unusual path of the reaction between TSI and the *Z*-1,2-bis(trimethylstannyl)-1-alkenes is probably due firstly to the electronic structure of TSI (the mesomeric interaction between the SO_2-group and the electron pair of the nitrogen atom causes an increase of the electrophilic character of the isocyanate carbon) and secondly to the spatial proximity of the trialkylstannyl groups.

The importance of the proximity of the stannyl groups is shown by the fact that the reaction of the *E*-isomer of the distannylalkene **3a** with TSI does not lead to a heterocycle but proceeds via destannylation of the β-trimethylstannyl group (Eq. (9)), so that a monostannyl carboxamide is formed. An increase of the reaction temperature to 40°C is necessary for this reaction; at room temperature no conversion is observed.



(9)

Other isocyanates such as benzoylisothiocyanate (PhCONCS), ethoxycarbonylisothiocyanate (EtOCONCS), phenyl isocyanate (PhNCO) and phenyl isothiocyanate (PhNCS) show no reaction toward *Z*-1,2-bis(trimethylstannyl)styrene under the same conditions. The electrophilic character of these isocyanates is not sufficient to lead to the formation of a destannylation product such as **8**. The addition of the Lewis acid $AlCl_3$ activates the 2:1 reaction with phenyl isocyanate (Eq. (10)); here only the biscarboxamide **11** is obtained.

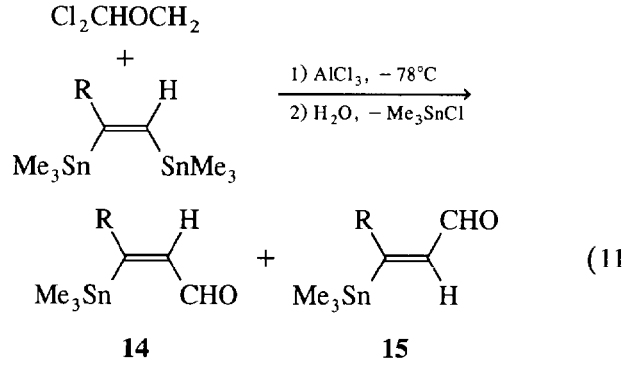


(10)

2.2.2. Reaction with DCME

DCME (**13**) reacts with simple vinyltins at −78°C in the presence of $AlCl_3$ as a catalyst to form α,β-unsaturated aldehydes [1]. This reaction is also applicable to *Z*-1,2-bis(trimethylstannyl)-1-alkenes. **2a** reacts with DCME in an equimolar ratio with cleavage of the trimethylstannyl group in the 1-position (Eq. (11)). However (in contrast to the behaviour of simple vinyltins), the reaction proceeds with partial isomerisation of the double bond, so that a mixture of 60% *Z*- and 40% *E*-isomer (**14a** and **15a**) results. Thus the reaction appears to take place predominantly via an addition–elimination sequence, as postulated by Saihi and Pereyre for other destannylations [9]. This mechanism is preferred because the cation formed during the reaction is not only stabilised via the β-effect of the trialkylstannyl group, but also because it is benzylic in nature.

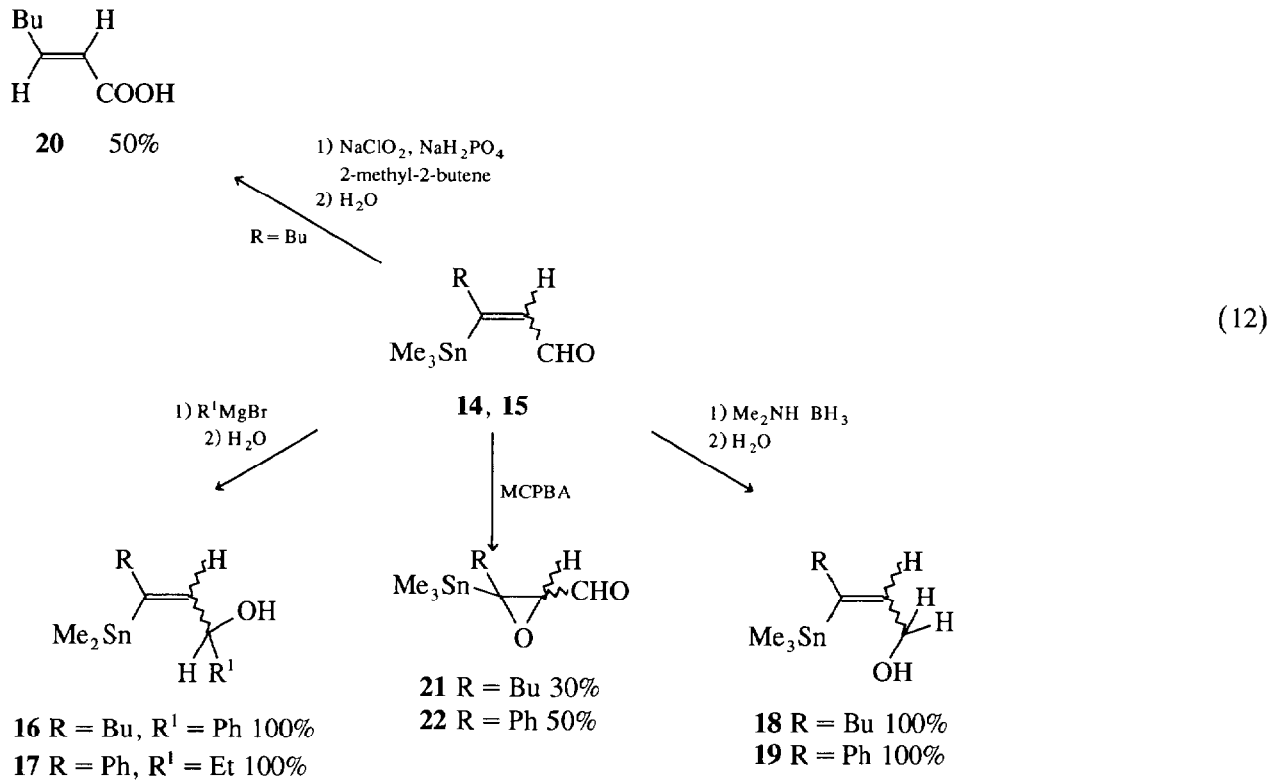
The reaction of the butyl compound **2b** with DCME under the same conditions leads to the analogous aldehydes (**14b** and **15b**). The amount of *E*-isomer formed is, however, only about 5%. A mechanism involving a four-centred transition state [16] is thus probable in this case, the reaction path via the cationic intermediate being of only secondary importance.



(11)

No formylation of the 2-trimethylstannyl group is observed even when 2 equivalents of DCME are used. The reactivity of the 2-trimethylstannyl group is thus clearly much lower than that of the 1-stannyl residue.

These α,β-unsaturated aldehydes should be interesting intermediates in organic synthesis as they still bear a reactive stannyl moiety. The reaction of **14** and **15** with Grignard reagents yields (after hydrolysis) secondary allylic alcohols. No transmetalation of the trimethylstannyl group by the Grignard reagent was observed (Eq. (12)).



(12)

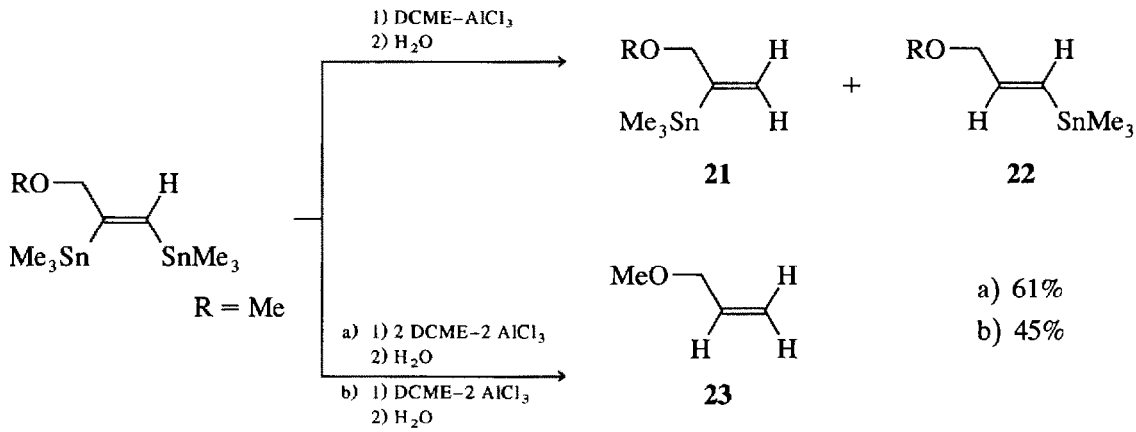
The reduction with dimethylamineborane [17] yields the unsubstituted allylic alcohols **18** and **19** without destannylation.

A method for oxidation of the aldehyde function without simultaneous oxidation of the double bond involves the use of a combination of sodium chlorite and sodium dihydrogen phosphate in the presence of 2-methyl-2-butene [18]. The aldehyde function is oxidised to the acid, but during the acidic workup the remaining trimethylstannyl group is removed, so that hept-2-enoic acid results.

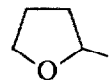
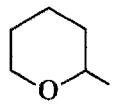
An attempt to oxidise the aldehyde function or the double bond of the compound **15** with $KMnO_4$ was unsuccessful; the unchanged starting material was recovered.

Epoxidation of **14** and **15** appeared possible, since α,β-unsaturated aldehydes [19], as well as vinyltins [20] and *Z*-1,2-bis(trimethylstannyl)-1-alkenes [5], can be converted into the corresponding epoxides by MCPBA. The compounds **14** and **15** form the expected stannylated epoxides with MCPBA but the yields are only poor (30 and 50%).

As the vinyltins containing an aldehyde function appear to be interesting and useful tools in organic synthesis, we attempted to enlarge this class of substances. Surprisingly, the distannylalkene **2d** bearing a methoxy group does not give the expected aldehyde when treated with DCME–$AlCl_3$ but rather the product **21a** of protodestannylation at the β-position. A change of the Lewis acid to $TiCl_4$ results in the same product though the yield is lower. If DCME or the Lewis acid is used in a twofold excess, both of the stannyl groups are removed to yield the tin-free ether **23** (Eq. (13)).



(13)

R	yield (%)	21	22	
Me ($AlCl_3$)	81	100%		**a**
Me ($TiCl_4$)	68	100%		**a**
	65	75%	25%	**b**
	71	90%	10%	**c**

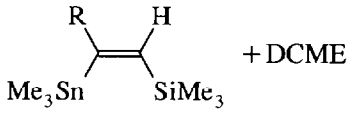
The reaction of the distannylalkenes **2f** and **2g**, bearing an acetal function, with an equimolar amount of DCME results in the formation of monodestannylation products. However, not only the 1-trimethylstannyl group but also that in 2-position is substituted by a proton, though to a lesser extent. No reaction is observed if distannylalkenes with an amino function are used, the distannylalkenes remaining unchanged in this case.

The unusual behaviour of these distannylalkenes is obviously due to the presence of the heteroatom. Apparently, the electrophile or the Lewis acid coordinates at the oxygen or nitrogen atom of the distannylalkene, so that the electrophile cannot attack the stannyl group and no aldehyde is obtained.

Even the trialkylsilyl group can be employed for electrophilic demetalation reactions [21]. 1-Trimethylstannyl-2-trimethylsilylalkenes, which are easily accessible via palladium-catalysed addition of trimethylsi-

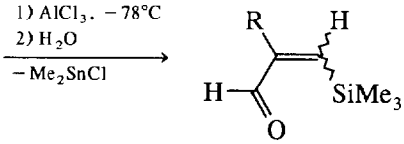
lyltrimethylstannane to terminal alkynes [22], demonstrate the relative tendency of trimethylsilyl and trimethylstannyl groups bonded to a vinylic centre to be cleaved off.

In the reaction of the silylstannylalkenes **24a** and **b** with DCME only the trimethylstannyl group is replaced by the aldehyde function, so that the trimethylsilyl-substituted α,β-unsaturated aldehydes **25** and **26** are formed. The formylation proceeds ipso-specifically at the stannyl function but not stereospecifically; apart from the *Z*-isomer, which is the main product, the *E*-isomer is also formed. The increased reactivity of the 2-trimethylstannyl group, which does not react in the case of *Z*-1,2-bis(trimethylstannyl)-1-alkenes, may involve activation by the neighbouring silyl function.



24a R = Bu

24b R = Ph



(14)

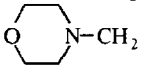
25 = Bu, 67%, *E*:*Z* = 1.0:1.5

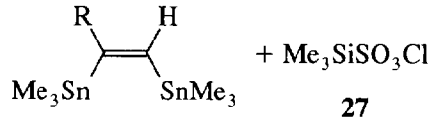
26 R = Ph, 58%, *E*:*Z* = 1.0:1.5

2.2.3. Reaction with trimethylsilyl chlorosulphonate 27

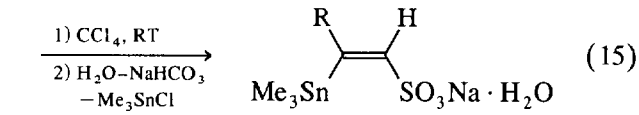
A mild reagent which has been used for the preparation of sulphonic acids and their salts is trimethylsilyl chlorosulphonate **27**, which is easily accessible [23]. **27** reacts with aryl- and vinyltins [11] to give the sodium salts of the corresponding sulphonic acids (after hydrolysis with saturated sodium bicarbonate). The reaction of **2a** with **27** in an equimolar ratio leads to the sodium sulphonate **28a**, though in low yield (16%) (Eq. (15)). The yield can be increased to 81% if the electrophile is taken in excess. Substitution of the stannyl group in the 2-position does not occur, even if the reaction is carried out under reflux or the amount of **27** is increased further. Other *Z*-1,2-bis(trimethylstannyl)-1-alkenes react under similar conditions to give the analogous sodium sulphonates in good yields. The conversion proceeds in an ipso- and stereospecific manner in each case (Table 4).

Table 4
Products of the reaction of *Z*-1,2-bis(trialkylstannyl)-1-alkenols **2** with trimethylsilyl chlorosulfoneate **27**

R	*T* (°C)	Ratio **2**:**27**	Yield (%)	Product
Ph	20	1:1	16	**28a**
Ph	20	1:2	81	**28a**
Ph	80	1:2	80	**28a**
Ph	80	1:4	76	**28a**
$MeOCH_2$	20	1:2	88	**28b**
Me_3SiOCH_2	20	1:2	77	**28c**
$PhOCH_2$	20	1:2	54	**28d**
$Me(CO)OCH_2$	20	1:2	73	**28e**
	20	1:2	65	**28f**
Me_2NCH_2	20	1:2	0	



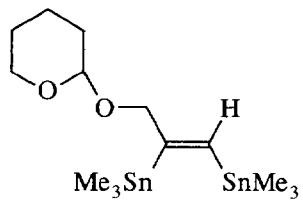
2



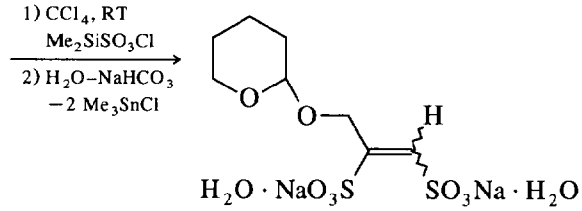
(15)

28

An exception to this mode of reaction is shown by the distannylalkene **2g**, which contains an acetal function. Here both trialkylstannyl groups are cleaved to give an α,β-unsaturated bissulphonate. However, the reaction is not stereospecific and results in a 1:1 mixture of the *E*- and the *Z*-isomers (Eq. (16)). In this case the 2-trimethylstannyl group appears to possess a higher reactivity than in the other *Z*-1,2-bis(trimethylstannyl)-1-alkenes. This effect may be due to the presence of the acetal function, which enables coordination of the trimethylstannyl group by oxygen.



2g



50%

E:*Z* = 1:1

29a, b

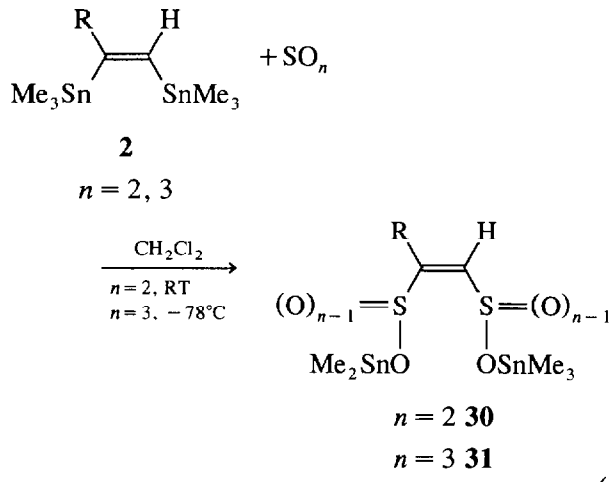
(16)

Z-1,2-bis(trimethylstannyl)-3-*N*,*N*-dimethylamino-1-propene **2h** shows no reaction towards the electrophile.

2.2.4. Reaction with SO_2 and SO_3

The insertion of SO_2 [23] and SO_3 [24] into the tin–carbon bond of aryl- and vinyltins is a well known reaction of stannanes.

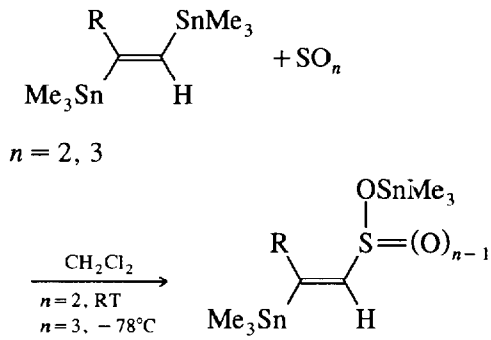
In all cases, the reaction of *Z*-1,2-bis(trimethylstannyl)-1-alkenes with SO_2 or SO_3 proceeds under insertion of the sulphur oxides into both Sn–C bonds. Thus, bissulphinic and bissulphonic bis(trimethylstannyl) esters derived from the compounds **2a–l** are obtained in high yields (Table 5).



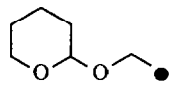
(17)

Here, no difference in the reactivities of the 1- and 2-trimethylstannyl groups can be observed. The reason may be that SO_2 or SO_3 is inserted first into the more reactive 1-Sn–C bond. This SO_n-group now coordinates via the oxygen to the tin atom in the 2-position, thus weakening the tin–sp^2 carbon bond so that insertion of the sulphur oxide into the less reactive 2-Sn–C bond is facilitated. While the reaction with SO_2 can be carried out at room temperature, that with SO_3 must be run at −78°C, because of the higher reactivity of SO_3. A fourfold insertion of SO_2 or SO_3 into the tetrastannylated bisallyl ether **5a** is possible.

The *E*-isomers of the 1,2-bis(trimethylstannyl)-1-alkenes investigated generally show a different behaviour towards the sulphur oxides, the insertion involving only the much more reactive 1-trimethylstannyl group (Eq. (18)).



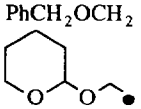
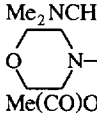
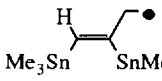
(18)

R	n		Yield (%)	B.p. (°C/Torr)
Ph	2	**32a**	67	110/0.01
$MeOCH_2$	2	**32b**	69	90/0.01
	3	**33a**	63	110/0.01

This reaction is understandable because the spatial proximity between the 2-trimethylstannyl group and the trimethylstannyl ester in the 1-position is now missing, so that the weakening of the tin–carbon bond is not observed and no insertion of the sulphur oxide occurs.

An exception is the distannylalkene bearing a 1-trimethylsilyloxy function, where the sulphur oxides are

Table 5
Products of the reaction of SO_2 and SO_3 with *Z*-1,2-bis(trimethylstannyl)-1-alkenes

R	Yield (SO_2) (%)	Product	B.p. (°C/Torr)	Yield (SO_3) (%)	Product	B.p. (°C/Torr)
Ph	73	**30a**	197 (dec.) [a]	76	**31a**	99 [a]
Bu	84	**30b**	150/0.01	84	**31b**	65 [a]
	92	**30c**	150/0.01	93	**31c**	150/0.01
$MeOCH_2$	65	**30d**	130/0.01	—		
$PhCH_2OCH_2$	89	**30e**	148–151 [a]	91	**31d**	150/0.01
	71	**30f**	150/0.01	73	**31e**	150/0.01
Me_3SiOCH_2	77	**30g**	120/0.01	85	**31f**	140/0.01
Me_2NCH_2	83	**30h**	130/0.01	91	**31g**	85 [a]
	87	**30i**	150/0.01	85	**31h**	110 [a]
$Me(CO)OCH_2$	62	**30j**	120/0.01	77	**31j**	120/0.01
MeO(CO)	69	**30k**	125/0.01	48	**31j**	140/0.01
	87	**30l**	169–175 [a]	84	**31k**	143–154 [a]

[a] M.p.

Table 6
^{119}Sn and ^{13}C NMR data of 1,2-bis(trimethylstannyl)alkenes $HCSn^1Me_3=CRSn^2Me_3$ (δ in ppm, ^nJ in Hz)

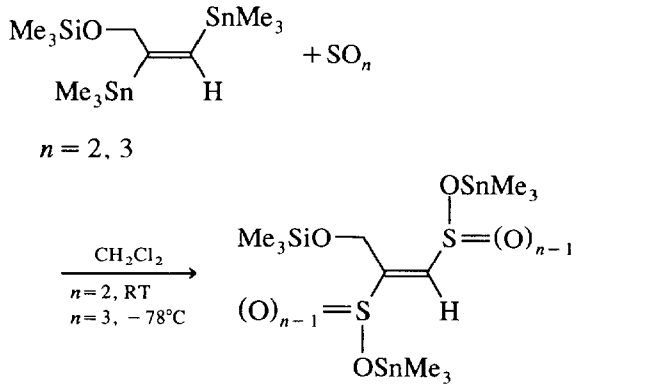
	δ(Sn(1)) ($^3J_{SnSn}$)	δ(Sn(2))	δ(Me_3Sn(1)) ($^1J_{SnC}$)	δ(Me_3Sn(2)) ($^1J_{SnC}$)	δ(C(1)) ($^1J_{Sn(1)}$/ $^2J_{Sn(2)}$)	δ(C(2)) ($^2J_{Sn(1)}$/ $^1J_{Sn(2)}$)	δ(C(3)) ($^2J_{Sn(1)}$/ $^3J_{Sn(2)}$)	δ(other)
2c	−48.9	−58.5	−7.2	−7.3	170.4	141.7	—	22.4, 23.1, 25.7, 28.0 (all CH_2), 123.6
	(392)		(328)	(341)	(503/38)	(74/505)	(—)	(CH), 145.8 (C_q)
3b	−43.2	−66.8	−7.3	−8.5	170.6	140.0	—	22.2, 22.8, 25.2, 29.3 (all CH_2),
	(897)		(332)	(323)	(402/32)	(n.d./425)	(—)	119.4 (CH), 146.7 (C_q)
2l [a]	−51.7	−59.7	−7.2	−7.5	168.2	141.2	74.3	−0.3 ($SiMe_3$)
	(372)		(337)	(346)	(498/39)	(67/502)	(66/108)	
3c [b]	−48.5	−66.6	−7.9	−8.4	169.4	137.6	69.8	−0.5 ($SiMe_3$)
	(883)		(333)	(337)	(434/52)	(n.d./394)	(53/73)	
2f	−49.4	−60.0	−7.5	−7.6	164.7	144.4	78.9	23.6, 32.4, 67.1 (all CH_2), 100.1 (CH)
	(364)		(336)	(346)	(493/39)	(67/495)	(57/111)	
3d	−45.6	−66.7	−8.0	−8.7	165.6	140.7	74.7	23.5, 32.4, 67.0 (all CH_2), 103.3 (CH)
	(854)		(333)	(337)	(426/42)	(n.d./389)	(51/70)	
2g	−50.2	−60.1	−7.5	−7.7	164.7	143.8	78.6	19.2, 25.4, 30.5, 61.7 (all CH_2),
	(368)		(337)	(336)	(496/41)	(66/506)	(56/107)	97.4 (CH)
3e	−46.0	−66.8	−8.1	−8.6	165.8	140.6	75.0	19.1, 25.4, 30.4, 61.5 (all CH_2),
	(854)		(333)	(337)	(427/41)	(15/389)	(47/70)	97.8 (CH)
2i	−55.0	−63.0	−7.3	−7.8	167.0	144.2	74.6	59.1 (CH_2N), 66.7 (CH_2O)
	(380)		(336)	(343)	(514/39)	(75/497)	(55/106)	
2k	−47.1	−57.8	−7.6	−7.7	160.8	146.6	75.7	128.3, 129.5, 130.1 (all CH),
	(371)		(339)	(332)	(476/43)	(66/483)	(67/109)	132.8 (C_q), 165.8 (C=O)
1e	−49.6	−58.9	−6.6	−7.4	171.1	143.6	147.7	16.5 (CH_3), 59.6 (CH_2), 121.1 (CH)
	(362)		(331)	(346)	(487/742)	(69/493)	(62/104)	
5a	−50.9	−59.7	−7.5	−7.7	164.9	143.9	81.0	—
	(374)		(336)	(345)	(490/39)	(64/498)	(64/107)	
5b	−48.2	−59.8	−7.5	−7.7	164.1	145.9	81.4	56.7 (CH_2), 74.3 (C_q), 79.7 (CH)
	(354)		(338)	(345)	(482/39)	(65/488)	(57/109)	
5c	−52.4	−60.9	−7.1	−7.6	165.1	143.1	79.8	—
	(377)		(335)	(348)	(486/38)	(64/498)	(61/104)	
	−57.4	−61.5	−6.2	−7.2	172.2	143.2	87.1	22.4 (CH_3)
	(384)		(338)	(340)	(484/33)	(66/484)	(56/104)	
5d	−49.0	−59.6	−7.4	−7.7	159.7	145.3	83.7	22.4 (CH_3), 64.2 (CH_2), 69.3 (CH),
	(358)		(338)	(347)	(483/36)	(66/496)	(60/104)	77.2 (C_q)
5e	−49.0	−59.6	−7.4	−7.7	164.5	145.2	80.6	20.0 (CH_3), 55.5, 73.1 (all CH),
	(358)		(338)	(347)	(487/38)	(66/490)	(58/109)	80.9 (C_q)
5f	−47.5	−58.4	−7.4	−7.6	159.8	143.8	81.4	27.3 (CH_3), 72.5 (C_q), 67.5 (CH),
	(355)		(334)	(346)	(451/41)	(63/497)	(63/102)	76.0 (C_q)
6a	−55.3	−59.1	−6.5	−7.3	172.9	139.6	78.3	29.2, 53.7 (all CH_3)
	(382)		(338)	(341)	(476/38)	(64/488)	(55/108)	
6b	−54.9	−58.0	−6.7	−7.3	166.9	143.6	81.6	21.3 (CH_3), 128.2, 129.4, 132.7
	(378)		(338)	(346)	(482/38)	(66/496)	(58/102)	(all CH), 130.2 (C_q), 165.5 (C=O)
6c	−57.7	−58.2	−4.9	−7.0	178.2	137.3	78.6	22.2 (CH_3), 25.4, 37.3, 46.0
	(439)		(333)	(334)	(521/32)	(71/507)	(43/90)	(all CH_2), 165.6 (C=O)
6d	−57.4	−57.9	−4.9	−7.1	178.2	137.1	78.4	25.3, 37.2, 45.6 (all CH_2), 127.7, 128.1,
	(441)		(332)	(343)	(500/31)	(69/506)	(43/92)	129.2 (all CH), 133.8 (C_q), 171.3 (C=O)
6e	−47.7	−57.7	−6.8	−7.4	171.0	143.9	150.1	16.8, 21.0 (CH_3), 61.5 (CH_2),
	(356)		(331)	(347)	(475/39)	(67/490)	(26/n.d.)	114.3 (CH), 167.0 (C=O)
6f	−48.2	−58.0	−6.7	−7.5	169.5	142.7	150.8	16.9 (CH_3), 62.0 (CH_2), 117.3, 128.2,
	(360)		(331)	(344)	(475/39)	(68/488)	(26/109)	129.5, 132.7 (CH), 130.4 (C_q), 166.4 (C=O)
6g	−46.9	−58.1	−7.7	−7.8	160.7	145.9	75.0	117.6, 127.8, 128.6, 130.1 (all CH),
	(342)		(340)	(346)	(477/42)	(62/483)	(66/108)	134.6 (C_q), 165.8 (C=O)
6h	−45.4	−56.8	−6.1	−6.2	160.9	148.4	77.0	11.2, 18.2 (CH_3), 30.4, 32.3 (CH_2), 55.6,
	(330)		(341)	(345)	(467/46)	(61/479)	(75/106)	56.2, 92.4, 168.4, 179.4 (C_q)
6i	−49.6	−58.7	−7.6	−7.8	165.7	147.8	74.7	125.1, 128.4, 132.2 (CH), 141.2 (C_q)
	(366)		(335)	(346)	(467/n.d.)	(66/492)	(67/108)	
6m	−57.7	−58.4	−5.0	−7.1	178.2	137.0	78.4	22.0, 25.3, 37.7 (all CH_2), 69.4 (CH_3)
	(441)		(330)	(345)	(524/32)	(71/507)	(43/93)	
6n	−57.8	−58.8	−5.0	−7.1	178.2	137.0	78.4	21.9, 25.3, 37.1, 69.3, 115.6 (all CH_2),
	(444)		(346)	(346)	(524/30)	(70/509)	(47/100)	136.7 (CH)

Table 6 (continued)

	δ(Sn(1)) ($^3J_{SnSn}$)	δ(Sn(2))	δ(Me_3Sn(1)) ($^1J_{SnC}$)	δ(Me_3Sn(2)) ($^1J_{SnC}$)	δ(C(1)) ($^1J_{Sn(1)}$/ $^2J_{Sn(2)}$)	δ(C(2)) ($^2J_{Sn(1)}$/ $^1J_{Sn(2)}$)	δ(C(3)) ($^2J_{Sn(1)}$/ $^3J_{Sn(2)}$)	δ(other)
6o	−48.5 (378)	−58.5	−6.7 (331)	−7.6 (344)	171.1 (484/38)	143.3 (71/498)	148.6 (42/97)	16.3, 53.8 (CH_3), 69.0 (CH_2), 120.3 (CH)
6p	−48.7 (366)	−58.5	−6.9 (335)	−7.6 (347)	171.0 (463/41)	143.2 (69/482)	148.3 (48/99)	16.4 (CH_3), 69.3, 70.4, 116.5 (CH_2), 120.0, 134.7 (CH)
6q [c]	−58.6 (368)	−59.6	−5.8 (337)	−7.3 (344)	175.1 (507/32)	138.6 (69/503)	80.4 (50/109)	−0.3 ($SiMe_3$)
6r [d]	−57.4 (441)	−57.9	−4.9 (333)	−6.9 (346)	178.3 (521/30)	137.3 (71/507)	78.6 (42/90)	1.01 ($SiMe_3$), 22.5, 25.5, 37.3 (CH_2)
6s [e]	−38.6 (368)	−58.5	−6.6 (329)	−7.4 (343)	171.3 (463/38)	143.3 (70/496)	145.7 (52/97)	−0.2 ($SiMe_3$), 16.5 (CH_3), 59.9 (CH_2), 124.0 (CH)

^{29}Si NMR: [a] 17.2; [b] 17.8; [c] 15.1; [d] 17.1; [e] 17.8.

inserted into both Sn–C bonds (Eq. (19)). Apparently, the missing coordinating effect of the trimethylstannyl group is compensated by the trimethylsilyloxy group.



(19)

34 $n = 2$, 88%, m.p. 71–72°C

35 $n = 3$, 63%, b.p. 150°C/0.01 Torr

3. Experimental

All manipulations involving organotin compounds were carried out under argon. NMR spectra were recorded for solutions in $CDCl_3$ using a Bruker AM-300 spectrometer. Mass spectra were recorded with an MAT 8230 and IR-spectra with a Perkin–Elmer 577 spectrometer. The elemental analyses were carried out using an Elemental Analyser Mod. 1106 (Carlo Erba). GC-MS spectra were recorded with an IDT 800 (Finnigan) in combination with an 8521 A (Dani) and GC-FT-IR with a 4130 GC instrument (Carlo Erba) in combination with a Bruker IFS 48 spectrometer.

3.1. Preparation of 1,2-bis(trimethylstannyl)-1-alkenes

3.1.1. From terminal alkynes

A mixture of hexamethylditin (75.0 mmol) and the terminal alkyne (75 mmol) is stirred in the presence of $Pd_2(dba)_3$ (3 mmol) at the temperature shown in Table 1. The distannylalkene is distilled in vacuo. The corresponding *E*-isomers are obtained via photochemical isomerisation using a mercury lamp (TQ 150, Heraeus).

3.1.2. From Z-1,2-bis(trimethylstannyl)-1-alkenols and acid chlorides

The *Z*-1,2-bis(trimethylstannyl)-1-alkenol (5.00 mmol) is dissolved in 25 ml of anhydrous triethylamine and the acid chloride (5.00 mmol) added over 5 min. After stirring at 70°C for 24 h the reaction mixture is hydrolysed with 25 ml of water. The organic layer is separated and the inorganic layer extracted twice with 25 ml of diethyl ether. The organic layer is dried over $MgSO_4$ and the solvent distilled off.

3.1.3. From Z-1,2-bis(trimethylstannyl)-1-alkenols and organic halides

A mixture of potassium hydroxide (5.00 mmol), the *Z*-1,2-bis(trimethylstannyl)-1-alkenol (5.00 mmol), and the organic halide (5.00 mmol) in 25 ml of anhydrous acetone is heated under reflux for 24 h. After hydrolysis with 25 ml of water, extraction with diethyl ether and drying over $MgSO_4$ the solvents are distilled off, leaving the products as colourless oils.

3.1.4. From Z-1,2-bis(trimethylstannyl)-1-alkenols and Me_3SiCl

The *Z*-1,2-bis(trimethylstannyl)-1-alkenol (5.00 mmol) is dissolved in a mixture of 15 ml of anhydrous triethylamine, 15 ml of diethyl ether and 0.5 ml of DMSO. Me_3SiCl (5.00 mmol) is added and the mixture heated for 24 h under reflux and worked up as described above NMR data are list in Tables 6 and 7.

3.2. Reaction of Z-1,2-bis(trialkylstannyl)-1-alkenes with isocyanates

A mixture of the 1,2-bis(trialkylstannyl)-1-alkene (5.00 mmol) and the isocyanate (10.0 mmol) is dissolved in 25 ml of anhydrous dichloromethane and

Table 7
^{1}H NMR data of 1,2-bis(trimethylstannyl)alkenes $HCSn^1Me_3=CRSn^2Me_3$ (δ in ppm, ^nJ in Hz)

	$\delta(Me_3Sn(1))$ ($^2J_{Sn(1)H}$)	$\delta(Me_3Sn(2))$ ($^2J_{Sn(2)H}$)	$\delta(CH(1))$ ($^2J_{Sn(2)H}$ / $^3J_{Sn(1)H}$)	$\delta(C(1)(R))$ ($^3J_{Sn(1)H}$)	δ(other)
2c	0.17	0.18	6.70(s)	—	1.58 (m, 4H, CH_2), 2.06 (m, 4H, CH_2),
	(55.8)	(54.4)	(83.3/202.0)	(—)	5.10 (m, 1H, CH)
3b	0.08	0.11	6.02(s)	—	1.57 (m, 4H, CH_2), 2.00 (m, 4H, CH_2),
	(54.4)	(53.2)	(102.7/113.9)	(—)	5.22 (m, 1H, CH)
2l	0.17	0.17	6.81 (t, ^4J = 1.6)	4.21 (d, ^4J = 1.6)	0.10 (s, 9H, $SiMe_3$)
	(54.2)	(54.2)	(65.2/194.2)	(35.5)	
3c	0.11	0.14	6.21 (t, ^4J = 1.9)	4.24 (d, ^4J = 1.9)	0.10 (s, 9H, $SiMe_3$)
	(53.8)	(54.1)	(98.1/107.9)	(35.7)	
2f	0.12	0.13	6.84 (t, ^4J = 1.6)	3.95/4.31 (dd, ^2J = 12.5, ^4J = 1.6)	1.67–2.02 (m, 4H, CH_2), 3.71–3.92 (m, 2H, CH_2),
	(52.8)	(53.2)	(85.6/192.6)	(41.2)	5.06 (m, 1H, CH)
3d	0.10	0.16	6.29 (t, ^4J = 1.6)	4.39/4.01 (dd, ^2J = 12.3, ^4J = 1.6)	1.57–1.98 (m, 4H, CH_2), 3.86 (m, 2H, CH_2),
	(54.1)	(53.4)	(103.4/109.4)	(36.1)	5.11 (dd, 1H ^3J = 4.1)
2g	0.15	0.15	6.68 (t, ^4J = 1.5)	4.33/4.04 (dd, ^2J = 11.9, ^4J = 1.5)	1.51 (m, 6H, CH_2), 3.48 (m, 1H, CH),
	(54.4)	(54.4)	(84.7/191.5)	(46.4)	3.83 (m, 1H, CH), 4.59 (t, 1H, ^3J = 3.2)
3e	0.11	0.14	6.29 (t, ^4J = 1.9)	4.00/4.41 (dd, ^2J = 12.8, ^4J = 1.9)	1.61 (m, 6H, CH_2), 3.48 (m, 1H, CH_2),
	(54.1)	(54.1)	(96.7/107.0)	(44.0)	3.79 (m, 1H, CH_2), 4.61 (m, 1H, CH)
2i	0.09	0.12	6.71 (t, ^4J = 1.6)	4.21 (d, ^4J = 1.6)	2.32 (m, 4H, CH_2N), 3.60 (m, 4, CH_2O)
	(54.1)	(53.8)	(88.9/199.1)	(48.2)	
2k	0.20	0.23	7.03 (t, ^4J = 1.6)	4.94 (t, ^4J = 1.6)	7.37–8.07 (m, 5H, aryl)
	(55.2)	(59.2)	(79.4/183.4)	(38.4)	
1e	0.15	0.17	6.72(s)	—	1.70 (s, 3H, CH_3), 1.78 (s, 1H, OH),
	(54.4)	(53.2)	(83.7/192.9)	(—)	4.13 (m, 2H, CH_2), 5.26 (m, 1H, CH)
5a	0.16	0.17	6.86 (t, ^4J = 1.6)	4.03 (d, ^4J = 1.6)	—
	(53.8)	(54.4)	(86.3/192.6)	(36.0)	
5b	0.16	0.17	6.91 (t, ^4J = 1.6)	4.14 (m)	2.38 (t, 1H, CH, ^4J = 2.2), 4.07 (d, 2H, CH_2, ^4J = 2.2)
	(54.1)	(54.4)	(84.6/187.8)	(40.6)	
5c	0.19	0.23	6.85 (t, ^4J = 1.6)	4.00 (d, ^4J = 1.6)	—
	(54.2)	(54.2)	(81.6/196.8)	(47.2)	
	0.22	0.25	6.79 (t, ^4J = 1.3)	3.85 (qd, ^3J = 6.5, ^4J = 1.3)	1.23 (d, 3H, CH_3, ^3J = 6.4)
	(53.8)	(54.1)	(86.9/194.2)	(47.8)	
5d	0.22	0.25	6.04 (d, ^4J = 1.3)	4.16 (q, ^4J = 1.3)	1.39 (d, 3H, ^3J = 6.3), 2.39 (t, 1H, CH, ^4J = 1.4),
	(52.8)	(54.1)	(85.8/173.9)	(n.d.)	4.56 (t, 2H, CH_2, ^4J = 1.4)
5e	0.21	0.22	6.96 (t, ^4J = 1.3)	4.44 (d, ^4J = 1.3)	1.47 (d, 3H, CH_3, ^3J = 6.5), 2.44 (s, 1H, CH),
	(52.7)	(54.3)	(81.1/187.3)	(n.d.)	4.17 (q, 1H, CH, ^3J = 6.5)
5f	0.20	0.21	5.94 (t, ^4J = 1.4)	4.50 (d, ^4J = 1.4)	1.36 (s, 6H, CH_3), 2.45 (s, 1H, CH)
	(53.1)	(52.8)	(82.2/173.6)	(38.0)	
6a	0.12	0.15	6.76 (d, ^4J = 1.4)	5.26 (qd, ^3J = 6.2, ^4J = 1.4)	1.22 (d, 3H, CH_3, ^3J = 6.2), 1.97 (s, CH_3)
	(55.7)	(54.0)	(78.9/194.5)	(46.6)	
6b	0.17	0.21	6.92 (d, ^4J = 1.4)	5.26 (qd, ^3J = 6.2, ^4J = 1.4)	1.40 (d, 3H, CH_3, ^3J = 6.2), 7.39 (m, 5H, aryl)
	(52.9)	(53.2)	(74.1/183.5)	(38.0)	
6c	0.12	0.13	6.65 (s)	—	1.31–1.69 (m, 10H, CH_2), 1.97 (s, 3H, CH_3)
	(52.8)	(53.2)	(71.9/212.9)	(—)	
6d	0.12	0.13	6.65 (s)	—	1.34–1.65 (m, 10H, CH_2), 7.22–8.01 (m, 5H, aryl)
	(52.5)	(52.8)	(72.1/213.2)	(—)	
6e	0.21	0.22	6.78 (s)	—	1.79 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 4.63 (d, 2H,
	(54.4)	(53.2)	(83.4/190.0)	(—)	CH_2, ^3J = 7.5), 5.34 (tq, 1H, CH ^2J = 7.5, ^4J = 1.3)
6f	0.24	0.26	6.84 (s)	—	1.88 (s, 3H, CH_3), 4.91 (d, 2H, CH_2, ^3J = 7.2),
	(54.4)	(53.4)	(84.0/190.6)	(—)	5.40 (tq, 1H, CH, ^3J = 7.2, ^4J = 1.3),
					7.37–8.16 (m, 5H, aryl)
6g	0.22	0.26	7.00 (t, ^4J = 1.3)	4.85 (d, ^4J = 1.3)	6.45 (d, 1H, CH, ^2J = 17.1), 7.19–7.58 (m, 5H, aryl),
	(52.9)	(52.8)	(84.0/180.4)	(34.8)	7.72 (d, 1H, ^2J = 17.1)
6h	0.14	0.19	6.90 (t, ^4J = 1.3)	4.78 (d, ^4J = 1.3)	0.91, 1.03, 1.06 (s, 9H, CH_3), 1.55–2.04 (m, 2H,
	(54.8)	(54.4)	(78.0/178.8)	(32.2)	CH_2), 2.31–2.67 (m, 2H, CH_2)
6i	0.20	0.21	7.30 (t, ^4J = 1.6)	4.28 (d, ^4J = 1.6)	7.46–7.71 (m, 5H, aryl)
	(54.4)	(53.8)	(85.4/192.5)	(32.0)	
6m	0.14	0.14	6.65 (s)	—	3.17 (s, 3H, CH_3), 1.30–1.76 (m, 10H, CH_2)
	(52.6)	(52.6)	871.5/214.4)	(—)	
6n	0.16	0.16	6.69 (s)	—	1.37–1.93 (m, 10H, CH_2), 3.83 (m, 2H, CH_2), 4.96
	(52.8)	(52.8)	(71.8/213.2)	(—)	(dq, CH, ^2J = 17.4, ^4J = 1.3), 5.17 (dq, ^2J = 17.4,
					^4J = 1.3), 5.77 (m, 1H, CH)

Table 7 (continued)

	$\delta(Me_3Sn(1))$ ($^2J_{Sn(1)H}$)	$\delta(Me_3Sn(2))$ ($^2J_{Sn(2)H}$)	$\delta(CH(1))$ ($^2J_{Sn(2)H}/^3J_{Sn(1)H}$)	$\delta(C(1)(R))$ ($^3J_{Sn(1)H}$)	δ(other)
6o	0.18	0.20	6.75 (s)	—	1.73 (d, 3H CH_3, $^4J = 0.6$), 3.32 (s, 3H, CH_3), 3.97
	(54.1)	(52.9)	(83.3/162.0)	(—)	(dd, 2H, CH_2, $^3J = 6.2$), 5.22 (tq, $^3J = 6.2$, $^4J = 1.3$)
6p	0.18	0.21	6.76 (s)	—	1.76 (s, 3H, CH_3), 3.97–4.25 (m, 4H, CH_2);
	(52.8)	(51.9)	(84.0/193.3)	(—)	4.89–5.43 (m, 3H, CH_2 + CH),
					5.84–6.02 (m, 1H, CH)
6q	0.13	0.16	6.61 (d, $^4J = 1.4$)	4.22 (qd, $^3J = 6.2$, $^4J = 1.4$)	0.08 (s, 9H, $SiMe_3$), 1.17 (d, 3H, CH_3, $^3J = 6.2$)
	(54.3)	(54.1)	(79.37/199.2)	(54.4)	
6r	0.15	0.16	6.68(s)	—	0.04 (s, 9H, $SiMe_3$), 1.30–1.77 (m, 10H, CH_2)
	(53.0)	(53.2)	(71.2/211.8)	(—)	
6s	0.18	0.14	6.71(s)	—	0.02 (s, 9H, $SiMe_3$), 1.74 (s, 3H, CH_3), 3.90 (dq, 2H
	(54.2)	(53.8)	(81/191.4)	(—)	CH_2, $^3J = 6.5$, $^4J = 1.3$), 5.20 (tq, $^3J = 6.5$, $^4J = 1.3$)

stirred for the time given in Table 3. The precipitated product is filtered off and recrystallised from dichloromethane. NMR data are given in Tables 8 and 9; the elemental analysis values are in Table 10.

8a. IR: $\nu = 597$ cm^{-1} (νNSn), 1153 (νRSO_2N), 1342 (νRSO_2N), 1624 ($\nu CONR_2$), 3025 (νCH), 3065 (νCH).

8b. IR: $\nu = 594$ cm^{-1} (νSnN), 1156 (νRSO_2N), 1344 (νRSO_2N), 3030 (νCH), 3060 (νCH).

8c. IR: $\nu = 617$ cm^{-1} (νSnN), 815 (1,4-disubstituted arene), 1150 (νRSO_2N), 1324 (νRSO_2N), 1614 (νCONRR'), 2855 (νCH), 2920 (νCH). MS: (70 eV) $m/e = 414$ (1%, $M^+ - CH_3$), 365 (45%, $M^+ - SO_2$), 179 (33%, $H_3CC_6H_4SO_2NH$), 155 (13%, $H_3CC_6H_5$-SO_2^+), 135 (15%, $SnMe^+$), 121 (17%, SnH^+), 91 (100%, $H_3CC_6H_4^+$).

8d. IR: $\nu = 596$ cm^{-1} (νSnN), 811 (1,4-disubstituted arene), 1149 (νRSO_2N), 1306 (νRSO_3N), 1600 (νC=C), 1639 (νCONRR'), 2965 (νCH), 2930 (m, νCH). MS: (70 eV) $m/e = 453$ (4%, M^+), 438 (2%, $M^+ - CH_3$), 389 (78%, $M^+ - SO_2$), 298 (19%, $M^+ - SO_2C_6H_4CH_3$), 282 (81%, $M^+ - C_6H_4CH_3$, $-C_6H_9$, +H), 155 (51%, $C_6H_4CH_3^+$), 135 (28%, $SnMe^+$), 91 (100%, $C_6H_4CH_3^+$), 81 (52%, $C_6H_9^+$), 65 (32%, HSO_2^+).

8e. IR: $\nu = 618$ cm^{-1} (νSnN), 811 (1,4-disubstituted arene), 1085 (νC–O–C), 1156 (νRSO_2N), 1326 (νRSO_2N), 1613 (νCONRR'), 2930 (νCH). MS: (70 eV) $m/e = 402$ (3%, $M^+ - CH_3$), 353 (54%, $M^+ - SO_2$), 246 (78%, $M^+ - H_3CC_6H_4SO_2NH$), 181 (45%, $M^+ - Me_2SnC(CH_2OCH_3)CH_2$, $-CH_3$), 155 (28%, $H_3CC_6H_4SO_2^+$), 91 (100%, $C_6H_4CH_3^+$), 65 (39%, SO_2H^+), 45 (10%, $CH_2OCH_3^+$).

8f. IR: $\nu = 593$ cm^{-1} (νSnN), 665 (νSiC), 846 (m, 1,4-disubstituted arene), 1088 (νSiO), 1156 (νC–O–C), 1322 (νRSO_2N), 1602 (νCONRR'), 2905 (νCH), 2965

Table 8
^{119}Sn and ^{13}C NMR data of **8** in $CDCl_3$ (δ in ppm, ^nJ in Hz)

	δ(Sn)	$\delta(SnMe_2)$ ($^1J_{SnC}$)	δ(CH) ($^2J_{SnCH}$)	$\delta(C_q)$ ($^1J_{SnC}$)	δ(C=O) ($^{2+3}J_{SnC}$)	δ(C(1)(R)) ($^2J_{SnC}$)	δCH_3	$\delta(C_{ar})$(CH/CH/C_q/C_q)	δ(others)
8a	−30.7	2.0	128.0	146.1	167.6	—	21.8	127.3 (C_q), 128.0, 128.1, 128.5 (CH),	
		(475)	(72)	(501)	(67)	(—)		129.1 (C_q), 129.7, 134.5, 139.8 (CH)	
8b	−46.9	—	128.0	143.8	170.5	—	21.5	127.5 (C_q), 127.6 (CH), 13.4 (CH_3), 19.7, 26.7, 27.7 (CH_2)	
			(70)	(498)	(66)	(—)		127.8 (C_q), 128.8, 129.1, 134.3, 137.5 (CH)	
8c	−37.2	0.67	133.2	163.1	171.8	21.9	21.3	127.3/129.2/	13.6 (CH_3), 30.0 (CH_2, $^3J_{SnC} = 114$),
		(492)	(71)	(322)	(58)	(52)		137.2/143.5	36.4 (CH_2)
8d	−27.4	−1.7	139.3	166.0	170.3	143.7	21.5	127.9/129.6/	21.8, 22.0, 23.5, 26.9 (CH_2), 125.3 (CH)
		(470)	(n.d.)	(436)	(96)	(n.d.)		136.9/138.1	
8e	−28.6	0.3	131.4	169.4	171.3	74.3	21.5	127.5/129.2/	58.8 (CH_3)
		(478)	(71)	(498)	(66)	(60)		137.7/143.6	
8g	−27.3	−2.1	134.6	165.9	169.9	74.1	21.4	127.7/128.9/	20.7, 24.9, 31.6, 66.8 (CH_2), 106.9 (OCH)
		(452)	(69)	(456)	(94)	(79)		137.7/143.1	
8h	−29.6	0.30	129.3	170.0	171.7	72.3	21.4	127.1/129.1/	72.4 (CH_2), 126.1, 127.4, 129.1 (CH),
		(496)	(70)	(491)	(60)	(n.d.)		143.6/163.2	143.6, 163.2 (C_q)
8i	−31.3	−1.1	136.0	160.9	169.5	69.5	21.3	127.6/129.0/	21.4 (CH_3), 175.2 (C_q)
		(506)	(56)	(497)	(61)	(57)		137.1/143.5	

Table 9
^{1}H NMR data of **8** in $CDCl_3$ (δ in ppm)

	$\delta(CH_3Sn)$ ($^2J_{SnH}$)	$\delta(CH)$ ($^3J_{SnH}$)	$\delta(CH(1)(R))$ ($^3J_{SnH}$)	$\delta(CH_3)$	$\delta(H_{ar})$	δ(others)
8a	0.62 (72.3)	6.53(s) (146.7)	— (—)	2.40	7.54 (m, 9H)	
8b	— (—)	6.68(s) (121.6)	— (—)	2.35	7.46 (m, 9H)	0.79 (t, 6H, CH_3), 1.28 (m, 4H, CH_2), 1.67 (m, 8h, CH_2)
8c	0.91 (63.3)	6.32(s) (167.6)	(—)	2.39	7.29 (d, 2H), 7.77 (d, 2H)	0.78 (t, 3H, CH_3), 1.00–1.34 (m, 6H, CH_2)
8d	0.55 (64.0)	6.48(s) (146.0)	— (—)	2.46	7.30 (d, 2H), 7.90 (d, 2H)	1.66 (m, 4H, CH_2), 2.40 (m, 4H, CH_2), 5.32 (s, 1H, CH)
8e	0.92 (69.9)	6.55 (t, ^4J = 1.4) (157.9)	4.01 (d, ^4J = 1.4) (n.d.)	2.40	7.27 (d, 2H), 7.78 (d, 2H)	3.28 (s, 3H, CH_3)
8f [a]	0.89 (76.0)	6.57 (t, ^4J = 1.3) (166.6)	4.65 (d, ^4J = 1.3) (40.6)	2.65	7.75 (d, 2H), 7.87 (d, 2H)	0.24 (s, 9H, $SiMe_3$, $^2J_{SiH}$ = 41.6)
8g	0.62 (73.4)	7.30(m) (176.3)	4.06(m) (n.d.)	2.46	7.38 (d, 2H), 7.94 (d, 2H)	1.58 (m, 6H, CH_2), 3.57 (m, 1H), 3.77 (m, 1H), 4.68 (m, 1H)
8h	0.92 (70.8)	6.71 (t, ^4J = 1.3) (154.1)	4.47 (59.8)	2.41	7.10 (d, 2H), 7.58 (d, 2H)	4.31 (s, 2H, OCH_2), 7.29 (m, 5H, aryl)
8i	0.94 (72.2)	6.55 (t, ^4J = 1.3) (148.2)	4.89(d, ^4J = 1.3) (49.5)	2.41	7.28 (d, 2H), 7.88 (d, 2H)	2.16 (s, 3H, CH_3)
8j [a]	0.80 (79.4)	6.61 (t, ^4J = 1.3) (165.2)	4.89 (^4J = 1.3) (n.d.)	2.48	7.27 (d, 2H), 7.69 (d, 2H)	2.49 (s, 6H, CH_3)

[a] In DMSO (d_6).

(νCH). MS: (70 eV) m/e = 460 (9%, $M^+ - CH_3$), 411 (51%, $M^+ - SO_2$), 304 (97%, $M^+ - O$, $-SO_2C_6H_4CH_3$), 239 (100%, $Me_3SnOSiMe_2^+$), 155 (14%, $H_3CC_6H_4SO_2^+$), 135 (9%, $SnMe^+$), 91 (39%, $H_3CC_6H_4^+$), 77 (10%, $C_6H_5^+$), 73 (19%, $SiMe_3^+$), 65 (12%, $C_5H_5^+$).

8g. IR: ν = 610 cm^{-1} (νSnN), 812 (1,4-disubstituted arene), 1084 (νC–O–C), 1150 (νRSO_2N), 1308 (νRSO_2N), 1600 (νC=C), 1638 (νCONRR'), 2870 (νCH), 2955 (νCH). MS: (70 eV) m/e = 472 (7%, $M^+ - CH_3$), 423 (51%, $M^+ - SO_2$), 372 (39%, $M^+ - C_6H_{11}O_2$), 153 (22%, $H_3CC_6H_5SO_2^+$), 135 (28%, $SnMe^+$), 115 (47%, $C_6H_{11}O_2^+$), 91 (100%, $H_3CC_6H_5^+$), 85 (73%, $C_5H_9O^+$), 65 (8%, SO_2H^+).

8h. IR: ν = 613 cm^{-1} (νSnN), 669 (monosubstituted arene), 732 (monosubstituted arene), 811 (1,4-disubstituted arene), 1085 (νC–O–C), 1151 (νRSO_2N), 1304 (νRSO_2N), 1601 (νC=C), 1619 (νCONRR'), 2870 (νCH), 2930 (νCH). MS: (70 eV) m/e = 478 (3%, $M^+ - CH_3$), 429 (44%, $M^+ - SO_2$), 372 (31%, $M^+ - C_6H_5CH_2OCH_2$), 155 (24%, $H_3CC_6H_4SO_2^+$), 135 (17%, $SnMe^+$), 121 (11%, $C_6H_5CH_2OCH_2^+$), 91 (100%, $C_7H_7^+$), 77 (37%, $C_6H_5^+$), 65 (58%, SO_2H^+).

8i. IR: ν = 615 cm^{-1} (νSnN), 813 (1,4-disubstituted arene), 1085 (νC–O–C), 1153 (νRSO_2N), 1227 (νC–O), 1319 (νRSO_2N), 1614 (νCONRR'), 1747 (νC=O), 2930 (νCH), 3000 (m, νCH). MS: (70 eV) m/e = 430 (2%, $M^+ - CH_3$), 381 (8%, $M^+ - SO_2$), 274 (4%, $M^+ - SO_2C_6H_4CH_3$, $-O$), 209 (4%, $HSn[CH_3]CH_2OC[O]CH_3^+$), 197 (7%, $H_2CC_6H_4SO_2C[O]CH_3^+$), 171 (39%, $SO_3C_6H_4CH_3^+$), 155 (47%, $SO_2C_6H_4CH_3^+$), 107 (19%, $OC_6H_4CH_3^+$), 91 (100%, $C_6H_4CH_3^+$), 65 (27%, HSO_2^+).

Table 10
Elmental analysis values for compounds **8**

		M.w.	Calc.			Found		
			C	H	N	C	H	N
8a	$C_{18}H_{19}NO_3SSn$	448.10	48.25	4.27	3.13	48.0	4.4	3.1
8b	$C_{24}H_{31}NO_3SSn$	532.27	54.16	5.87	2.63	54.0	6.0	2.6
8c	$C_{16}H_{23}NO_3SSn$	428.11	44.89	5.42	3.27	44.7	5.5	3.1
8d	$C_{18}H_{23}NO_3SSn$	452.14	47.82	5.13	3.10	47.6	5.0	3.0
8e	$C_{14}H_{19}NO_4SSn$	416.06	40.42	4.60	3.37	40.3	4.7	3.3
8f	$C_{16}H_{25}NO_4SSiSn$	474.21	40.35	5.31	2.95	40.1	5.0	3.0
8g	$C_{18}H_{25}NO_5SSn$	486.15	44.47	5.18	2.88	44.5	5.0	2.6
8h	$C_{20}H_{23}NO_4SSn$	492.16	48.81	4.71	2.85	48.6	4.5	2.6
8i	$C_{15}H_{19}NO_5SSn$	444.07	40.57	4.31	3.15	40.7	4.4	3.0
8j	$C_{15}H_{22}N_2O_3SSn$	429.20	41.99	5.17	6.53	42.2	5.0	6.3

8j. IR: $\nu = 614\ cm^{-1}$ (νSnN), 824 (1,4-disubstituted arene), 1089 (νC–O–C), 1167 (νRSO_2N), 1336 (νRSO_2N), 1598 (νC=C), 1620 (νCONRR'), 2790 (νCH), 2965 (νCH), 3045 (m, νCH).

3.3. Reaction of 2a with phenyl isocyanate in the presence of $AlCl_3$

Phenyl isocyanate (10.0 mmol, 2.14 g) is added to $AlCl_3$ (10.0 mmol, 1.33 *g*) in 20 ml of anhydrous dichloromethane and the mixture stirred for 30 min. After addition of **2a** (5.00 mmol, 2.14 g) the mixture is stirred at 40°C for 12 h, then poured onto ca. 50 g of ice and stirred for 30 min. Separation of the organic layer is followed by extraction of the aqueous layer with two 15 ml portions of dichloromethane. The combined organic layers are treated with 10 ml of a saturated solution of KF in water, stirred vigorously for 3 h, and the precipitated Me_3SnF filtered off. The filtrate is extracted twice with 10 ml of dichloromethane. The combined organic layers are dried over $MgSO_4$ and concentrated in vacuo. Yield: 0.89 g (52%) of **11**, m.p. 131°C (from *n*-pentane).

^{1}H NMR(DMSO[d_6]): $\delta = 6.92–7.99$ (m, 15H, $H_{aromat.}$), 8.65 (s, 2H, NH). ^{13}C NMR(DMSO[d_6]): $\delta = 125.0$, 127.3, 129.2, 130.0, 132.7, (all CH), 133.3 (C_q), 139.3 (CH), 138.0, 150.7 (C_q), 163.3 (C_q, C=O). IR: $\nu = 696\ cm^{-1}$ (s, monosubstituted arene), 752 (s, monosubstituted arene), 1555 (νamide II), 1598 (νC=C), 1650 (νamide I), 2790 (νCH), 2970 (νCH), 3065 (νCH), 3290 (s, νNH). Anal. Found: C, 77.0; H, 5.1; N, 8.3. $C_{22}H_{18}N_2O_2$ (342.40). Calc.: C, 77.17; H, 5.30; N, 8.18%.

3.4. Reaction of 3a with 7

12 is obtained from 2.15 g (5.00 mmol) of **3a** and 1.97 g (10.0 mmol) of **7**. Yield: 1.57 g (68%), m.p. 174°C (from *n*-pentane).

^{1}H NMR ($CDCl_3$): $\delta = 0.17$ (s, 9H, CH_3, $^2J_{SnH} = 54.3$ Hz), 2.42 (s, 3H, CH_3), 6.06 (s, 1H, CH), 7.31 (m, 10H, H_{arene}, NH). ^{13}C NMR ($CDCl_3$): $\delta = -9.2$ ($SnMe_3$, $^1J_{SnC} = 346$ Hz), 21.6 (CH_3), 124.3 (C_q), 124.4 (CH), 124.5 (C_q), 127.4, 128.4, 129.3, 129.5, 130.7 (all CH), 166.0 (C=O). ^{119}Sn NMR ($CDCl_3$): $\delta = -58.5$. IR: $\nu = 1167\ cm^{-1}$ (νRSO_2N), 1324 (νRSO_2N), 1569 (νamide II), 1705 (νamide I), 2990 (νCH), 3065 (νCH), 3235 (νNH). Anal. Found: C, 49.5; H, 4.6; N, 3.0. $C_{19}H_{23}NO_3SSn$ (464.15). Calc.: C, 49.17; H, 4.99; N, 3.02%.

3.5. Reaction of Z-1,2-bis(trimethylstannyl)-1-alkenes with DCME

A suspension of $AlCl_3$ (5.00 mmol, 0.78 g or 10.0 mmol, 1.33 g) in 20 ml of anhydrous dichloromethane is cooled to −78°C under Ar. A solution of **13** and the *Z*-1,2-bis(trimethylstannyl)-1-alkene **2** in 5 ml of anhydrous dichloromethane is added over 15 min. After stirring at −78°C for 4 h the reaction mixture is hydrolysed with 25 ml of saturated aqueous NH_4Cl and the aqueous layer extracted three times with 25 ml of dichloromethane. The combined organic layers are treated with 15 ml of a saturated solution of KF in water, stirred vigorously for 3 h, and the precipitated Me_3SnF filtered off. The filtrate is extracted twice with 10 ml of dichloromethane. The combined organic layers are dried with $MgSO_4$ and the solvent distilled off. The residue is purified by distillation.

A mixture of **14a** and **15a** (40% of **15a** and 60% of **14a**) 1.31 g (89%), b.p. 80°C/0.01 Torr is obtained from 5.00 mmol of **2a**, 5.00 mmol of $AlCl_3$ and 5.00 mmol of **13**.

14a. ^{1}H NMR($CDCl_3$): $\delta = 0.30$ (s, 9H, $SnMe_3$, $^2J_{SnH} = 55.2$ Hz), 6.47 (d, 1H, CH, $^3J_{HH} = 7.8$ Hz, $^3J_{SnH} = 63.0$ Hz), 7.25–7.54 (m, 5H, $H_{aromat.}$). ^{13}C NMR($CDCl_3$): $\delta = -6.2$ ($SnMe_3$, $^1J_{SnC} = 364$ Hz), 126.2 (CH, $^3J_{SnC} = 18$ Hz), 127.0 (CH_p), 128.3 (CH_m), 139.6 (CH, $^2J_{SnC} = 15$ Hz), 144.4 ($C_{q,aromat.}$, $^2J_{SnC} = 24$ Hz), 175.2 (C_q, $^1J_{SnC} = 347$ Hz), 190.5 (C_q, C=O, $^3J_{SnC} = 60$ Hz). ^{119}Sn NMR($CDCl_3$): $\delta = -34.4$. GC-FT-IR: $\nu = 618\ cm^{-1}$ (νSnC), 701 (monosubstituted arene), 770 (monosubstituted arene), 1095 (νCC), 1653 (νC=C), 1696 (νC=O), 2720 (νC=O–H), 2832 (νCH), 2986 (νCH). GC-MS: (70 eV) $m/e = 297$ (2%, $M^+ + H$), 281 (100%, $M^+ - CH_3$), 250 (3%, $C_6H_5C{\equiv}CSnMe_3^+ - H$), 165 (2%, $SnMe_3^+$), 135 (6%, $SnMe^+$), 115 (15%, $M^+ - SnMe_3$, −O), 103 (5%, $M^+ - SnMe_3$, +H, −CHO), 77 (4%, $C_6H_5^+$), 51 (1%, $C_4H_4^+$).

15a. ^{1}H NMR($CDCl_3$): $\delta = 0.36$ (s, 9H, $SnMe_3$, $^2J_{SnH} = 54.1$ Hz), 6.85 (d, 1H, CH, $^3J_{HH} = 5.6$ Hz, $^3J_{SnH} = 62.3$ Hz), 7.04–7.22 (m, 5H, $H_{aromat.}$), 9.83 (d, 1H, CHO, $^3J_{HH} = 5.6$ Hz). ^{13}C NMR($CDCl_3$): $\delta = -9.1$ ($SnMe_3$, $^1J_{SnC} = 353$ Hz), 126.3 (CH, $^3J_{SnC} = 18$ Hz), 127.8 (CH_p), 128.2 (CH_m), 139.1 (CH, $^2J_{SnC} = 25$ Hz), 141.3 (C_q, $^2J_{SnC} = 21$ Hz), 177.2 (C_q, $^1J_{SnC} = 338$ Hz), 192.2 (C_q, C=O, $^3J_{SnC} = 34$ Hz). ^{119}Sn NMR($CDCl_3$): $\delta = -12.4$. GC-FT-IR: $\nu = 616\ cm^{-1}$ (νSnC), 698 (monosubstituted arene), 762 (monosubstituted arene), 820 (ρCH_3), 979 (νCC), 1698 (νC=O), 2710 (νC=O–H), 2831 (νCH), 2980 (m, νCH). GC-MS: (70 eV) $m/e = 297$ (7%, $M^+ + H$), 281 (100%, $M^+ - CH_3$), 251 (8%, $C_6H_5C{\equiv}CSnMe_3^+$), 165 (16%, $SnMe_3^+$), 135 (12%, $SnMe^+$), 115 (5%, $M^+ - SnMe_3$, −O), 103 (14%, $M^+ - SnMe_3$, +H, −CHO), 77 (11%, $C_6H_5^+$), 51 (6%, $C_4H_4^+$). Anal. Found: C, 49.0; H, 5.4. $C_{12}H_{16}OSn$ (294.95). Calc.: C, 48.87; H, 5.47%.

A mixture of **14b** and **15b** (95% of **14b** and 5% of **15b**) 1.15 g (84%), b.p. 50°C/0.01 Torr is obtained from 5.00 mmol of **2b**.

14b. ^{1}H NMR ($CDCl_3$): $\delta = 0.28$ (s, 9H, $SnMe_3$, $^2J_{SnH} = 55.2$ Hz), 0.93 (t, 3H, CH_3, $^3J_{HH} = 72$ Hz),

1.25–1.48 (m, 4H, CH_2), 2.43–2.55 (m, 2H, CH_2), 6.65 (d, 1H, CH, $^3J_{HH}$ = 5.9 Hz, $^3J_{SnH}$ = 114 Hz), 9.57 (d, 1H, CHO, $^3J_{HH}$ = 5.9 Hz). ^{13}C NMR($CDCl_3$): δ = −7.6 ($SnMe_3$, $^1J_{SnC}$ = 357 Hz), 13.8 (CH_3) 22.2, 31.0 (all CH_2), 40.7 (CH_2, $^2J_{SnC}$ = 32 Hz), 138.6 (CH, $^2J_{SnC}$ = 64 Hz), 181.9 (C_q, $^1J_{SnC}$ = 364 Hz), 192.4 (C_q, C=O, $^3J_{SnC}$ = 39 Hz). ^{119}Sn NMR($CDCl_3$): δ = −38.5. GC-FT-IR: ν = 629 cm^{-1} (νSnC), 1087 (νCC), 1462 (m, $\delta_{as}CH_3$), 1595 (νC=C), 1699 (νC=O), 2830 (νCH), 2885 (νCH), 2930 (νCH). MS: (70 eV) m/e = 275 (11%, $M^+ + H$), 261 (100%, $M^+ - CH_3$), 259 (94%, $M^+ - OH$), 165 (54%, $SnMe_3^+$), 135 (27%, $SnMe^+$), 111 (11%, $M^+ - SnMe_3$), 57 (6%, $C_4H_9^+$).

15b. ^{1}H NMR($CDCl_3$): δ = 0.24 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 55.1 Hz), 0.92 (t, 3H, CH_3, $^3J_{HH}$ = 7.2 Hz), 1.25–1.48 (m, 4H, CH_2), 2.43–2.55 (m, 2H, CH_2), 6.21 (d, 1H, CH, $^3J_{HH}$ = 7.8 Hz), 10.0 (d, 1H, CHO, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR($CDCl_3$): δ = −9.3 ($SnMe_3$), 13.5 (CH_3), 22.1, 29.8, 39.1 (all CH_2), 132.8 (CH), 187.6 (C_q), 193.8 (C_q, C=O). ^{119}Sn NMR($CDCl_3$): δ = −19.4. GC-FT-IR: ν = 631 cm^{-1} (νSnC), 940 (ρCH_2), 1087 (νCC), 1596 (νC=C), 1694 (νC=O), 2824 (νCH), 2812 (νCH), 2936 (νCH), 2972 (νCH). GC-MS: (70 eV) m/e = 275 (11%, $M^+ + H$), 261 (100%, $M^+ - CH_3$), 259 (94%, $M^+ - OH$), 165 (54%, $SnMe_3^+$), 135 (27%, $SnMe^+$), 111 (11%, $M^+ - SnMe_3$), 57 (6%, $C_4H_9^+$). Anal. Found: C, 43.4; H, 7.0. $C_{10}H_{20}OSn$ (274.96). Calc.: C, 43.68; H, 7.33%.

3.6. Reaction of *14b* and *15b* with phenylmagnesium bromide

A solution of phenylmagnesium bromide (6.00 mmol, 1.08 g) is added to a solution of **14b** and **15b** (5.00 mmol, 1.37 g) in 25 ml of anhydrous diethyl ether. The mixture is heated under reflux for 12 h and then hydrolysed with 25 ml of a saturated aqueous NH_4Cl solution; the organic layer is separated off and the aqueous layer extracted with 25 ml of diethyl ether. The solvent is removed after drying over $MgSO_4$. Yield: 100% of *E*-and *Z*-1-phenyl-3-trimethylstannyl-hept-2-ene-1-al (**16a** and **b**).

^{1}H NMR($CDCl_3$): δ = 0.36 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 53.4 Hz), 1.00 (t, 3H, CH_3, $^3J_{HH}$ = 7.2 Hz), 1.33–1.59 (m, 6H, CH_2), 3.40 (s, 1H, OH), 5.21 (d, 1H, CH, $^3J_{HH}$ = 7.5 Hz), 6.25 (d, 1H, CH, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 44.6 Hz), 7.12–7.58 (m, 5H, $H_{aromat.}$). ^{13}C NMR($CDCl_3$): δ = 1.0 ($SnMe_3$, $^1J_{SnC}$ = 348 Hz), 13.9 (CH_3), 22.3, 31.7 (all CH_2), 40.0 (CH_2, $^2J_{SnC}$ = 33 Hz), 75.9 (CHOH, $^3J_{SnC}$ = 108 Hz), 124.3, 126.7, 128.5 (all $CH_{aromat.}$), 141.1 (CH, $^2J_{SnC}$ = 68 Hz), 149.0 (C_q, $^1J_{SnC}$ = 360 Hz). ^{119}Sn NMR($CDCl_3$): δ = −47.8 (*Z*-isomer) (90%), −28.8 (*E*-isomer) (10%). GC-FT-IR: ν = 697 cm^{-1} (monosubstiuted arene), 761 (monosubstituted arene), 1604 (νC=C), 2884 (νCH), 2934 (νCH), 2982 (νCH), 3073 (νCH), 3639 (m, νOH). GC-MS: (70 eV) m/e = 355 (52%, $M^+ + H$), 339 (12%, $M^+ - CH_3$), 267 (30%, $M^+ - C_4H_9$, −CHOH), 165 (20%, $SnMe_3^+$), 135 (63%, $SnMe^+$), 77 (100%, $C_6H_5^+$), 73 (90%, $C_4H_9O^+$).

3.7. Reaction of *14a* and *15a* with ethylmagnesium bromide

Yield: 100% of *E*- and *Z*-1-phenyl-1-trimethylstannyl-hept-2-ene-1-al (**17a** 60% and **17b** 40%) (carried out as above).

17a. ^{1}H NMR($CDCl_3$): δ = 0.18 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 53.4 Hz), 1.29 (t, 3H, CH_3, $^3J_{HH}$ = 6.8 Hz), 3.55 (q, 2H, CH_2, $^3J_{HH}$ = 6.8 Hz), 3.46 (s, 1H, OH), 4.18 (m, 1H, CHO), 5.86 (d, 1H, CH, $^3J_{HH}$ = 8.8 Hz, $^3J_{SnH}$ = 72.3 Hz), 7.07–7.56 (m, 5H, H_{aromat}). ^{13}C NMR($CDCl_3$): δ = 1.0 ($SnMe_3$, $^1J_{SnC}$ = 344 Hz), 9.7 (CH_3), 30.1 (CH_2), 65.8 (CHOH, $^3J_{SnC}$ = 100 Hz), 126.3, 128.1, 128.4 (all $CH_{aromat.}$), 130.4 ($C_{q,\ aromat.}$), 142.7 (CH, ^{2}iJ$_{SnC}$ = 65 Hz), 148.2 (C_q, $^1J_{SnC}$ = 385 Hz). ^{119}Sn NMR($CDCl_3$): δ = −22.4. GC-FT-IR: ν = 702 cm^{-1} (monosubstituted arene), 740 (monosubstituted arene), 1610 (νC=C), 2887 (νCH), 2937 (νCH), 2975 (νCH), 3066 (νCH), 3420 (νOH). GC-MS: (70 eV) m/e = 327 (11%, $M^+ + H$), 326 (20%, M^+), 311 (18%, $M^+ - CH_3$), 165 (10%, $SnMe_3^+$), 161 (31%, $M^+ - SnMe_3$), 135 (21%, $SnMe^+$), 77 (16%, $C_6H_5^+$).

17b. ^{1}H NMR($CDCl_3$): δ = 0.22 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 51.8 Hz), 1.23 (t, 3H, CH_3, $^3J_{HH}$ = 6.8 Hz), 3.55 (q, 2H, CH_2, $^3J_{HH}$ = 6.8 Hz), 3.46 (s, 1H, OH), 4.24 (m, 1H, CHO), 6.20 (d, 1H, CH, $^3J_{HH}$ = 7.8 Hz, $^3J_{SnH}$ = 70.0 Hz), 7.07–7.56 (m, 5H, $H_{aromat.}$). ^{13}C NMR($CDCl_3$): δ = 1.1 ($SnMe_3$, $^1J_{SnC}$ = 342 Hz), 10.6 (CH_3), 30.5 (CH_2), 69.9 (CHOH, $^3J_{SnC}$ = 101 Hz), 126.3, 128.1, 128.4 (all $CH_{aromat.}$), 132.3 ($C_{q,aromat.}$), 143.7 (CH, $^2J_{SnC}$ = 61 Hz), 148.6 (C_q, $^1J_{SnC}$ = 390 Hz). ^{119}Sn NMR($CDCl_3$): δ = −45.8.

3.8. Reaction of *14* and *15* with dimethylamine borane

The dimethylamine borane complex is added to a solution of the aldehyde in 25 ml of anhydrous diethyl ether and the mixture stirred for 5 h at room temperature. 25 ml of water are added, the organic layer is separated off and the aqueous layer extracted with 25 ml of diethyl ether. The solvent is distilled off after drying over $MgSO_4$.

Z- and *E*-3-trimethylstannylhept-2-ene-1-ol (**18a** and **b**) are obtained from **15**.

18. ^{1}H NMR($CDCl_3$): δ = 0.15 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 52.9 Hz), 0.97 (t, 3H, CH_3, $^3J_{HH}$ = 7.5 Hz), 1.25–1.98 (m, 6H, CH_2), 3.37 (d, 2H, CH_2O, $^3J_{HH}$ = 5.9 Hz), 4.35 (s, 1H, OH), 7.07 (d, 1H, CH, $^3J_{HH}$ = 5.9 Hz, $^3J_{SnH}$ = 99.2 Hz). ^{13}C NMR($CDCl_3$): δ = −6.9 ($SnMe_3$, $^1J_{SnC}$ = 352 Hz), 13.9 (CH_3), 21.9, 31.6, 39.8 (all CH_2),

63.2 (CH_2O, $^3J_{SnC}$ = 108 Hz), 139.1 (CH, $^2J_{SnC}$ = 64 Hz), 155.4 (C_q, $^1J_{SnC}$ = 368 Hz). ^{119}Sn NMR($CDCl_3$): δ = −23.2 (*Z*-isomer); −49.2 (*E*-isomer). GC-MS: (70 eV) *m/e* = 278 (8%, M^+), 165 (90%, $SnMe_3^+$), 135 (24%, $SnMe^+$), 121 (10%, SnH^+), 113 (31%, $M^+ - SnMe_3$), 57 (100%, $C_4H_9^+$).

3.9. Z- and E-3-Phenyl-3-trimethylstannyl-prop-2-ene-1-ol (*19a and b*)

19a. ^{1}H NMR($CDCl_3$): δ = 0.14 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 54.4 Hz), 2.39 (s, 1H, OH), 4.39 (d, 2H, CH_2O, $^3J_{HH}$ = 5.6 Hz), 7.11 (d, 1H, CH, $^3J_{HH}$ = 5.6Hz, $^3J_{SnH}$ = n.d.), 7.17–7.55 (m, 5H, $H_{aromat.}$). ^{13}C NMR($CDCl_3$): δ = −7.3 ($SnMe_3$, $^1J_{SnC}$ = 330 Hz), 65.7 (CH_2, $^3J_{SnC}$ = 104 Hz), 126.6, 126.7, 128.0 (all $CH_{aromat.}$), 133.7 ($C_{q,aromat.}$), 141.3 (CH, $^2J_{SnC}$ = 63 Hz), 151.0 (C_q, $^1J_{SnC}$ = 356 Hz). ^{119}Sn NMR($CDCl_3$): δ = −43.8.

19b. ^{1}H NMR($CDCl_3$): δ = 0.19 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 55.3 Hz), 2.39 (s, 1H, OH), 4.37 (d, 2H, CH_2O, $^3J_{HH}$ = 5.2 Hz), 7.00 (d, 1H, CH, $^3J_{HH}$ = 5.2 Hz, $^3J_{SnH}$ = 156.4 Hz), 7.17–7.55 (m, 5H, $H_{aromat.}$). ^{13}C NMR($CDCl_3$): δ = −9.2 ($SnMe_3$, $^1J_{SnC}$ = 346 Hz), 65.1 (CH_2, $^3J_{SnC}$ = n.d.), 126.6, 126.7, 128.0 (all $CH_{aromat.}$), 133.7 ($C_{q,aromat.}$), 139.0 (CH, $^2J_{SnC}$ = 66 Hz), 153.1 (C_q, $^1J_{SnC}$ = 360 Hz). ^{119}Sn NMR($CDCl_3$): δ = −23.4.

3.10. Reaction of *15* with $NaClO_2$–NaH_2PO_4

The aldehyde (5.00 mmol, 1.37 g) is dissolved in a mixture of 50 ml of *tert*-butanol and 25 ml of 2-methyl-2-butene; a solution of sodium chlorite (30.0 mmol, 4.20 g) and sodium dihydrogenphosphate (29.0 mmol, 4.10 g) in 30 ml of water is added over 30 min. The reaction mixture is stirred for 24 h at room temperature. The volatile compounds are distilled off in vacuo at room temperature and the residue dissolved in 30 ml of water and washed twice with 25 ml of hexane. The aqueous layer is acidified with HCl until the pH reaches 3. After extraction with 50 ml of diethyl ether and drying over $MgSO_4$ the solvent is distilled off. Yield: 0.32 g (50%) of *E*-hept-2-enoic acid (**20**), b.p. 120°C/15 Torr 129–132°C/20 Torr [25].

3.11. Epoxidation of *14* and *15* with MCPBA

A solution of MCPBA (6.00 mmol, 0.94 g) in 10 ml of trichloromethane is added to a solution of the aldehyde (3.00 mmol) in 10 ml of trichloromethane at 0°C. The reaction mixture is stirred for 4 h at room temperature, 3 g of KF added and the mixture stirred vigorously for an additional 2 h. The mixture is filtered through 10 g of $MgSO_4$ and the solvent removed in vacuo.

3.11.1. *21: 30% of 3-butyl-3-trimethylstannyl-epoxypropanal*

^{1}H NMR($CDCl_3$): δ = 0.21 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 54.4 Hz), 0.92 (t, 3H, CH_3, $^3J_{HH}$ = 7.2 Hz), 1.17–1.70 (m, 4H, CH_2), 2.42–2.54 (m, 2H, CH_2), 3.34 (d, 1H, CH, $^3J_{HH}$ = 7.8 Hz, $^3J_{SnH}$ = 90.6 Hz), 9.51 (d, 1H, COH, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR($CDCl_3$): δ = −8.9 ($SnMe_3$, $^1J_{SnC}$ = 351 Hz), 13.8 (CH_3), 22.3, 32.3, 38.5 (all CH_2), 67.1 (CH, $^2J_{SnC}$ = 47 Hz), 77.1 (C_q, $^1J_{SnC}$ = 404 Hz), 192.9 (CH, C=O, $^3J_{SnC}$ = 84 Hz). ^{119}Sn NMR($CDCl_3$): δ = −5.8.

3.11.2. *22: 50% of Z- and E-3-phenyl-3-trimethylstannylepoxypropanal (65% of 22a and 35% of 22b)*

22a. ^{1}H NMR ($CDCl_3$): δ = 0.29 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 55.2 Hz), 2.73 (s, 1H, CH, $^3J_{SnH}$ = 108 Hz), 7.00–7.56 (m, 5H, $H_{aromat.}$), 9.80 (s, 1H, CHO). ^{13}C NMR($CDCl_3$): δ = −8.0 ($SnMe_3$, $^1J_{SnC}$ = 333 Hz), 66.2 (CH, $^2J_{SnC}$ = n.d.), 77.2 (C_q, $^1J_{SnC}$ = n.d.), 125.1, 126.2, 127.7 (all $CH_{aromat.}$), 140.2 ($C_{q,aromat.}$, $^2J_{SnC}$ = n.d.), 192.4 (CH, C=O). ^{119}Sn NMR($CDCl_3$): δ = −11.6.

22b. ^{1}H NMR($CDCl_3$): δ = 0.26 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 53.0 Hz), 2.66 (s, 1H, CH, $^3J_{SnH}$ = 96.0 Hz), 7.00–7.58 (m, 5H, $H_{aromat.}$), 9.79 (s, 1H, CHO). ^{13}C NMR($CDCl_3$): δ = −10.2 ($SnMe_3$, $^1J_{SnC}$ = 340 Hz), 66.2 (CH, $^2J_{SnC}$ = n.d.), 77.2 (C_q, $^1J_{SnC}$ = n.d.), 128.2, 128.4, 129.4 (all $CH_{aromat.}$), 139.7 ($C_{q,aromat}$), 192.4 (CH, C=O). ^{119}Sn NMR($CDCl_3$): δ = 4.3.

3.12. 3-Methoxy-2-trimethylstannylpropene (*21*)

21 is obtained from 5.00 mmol (1.99 g) of **2d**, 5.00 mmol (0.50 g) of **13**, and 5.00 mmol (0.67 g) of $AlCl_3$. Yield: 0.94 g (81%) of **21**, b.p. 80°C/15 Torr. ^{1}H NMR($CDCl_3$): δ = 0.60 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 55.8 Hz), 3.32 (s, 3H, OCH_3), 4.09 (t, 2H, OCH_2, $^4J_{HH}$ = 1.6 Hz, $^3J_{SnH}$ = 39.4 Hz), 5.32 (d, 1H, CH_2, $^2J_{HH}$ = 1.9 Hz, $^3J_{SnH}$ = 69.9Hz), 5.72 (s, 1H, CH_2, $^2J_{HH}$ = 1.9 Hz, $^3J_{SnH}$ = 140.9 Hz). ^{13}C NMR($CDCl_3$): δ = −9.6 ($SnMe_3$, $^1J_{SnC}$ = 348 Hz), 57.9 (OCH_3), 79.3 (OCH_2, $^2J_{SnC}$ = 33 Hz), 124.4 (CH_2, $^2J_{SnC}$ = 33 Hz), 153.4 (C_q, $^1J_{SnC}$ = 438 Hz). ^{119}Sn NMR($CDCl_3$): δ = −34.8. GC-FT-IR: ν = 1113 cm^{-1} (νC–O–C), 2830 (νCH), 2927 (νCH), 2989 (νCH). GC-MS: (70 eV) *m/e* = 236 (10%, M^+), 221 (100%, $M^+ - CH_3$), 181 (30%, $Me_2SnOCH_3^+$), 165 (8%, $SnMe_3^+$), 151 (40%, $HSnMe_2^+$), 135 (5%, $SnMe^+$), 71 (15%, $M^+ - SnMe_3$), 59 (80%, $MeOCH_2CH_2^+$). Anal. Found: C, 35.5; H, 7.0. $C_7H_{16}OSn$ (234.89). Calc.: C, 35.79; H 6.87.

3.13. 3-Methoxy-1-propene (*23*)

23 is obtained from 5.00 mmol (1.99 g) of **2d**, 5.00 mmol (0.50 g) of **13**, and 10.0 mmol (1.34 g) of $AlCl_3$,

yield: 0.19 g (45%). Or, from 5.00 mmol (1.99 g) of **2d**, 10.0 mmol (1.00 g) of **13**, and 10.0 mmol (1.34 g) of $AlCl_3$, yield: 0.23 g (61%). ^{1}H NMR(acetone[d_6]): $\delta = 3.37$ (s, 3H, CH_3), 4.50 (m, 2H, OCH_2), 4.79 (m, 1H, CH_2), 5.65 (m, 1H, CH_2), 7.00 (m, 1H, CH). ^{13}C NMR(acetone[d_6]): $\delta = 55.8$ (CH_3), 75.5 (OCH_2), 121.9 (CH_2), 143.8 (CH), 153.8(C_q). GC-FT-IR: $\nu =$ 1087 cm^{-1} (νC–O–C), 2841 (νCH), 2921 (νCH), 3000 (m, νCH). GC-MS: (70 eV) $m/e = 73$ (100%, $M^+ + H$), 72 (53%, M^+), 59 (25%, $MeOCH_2CH_2^+$).

3.14. 2-(2-Trimethylstannyl-3-allyloxy)tetrahydrofuran (21b) and 2-(1-trimethylstannyl-3-allyloxy)tetrahydrofuran (22b)

A mixture of **21b** (75%) and **22b** (25%) is obtained from 5.00 mmol (2.27 g) of **2f**, 5.00 mmol (0.50 g) of **13**, and 5.00 mmol (0.67 g) of $AlCl_3$. Yield: 0.94 g (65%), b.p. 50°C/0.01 Torr.

21b. ^{1}H NMR($CDCl_3$): $\delta = 0.10$ (s, 9H, $SnMe_3$, $^2J_{SnH} = 54.1$ Hz), 1.52–2.11 (m, 4H, CH_2), 3.25–3.43 (m, 2H, OCH_2), 3.55 (dt, 1H, OCH_2, $^2J_{HH} = 12.9$ Hz, $^4J_{HH} = 1.4$ Hz, $^3J_{SnH} = 51.2$ Hz), 3.84 (dt, 1H, OCH_2, $^2J_{HH} = 12.9$ Hz, $^4J_{HH} = 12.9$ Hz, $^3J_{SnH} = 48.5$ Hz), 4.09 (m, 1H, OCH), 5.17 (m, 1H, CH_2, $^3J_{SnH} = 79.4$ Hz), 5.88 (m, 1H, CH_2, $^3J_{SnH} = 143.2$ Hz). ^{13}C NMR($CDCl_3$): $\delta = -9.6$ ($SnMe_3$, $^1J_{SnC} = 348$ Hz), 23.3, 32.1 (all CH_2), 66.6 (OCH_2), 74.2 (OCH_2, $^2J_{SnC}$ = n.d.), 103.5 (OCH), 116.5 (CH_2, $^2J_{SnC} = 44$ Hz), 160.9 (C_q, $^1J_{SnC} = 452$ Hz). ^{119}Sn NMR($CDCl_3$): $\delta = -34.9$.

22b. ^{13}C NMR($CDCl_3$): $\delta = -9.7$ ($SnMe_3$), 13.3, 33.0 (all CH_2), 66.7 (OCH_2), 74.0 (OCH_2), 103.0 (OCH), 137.4 (CH), 152.7 (CH). ^{119}Sn NMR($CDCl_3$): $\delta = -36.0$. Anal. Found: C, 41.5: H 7.1. $C_{10}H_{20}O_2Sn$ (290.96). Calc.: C, 41.28; H, 6.93%.

3.15. 2-(2-Trimethylstannyl-3-allyloxy)tetrahydropyran (21c) and 2-(1-trimethylstannyl-3-allyloxy)tetrahydropyran (22c)

A mixture of **21c** (90%) and **22c** (10%) is obtained from 5.00 mmol (2.33 g) of **2g**, 5.00 mmol (0.50 g) of **13**, and 5.00 mmol (0.67 g) of $AlCl_3$. Yield: 1.08 g (71%), b.p. 50°C/0.01 Torr.

21c. ^{1}H NMR($CDCl_3$): $\delta = 0.15$ (s, 9H, $SnMe_3$, $^2J_{SnH} = 55.5$ Hz), 1.44–1.93 (m, 6H, CH_2), 3.51 (m, 1H, CH_2), 3.83 (m, 1H, CH_2), 4.06 (dt, 1H, OCH_2, $^2J_{HH} = 12.8$ Hz, $^4J_{HH} = 1.6$ Hz, $^3J_{SnH} = 50.6$ Hz), 4.42 (dt, 1H, CH_2, $^2J_{HH} = 12.8$ Hz, $^4J_{HH} = 1.6$ Hz, $^3J_{SnH} = 49.8$ Hz), 5.26 (m, 1H, CH_2, $^3J_{SnH} = 73.5$ Hz), 5.82 (m, 1H, CH_2, $^3J_{SnH} = 146.9$ Hz). ^{13}C NMR($CDCl_3$): $\delta = -9.4$ ($SnMe_3$, $^1J_{SnC} = 351$ Hz), 19.1, 25.4, 30.4 (all CH_2), 61.6 (OCH_2), 73.8 (OCH_2, $^2J_{SnC} = 36$ Hz), 97.7 (OCH), 123.8 (CH_2, $^2J_{SnC} = 25$ Hz), 152.9 (C_q, $^1J_{SnC} = 443$ Hz). ^{119}Sn NMR($CDCl_3$): $\delta = -35.1$. GC-MS: (70 eV) $m/e = 307$ (5%, $M^+ - H$), 306 (3%, M^+), 291 (100%, $M^+ - CH_3$), 251 (26%, $M^+ - CHCH_2CH_2CH_2$), 207 (14%, $M^+ - OCH[CH_2]_5$), 165 (26%, $SnMe_3^+$), 141 (69%, $M^+ - SnMe_3$), 85 (74%, $OCH[CH_2]_4^+$), 69 (21%, $C_5H_9^+$).

22c. ^{13}C NMR($CDCl_3$): $\delta = -9.6$ ($SnMe_3$), 19.3, 25.2, 30.6 (all CH_2), 62.4 (OCH_2), 75.8 (OCH_2), 98.7 (OCH), 122.6 (CH), 134.5 (CH). ^{119}Sn NMR($CDCl_3$): $\delta = -35.8$.

3.16. Z- and E-2-Butyl-3-trimethylsilyprop-2-ene-1-al (25a and b)

A mixture of 60% **25a** and 40% of **25b** is obtained from 5.00 mmol (1.59 g) of **24a**, 5.00 mmol (0.50 g) of **13**, and 5.00 mmol (0.67 g) of $AlCl_3$. Yield: 0.62 g (67%), b.p. 70–80°C/0.5 Torr (68–80°C/1.0 Torr [21])

25a. ^{1}H NMR($CDCl_3$): $\delta = 0.07$ (s, 9H, $SiMe_3$), 0.91 (t, 3H, CH_3, $^3J_{HH} = 7.2$ Hz), 1.24–1.49 (m, 4H, CH_2), 2.02–2.39 (m, 2H, CH_2), 6.41 (s, 1H, CH), 9.82 (s, 1H, CHO). ^{13}C NMR($CDCl_3$): $\delta = -1.53$ ($SiMe_3$), 13.8 (CH_3), 22.8, 31.1, 37.0 (all CH_2), 134.6 (CH), 159.4 (C_q), 193.3 (CHO). ^{29}Si NMR($CDCl_3$): $\delta = -9.2$. GC-FT-IR: $\nu = 685$ cm^{-1} (νSiC), 1697 (νC=O), 2750 (νC=O–H), 2850 (νCH).

25b. ^{1}H NMR($CDCl^3$): $\delta = 0.08$ (s, 9H, $SiMe_3$), 0.91 (t, 3H, CH_3, $^3J_{HH} = 7.2$ Hz), 1.24–1.43 (m, 4H, CH_2), 2.02–2.39 (m, 2H, CH_2), 6.18 (s, 1H, CH), 9.96 (s, 1H, CHO). ^{13}C NMR($CDCl_3$): $\delta = -0.5$ ($SiMe_3$, $^1J_{SiC} = 58$ Hz), 13.9 (CH_3), 22.4, 31.2, 35.7 (all CH_2), 136.1 (CH, $^1J_{SiC} = 72$ Hz), 152.0 (C_q), 190.3 (CHO). ^{29}Si NMR($CDCl_3$): $\delta = 2.3$ Anal. Found: C, 65.0; H, 10.5. $C_{10}H_{20}OSi$ (184.35). Calc.: C, 65.15; H 10.93%.

3.17. Z- and E-2-Phenyl-3-trimethylsilyl-prop-2-ene-1-al (26a and b)

A mixture of 75% of **26a** and 25% of **26b** is obtained from 5.00 mmol (1.69 g) of **24b**, 5.00 mmol (0.50 g) of **13**, and 5.00 mmol (0.67g) of $AlCl_3$. Yield: 0.59 g (58%), b.p. 100–105°C/0.5 Torr. (54–56°C/0.002 Torr [21]).

26a. ^{1}H NMR($CDCl_3$): $\delta = 0.23$ (s, 9H, $SiMe_3$), 6.57 (s, 1H, CH), 7.23–7.57 (m, 5H, $H_{aromat.}$), 9.44 (s, 1H, CHO). ^{13}C NMR($CDCl_3$): $\delta = 0.4$ ($SiMe_3$, $^1J_{SiC} =$ 52 Hz), 126.2, 127.8, 129.2 (all $CH_{aromat.}$), 138.1 ($C_{q,aromat.}$), 143.5 (CH, $^1J_{SiC} = 66$ Hz), 148.0 (C_q); 192.5 (CHO). ^{29}Si NMR($CDCl_3$): $\delta = -6.3$

26b. ^{1}H NMR($CDCl_3$): $\delta = 0.26$ (s, 9H, $SiMe_3$), 6.92 (s, 1H, CH), 7.23–7.57 (m, 5H, $H_{aromat.}$), 9.68 (s, 1H, CHO). ^{13}C NMR($CDCl_3$): $\delta = -0.9$ ($SiMe_3$), 126.2, 127.8, 129.2 (all $CH_{aromat.}$), 137.3 ($C_{q.aromat.}$), 143.5 (CH), 150.7 (C_q), 193.3 (CHO). ^{29}Si NMR-($CDCl_3$): $\delta = -8.0$. Anal. Found: C, 70.1; H, 8.0. $C_{12}H_{16}OSi$ (204.34). Calc.: C, 70.53; H 7.89%.

Table 11
^{119}Sn and ^{13}C NMR data of sodium sulphonates **28** in D_2O

	δ(Sn)	δ($SnCH_3$) ($^1J_{SnC}$)	δ(CH) ($^2J_{SnC}$)	δ(C_q) ($^1J_{SnC}$)	δ(C(1)R) ($^2J_{SnC}$)	δ(others)
28a	−44.1	−5.8 (526)	133.1 (97)	156.2 (518)	— (—)	122.6, 123.6, 124.6 (all CH), 136.0 (C_q)
28b	−32.5	0.77 (539)	137.1 (n.d.)	160.2 (539)	76.8 (56)	60.7 (OCH_3)
28c [a]	−35.3	−2.4 (538)	141.8 (43)	164.0 (540)	77.0 (54)	0.6 ($SiMe_3$)
28d	−33.1	0.8 (529)	137.6 (98)	166.1 (517)	74.6 (58)	75.3 (OCH_2), 131.1, 131.2, 131.5 (all CH), 139.7 (C_q)
28e	−34.2	−0.22 (520)	134.1 (80)	163.0 (536)	66.1 (64)	25.5 (CH_3), 183.4 (C_q)
28f	−26.4	0.87 (524)	140.6 (94)	160.2 (521)	66.1 (58)	55.4 (NCH_2), 69.3 (OCH_2)

[a] ^{29}Si $\delta = 17.9$.

3.18. Reaction of 1,2-bis(trimethylstannyl)-1-alkenes with trimethylsilyl chlorosulfonate (27)

The *Z*-1,2-bis(trimethylstannyl)-1-alkene (5.00 mmol) is slowly added to a solution of **27** (10.0 mmol, 1.88 g) in 20 ml of anhydrous CCl_4. After 1 h the exothermic reaction is complete and the reaction mixture is hydrolysed with 30 ml of a saturated aqueous $NaHCO_3$ solution and stirred for 30 min. The layers are separated and the aqueous layer washed three times with 10 ml of diethyl ether. The water is removed from the aqueous layer in vacuo and the residue digested with 150 ml of boiling ethanol and filtered off. The ethanol is evaporated and the solid residue washed twice with 25 ml of *n*-pentane and dried in vacuo at 80°C. The products are obtained as hygroscopic solids with melting points above 320°C NMR data for **28** are given in Tables 11 and 12, and elemental analyses are in Table 13.

28a. IR: $\nu = 700\ cm^{-1}$ (monosubstituted arene), 755

Table 12
^1H NMR data of sodium solphonates **28** in D_2O

	δ($SnMe_3$) ($^2J_{SnH}$)	δ(CH) ($^3J_{SnH}$)	δ(CH(R)) ($^3J_{SnH}$)	δ(others)
28a	0.48 (70.8)	6.87 (s) (139.6)	— (—)	7.14 (m, 5H, $H_{aromat.}$)
28b	0.39 (74.8)	6.98 (t, $^4J = 1.9$) (147.0)	4.23 (d, $^4J = 1.9$) (50.6)	3.28 (s, 3H, CH_3)
28c	0.37 (72.3)	6.19 (t, $^4J = 1.6$) (139.8)	3.76 (d, $^4J = 1.6$) (53.4)	0.13 (s, 9H, $SiMe_3$)
28d	0.38 (70.8)	7.02 (t, $^4J = 2.0$) (133.4)	4.31 (d, $^4J = 2.0$) (61.6)	4.45 (s, 2H, CH_2), 7.28 (m, 5H, H_{aromat})
28e	0.37 (72.3)	7.18 (t, $^4J = 1.6$) (138.2)	4.42 (d, $^4J = 1.6$) (66.4)	2.15 (s, 3H, CH_3)
28f	0.36 (73.6)	6.98 (t, $^4J = 1.6$) (144.8)	3.34 (d, $^4J = 1.6$) (50.4)	2.39 (m, 4H, NCH_2), 3.62 (m, 4H, OCH_2)

Table 13
Elemental analysis values for sodium sulphonates **28**

		M.w.	Calc.		Found	
			C	H	C	H
28a	$C_{11}H_{15}NaO_3SSn \cdot H_2O$	386.99	34.14	4.43	34.0	4.6
28b	$C_7H_{15}NaO_4SSn \cdot H_2O$	354.95	23.69	4.83	23.4	5.0
28c	$C_9H_{21}NaO_4SSiSn \cdot H_2O$	390.11	27.71	5.94	27.5	5.9
28d	$C_{13}H_{19}NaO_4SSn \cdot H_2O$	431.05	36.22	4.91	36.0	5.2
28e	$C_8H_{15}NaO_5SSn \cdot H_2O$	382.96	25.09	4.47	24.8	4.7
28f [a]	$C_{10}H_{20}NNaO_4SSn \cdot H_2O$	410.03	29.29	5.41	29.1	5.7

[a] N, calc.: 3.42; found: 3.3.

Table 14
^{119}Sn and ^{13}C NMR data of the SO_2 adducts **30** in $CDCl_3$

	δ(Sn)	δ($SnMe_3$)/($^1J_{SnC}$)	δ(CH)	δ(C_q)	δ(C(1)(R))	δ(others)
30a	−8.1	1.1/514	140.5	158.2	—	127.3, 128.7, 129.2 (all CH), 134.4 (C_q)
30b	−31.3	1.4/507	144.0	156.0	—	13.7 (CH_3), 22.3, 31.6, 35.0 (all CH_2)
30c	−17.7	1.4/501	143.4	157.4	—	21.6, 22.6, 25.5, 28.2 (all CH_2), 125.7 (CH), 145.8 (C_q)
30d	−0.2	1.3/520	142.3	152.2	75.3	58.4 (CH_3)
30e	−2.3	1.4/501	142.9	152.3	72.0	75.1 (CH_2), 126.3, 126.8, 127.9 (all CH), 137.1 (C_q)
30f	−4.0	1.4/505	142.4	152.5	78.6	19.4, 25.4, 30.5, 62.4 (all CH_2), 90.2 (CH)
30g [a]	−8.5	1.3/498	142.0	154.6	65.6	−0.5 ($SiMe_3$)
30h	−6.1	1.3/551	145.0	153.9	47.9	40.4 (CH_3)
30i	2.9	1.4/503	145.2	153.5	66.7	52.1 (NCH_2), 60.2 (OCH_2)
30j	−1.8	1.3/525	143.1	149.8	47.7	20.7 (CH_3), 170.1 (C=O)
30k	−52.1	1.4/474	146.1	160.9	—	53.2 (CH_3), 171.5 (C=O)
30l	0.2	1.2/521	143.2	153.1	75.4	—
34 [b]	8.2	1.7/498	141.5	172.7	47.6	−0.4 ($SiMe_3$)

^{29}Si NMR: [a] 20.8; [b] 20.0.

(monosubstituted arene), 1041 (ν_sSO_3), 1191 ($\nu_{as}SO_3$), 1600 (νC=C), 2925 (νCH), 3025 (νCH), 3450 (m, νOH).

28b. IR: $\nu = 1045\ cm^{-1}$ (ν_sSO_3), 1070 (νC–O–C), 1190 ($\nu_{as}SO_3$), 1616 (νC=C), 2855 (νCH), 2980 (νCH), 3480 (νCH).

28c. IR: $\nu = 638\ cm^{-1}$ (νSiC), 1053 (ν_sSO_3), 1071 (νSiO), 1196 ($\nu_{as}SO_3$), 1617 (νC=C), 2855 (νCH), 2920 (νCH), 3470 (m, νOH).

28d. IR: $\nu = 698\ cm^{-1}$ (monosubstituted arene), 743 (monosubstituted arene), 1047 (ν_sSO_3), 1098 (νC–O–C), 1212 ($\nu_{as}SO_3$), 1639 (νC=C), 2860 (νCH), 2929 (νCH), 3240 (νOH).

28e. IR: $\nu = 1042\ cm^{-1}$ (ν_sSO_3), 1196 ($\nu_{as}SO_3$), 1636 (νC=C), 1661 (νC=O), 2935 (νCH), 3435 (νOH).

28f. IR: $\nu = 1039\ cm^{-1}$ (ν_sSO_3), 1073 (νC–O–C), 1198 ($\nu_{as}SO_3$), 1277 (νC–N), 1640 (νC=C), 2820 (νCH), 2865 (νCH), 2925 (νCH), 2975 (νCH), 3420 (νOH).

29. ^1H NMR(D_2O): δ = 1.54 (m, 6H, CH_2), 3.48 (m, 1H, CH_2), 3.90 (m, 1H, CH_2), 4.00 (dd, 1H, CH_2, $^2J_{HH} = 6.5$ Hz, $^4J_{HH} = 1.6$ Hz), 4.19 (dd, 1H, CH_2, $^2J_{HH} = 6.5$ Hz, $^4J_{HH} = 1.6$ Hz), 4.52 (m, 1H, CH), 6.64 (t, 1H, CH, $^4J_{HH} = 1.6$ Hz), 7.06 (t, 1H, CH, $^4J_{HH} = 1.6$ Hz). ^{13}C NMR(D_2O): δ = 21.8, 23.2, 24.1, 24.2, 30.6, 30.8 (all CH_2), 59.8, 60.2, 68.9, 72.0 (all OCH_2), 119.7, 122.6 (all OCH), 134.6, 149.8 (all CH), 158.7, 158.8 (all C_q). IR: $\nu = 1015\ cm^{-1}$ (νC–O–C), 1045 (ν_sSO_3), 1225 ($\nu_{as}SO_3$), 1645 (νC=C), 2870 (νCH), 2945 (νCH), 3240 (νOH).

3.19. Reaction of 1,2-bis(trimethylstannyl)-1-alkenes with SO_2

A slow stream of SO_2, dried with concentrated sulphuric acid, is passed into a solution of the 1,2-bis(trimethylstannyl)-1-alkene (5.00 mmol) in 25 ml of anhydrous dichloromethane for 4 h at room temperature. The solvent and the surplus SO_2 are evaporated off and the

Table 15
^1H NMR data of the SO_2 adducts **30** in $CDCl_3$

	δ($SnMe_3$)/($^2J_{SnH}$)	δ(CH)	δ(CH(R))	δ(others)
30a	0.47/71.0	6.81(s)	—	7.26 (m, 5H, $H_{aromat.}$)
30b	0.62/68.9	6.90(t, $^4J = 1.6$)	—	0.93 (t, 3H, CH_3, $^3J = 7.3$), 1.25–1.78 (m, 4H, CH_2), 1.98–2.24 (m, 2H, CH_2)
30c	0.56/65.3	6.88(s)	—	1.61 (m, 4H, CH_2), 2.28 (m, 4H, CH_2), 5.60 (s, 1H, CH)
30d	0.50/67.9	7.10(t, $^4J = 1.6$)	4.32 (d, $^4J = 1.6$)	3.31 (s, 3H, CH_3)
30e	0.66/66.1	7.21 ($^4J = 1.5$)	4.21 (d, $^4J = 1.5$)	4.00 (s, 2H, OCH_2), 7.31 (m, 5H, $H_{aromat.}$)
30f	0.59/66.4	7.30($^4J = 1.5$)	4.38(dd, $^2J = 11.9$, $^4J = 1.5$)	1.62 (m, 6H, CH_2), 3.52 (m, 1H, CH_2), 3.88 (m, 1H, CH_2), 4.70 (t, 1H, CH, $^3J = 7.2$)
30g	0.50/51.8	7.20($^4J = 1.6$)	4.80(d, $^4J = 1.6$)	0.00 (s, 9H, $SiMe_3$)
30h	0.52/66.3	7.29($^4J = 1.6$)	3.71(d, $^4J = 1.6$)	2.35 (s, 6H, CH_3)
30i	0.51/72.1	7.17($^4J = 1.5$)	2.20(d, $^4J = 1.5$)	2.62 (m, 4H, NCH_2), 3.70 (m, 4H, OCH_2)
30j	0.56/69.6	7.10($^4J = 1.6$)	4.96(d, $^4J = 1.6$)	2.12 (s, 3H, CH_3)
30k	0.56/69.6	7.43(s)	—	3.75 (s, 3H, CH_3)
30l	0.58/68.6	5.89($^4J = 1.4$)	3.72 (d, $^4J = 1.4$)	—
34	0.44/51.8	6.78(t, $^4J = 1.6$)	4.78 (d, $^4J = 1.6$)	0.00 (s, 9H, $SiMe_3$)

residue distilled in vacuo. NMR data for **30** and **34** are given in Tables 14 and 15.

30a. IR: $\nu = 525$ cm^{-1} (νSn–O), 549 (νSn–C), 697 (νC–S), 771 (νS–O), 1070 (νSO_2), 1200 (νS=O), 1630 (νC=C), 2915 (νCH), 3000 (νCH), 3060 (νCH). MS: (70 eV) $m/e = 331$ (1%, $M^+ - SO_2$, $-SnMe_3$), 267 (21%, $M^+ - 2SO_2$, $-SnMe_3$), 165 (100%, $SnMe_3^+$), 135 (60%, $SnMe^+$), 121 (13%, SnH^+), 77 (21%, $C_6H_5^+$).

30b. IR: $\nu = 521$ cm^{-1} (νSn–O), 549 (νSn–C), 669 (νC–S), 763 (νS–O), 1050 (νSO_2), 1187 (νS=O), 1655 (νC=C), 2970 (νCH).

30c. IR: $\nu = 520$ cm^{-1} (Sn–O), 555 (νSn–C), 680 (νC–S), 781 (νS–O), 1189 (νS=O), 1656 (νC=C), 2870 (νCH).

30d. IR: $\nu = 524$ cm^{-1} (νSn–O), 554 (νSn–C), 649 (νC–S), 766 (νS–O), 1054 (νSO_2), 1186 (νSO_2), 1648 (νC=C), 2935 (νCH). MS: (70 eV) $m/e = 235$ (72%, $M^+ - 2SO_2$, $-SnMe_3$), 165 (100%, $SnMe_3^+$), 135 (72%, $SnMe^+$), 121 (16%, SnH^+), 64 (38%, SO_2).

30e. IR: $\nu =$ cm^{-1} 524 (νSn–O), 554 (νSnC), 697 (νC–S), 778 (νS–O), 1198 (νSO_2), 1660 (νC=C), 2920 (νCH), 3005 (νCH).

30f. IR: $\nu = 521$ cm^{-1} (νSn–O), 554 (νSn–C), 696 (νC–S), 773 (νS–O), 1080 (νC–O–C), 1196 (νSO_2), 1648 (νC=C), 2850 (νCH), 2950 (νCH).

30g. IR: $\nu = 512$ cm^{-1} (νSn–O), 553 (νSn–C), 687 (νC–S), 773 (νS–O), 1194 (νSO_2), 1658 (νC=C), 2925 (νCH).

30h. IR: $\nu = 529$ cm^{-1} (νSn–O), 553 (νSn–C), 785 (νS–O), 1197 (νSO_2), 1318 (νC–N), 1680 (νC=C), 2830 (νCH), 2925 (νCH).

30i. IR: $\nu = 511$ cm^{-1} (νSn–O), 552 (νSn–C), 800 (νS–O), 1192 (νSO_2), 1660 (νC=C), 2820 (νCH), 2920 (νCH).

30j. IR: $\nu = 417$ cm^{-1} (νSn–O), 426 (νSn–C), 687 (νC–S), 779 (νS–O), 1096 (νSO_2), 1625 (νC=C), 1736 (νC=C), 2910 (νCH), 2970 (νCH).

30k. IR: $\nu = 417$ cm^{-1} (νSn–O), 426 (νSn–C), 650 (νC–S), 773 (νS–O), 1096 (νSO_2), 1645 (νC=C), 1707 (νC–O), 2920 (νCH), 2970 (νCH).

30l. IR: $\nu = 514$ cm^{-1} (νS–O), 553 (νSn–C), 676 (νC–S), 773 (νS–O), 1075 (νC–O–C), 1197 (νSO_2), 1638 (νC=C), 2920 (νCH). MS: (70 eV) $m/e = 229$ (50%, $Me_3SnSO_2^+$), 165 (100%, $SnMe_3^+$), 150 (20%, $SnMe_2^+$), 121 (6%, SnH^+), 64 (11%, SO_2), 48 (9% SO^+).

32a. ^{1}H NMR($CDCl_3$): $\delta = 0.25$ (s, 18H, $SnMe_3$, $^2J_{SnH} = 51.0$ Hz), 0.49 (s, 9H, $SnMe_3$, $^2J_{SnH} = 68.2$ Hz), 6.24 (s, 1H, CH, $^3J_{SnH} = 132.2$ Hz), 7.25 (m, 5H, $H_{aromat.}$). ^{13}C NMR($CDCl_3$): $\delta = -8.9$ ($SnMe_3$, $^1J_{SnC} = 346$ Hz), 1.4 ($SnMe_3$, $^1J_{SnC} = 496$ Hz), 126.5, 127.9, 129.4 (all $CH_{aromat.}$), 136.7 ($C_{q,aromat.}$), 141.2 (CH, $^2J_{SnC}$ = n.d.), 151.3 (C_q, $^1J_{SnC} = 421$ Hz). ^{119}Sn NMR($CDCl_3$): $\delta = -21.1$ ($SnMe_3C$), 8.3 ($SnMe_3SO_2$). IR: $\nu = 678$ cm^{-1} (νC–S), 779 (νS–O), 1191 (νSO_2), 1655 (νC=C), 2920 (νCH), 2990 (νCH), 3060 (νCH).

32b. ^{1}H NMR($CDCl_3$): $\delta = 0.20$ (s, 9H, $SnMe_3$, $^2J_{SnH} = 55.2$ Hz), 0.59 (s, 9H, $SnMe_3$, $^2J_{SnH} = 64.5$ Hz), 3.34 (s, 3H, CH_3), 4.38 (d, 2H, OCH_2, $^4J_{HH} = 1.6$ Hz), 6.73 (t, 1H, CH, $^4J_H^H = 1.6$ Hz). ^{13}C NMR($CDCl_3$): $\delta = -8.6$ ($SnMe_3$, $^1J_{SnC} = 360$ Hz), 1.6 ($SnMe_3$, $^1J_{SnC} = 502$ Hz), 58.3 (CH_3), 72.8 (CH_2, $^2J_{SnC} = 33$ Hz), 147.0 (CH, $^2J_{SnC}$ = n.d.), 155.2 (C_q, $^1J_{SnC} = 412$ Hz). ^{119}Sn NMR($CDCl_3$): $\delta = -22.7$ ($SnMe_3C$), 9.9 ($SnMe_3SO_2$). IR: $\nu = 516$ cm^{-1} (νSn–O), 551 (νSn–C), 682 (νC–S), 772 (νS–O), 1191 (νSO_2), 1655 (νC=C), 2830 (νCH).

32c. ^{1}H NMR($CDCl_3$): $\delta = 0.19$ (s, 9H, $SnMe_3$, $^2J_{SnH} = 55.8$ Hz), 0.53 (s, 9H, $SnMe_3$, $^2J_{SnH} = 69.0$

Table 16
Elemental analysis values for SO_2 adducts **30**

		M.w.	Calc.		Found	
			C	H	C	H
30a	$C_{14}H_{24}O_4S_2Sn_2$	557.38	30.14	4.34	30.9	4.3
30b	$C_{12}H_{28}O_4S_2Sn_2$	537.85	26.80	5.25	27.0	5.2
30c			not possible			
30d	$C_{10}H_{24}O_5S_2Sn_2$	525.38	22.84	4.60	23.1	4.2
30e	$C_{16}H_{28}O_5S_2Sn_2$	601.90	31.93	4.69	32.0	4.9
30f			not possible			
30g	$C_{12}H_{30}O_5S_2SiSn_2$	583.95	24.08	5.18	24.0	5.0
30h [a]	$C_{11}H_{27}NO_4S_2Sn_2$	538.84	24.52	5.05	24.2	5.2
30i			not possible			
30j	$C_{11}H_{24}O_6S_2Sn_2$	553.81	23.86	4.37	23.5	4.1
30k			not possible			
30l	$C_{18}H_{42}O_9S_4Sn_4$	1005.53	21.50	4.21	21.9	4.0
32a	$C_{14}H_{24}O_2SSn_2$	493.78	34.05	4.90	33.8	4.7
32b	$C_{10}H_{24}O_3SSn_2$	461.74	26.01	5.24	26.3	5.1
32c	$C_{14}H_{30}O_4SSn_2$	531.83	31.62	5.69	31.4	5.9
34	$C_{12}H_{30}O_5S_2SiSn_2$	583.95	24.08	5.18	24.3	5.0

[a] N, calc.: 2.60, found: 2.4.

Table 17
^{119}Sn and ^{13}C NMR data of the SO_3 adducts **31** in $CDCl_3$

	δ(Sn)	δ($SnMe_3$)/($^1J_{SnC}$)	δ(CH)	δ(C_q)	δ(C(1)(R))	δ(others)
31a	94.2	1.6/474	142.8	153.1	—	126.5, 127.3, 128.8 (all CH), 139.2 (C_q)
31b	95.8	1.3/503	149.0	163.3	—	13.4 (CH_3), 30.7, 35.1, 40.0 (all CH_2)
31c	90.8	1.4/501	142.1	157.0	—	22.2, 22.8, 25.1, 29.7 (all CH_2), 125.7 (CH)
31d	27.4	1.4/515	142.9	152.0	74.3	78.8 (CH_2), 129.9, 127.3, 128.7 (all CH), 133.4 (C_q)
31e	55.3	1.4/512	142.5	151.2	69.7	24.1, 30.7, 41.7 (all CH_2), 59.4, 101.0 (all CH)
31f [b]	96.3	1.3/510	136.1	154.7	53.5	0.35 ($SiMe_3$, $^1J_{SiC}$ = 58)
31g	85.6	1.3/551	145.1	153.0	47.9	40.4 (CH_3)
31h	92.2	1.4/503	140.2	152.3	78.3	55.1 (NCH_2), 68.1 (OCH_2)
31i	90.1	0.8/475	143.4	164.3	41.1	29.7 (CH_3), 171.5 (C=O)
31j	95.9	1.4/475	141.5	168.0	—	50.6 (CH_3), 170.0 (C=O)
31k [a]	53.6	0.4/518	145.5	162.3	59.5	—
35 [c]	90.3	0.4/498	143.7	164.7	76.6	−1.2 ($SiMe_3$)

[a] In D_2O. ^{29}Si NMR: [b] 21.0; [c] 22.0.

Hz), 1.62 (m, 6H, CH_2), 3.52 (m, 1H, CH_2), 3.77 (m, 1H, CH_2), 4.30 (dd, 1H, CH_2, $^2J_{HH}$ = 11.9 Hz, $^4J_{HH}$ = 1.4 Hz), 4.42 (dd, 1H, CH_2, $^2J_{HH}$ = 11.9 Hz, $^4J_{HH}$ = 1.4 Hz), 4.70 (t, 1H, CH, $^3J_{HH}$ = 7.3 Hz), 7.30 (t, 1H, CH, $^4J_{HH}$ = 1.4 Hz, $^3J_{SnH}$ = 106 Hz). ^{13}C NMR($CDCl_3$): δ = −15.6 ($SnMe_3$, $^1J_{SnC}$ = 361 Hz), −5.5 ($SnMe_3$, $^1J_{SnC}$ = 520 Hz), 11.5, 18.0, 23.1 (all CH_2), 54.1 (OCH_2), 91.4 (OCH), 70.1 (OCH_2, $^2J_{SnC}$ = 66 Hz), 139.5 (CH, $^2J_{SnC}$ = 64 Hz), 147.3 (C_q, $^1J_{SnC}$ = 409 Hz). ^{119}Sn NMR($CDCl_3$): δ = −23.7 ($SnMe_3C$), 12.5 ($SnMe_3SO_2$). MS: (70 eV) *m/e* = 229 (53%, $Me_3SO_2^+$), 165 (100%, $SnMe_3^+$), 135 (29%, $SnMe^+$), 64 (5%, SO_2^+), 48 (3%, SO^+).

34. IR: ν = 522 (νSn–O), 549 (νSn–C), 688 (νC–S), 773 (νS–O), 1193 (νSO_2), 1658 (νC=C), 2925 (νCH).

The elemental analyses of **30**, **32** and **34** are given in Table 16.

3.20. Reaction of 1,2-bis(trimethylstannyl)-1-alkenes with SO_3

A solution of the 1,2-bis(trimethylstannyl)-1-alkene (5.00 mmol) in 25 ml of dichloromethane is cooled to −78°C, SO_3 (10.0 mmol, 0.80 g) is added and the mixture stirred for 4 h at −78°C. The solvent and the remaining SO_3 are removed in vacuo and the residue purified by distillation or recrystallized from *n*-pentane. The NMR data for **31** and **35** are given in Tables 17 and 18

31a. IR: ν = 529 cm^{-1} (νSn–O), 558 (νSnC), 697 (νC–S), 787 (νS–O), 1040 (νSO_3), 1190 (νS=O), 1657 (νC=C), 2930 (νCH), 3015 (νCH).

31b. IR: ν = 521 cm^{-1} (νSn–O), 557 (νSnC), 648 (νC–S), 782 (νS–O), 1042 (νSO_3), 1200 (νS=O), 1680 (νC=C), 2940 (νCH).

31c. IR: ν = 518 cm^{-1} (νSn–O), 551 (νSn–C), 676 (νC–S), 785 (νS–O), 1067 (νSO_3), 1191 (νS=O), 1655 (νC=C), 2865 (νCH).

Table 18
^1H NMR data of the SO_3 adducts **31** in $CDCl_3$

	δ($SnMe_3$)/($^2J_{SnH}$)	δ(CH)	δ(CH(1)(R))	δ(others)
31a	0.67/67.2	8.87 (s)	—	7.35 (m, 5H, $H_{aromat.}$)
31b	0.72/63.7	6.93 (t, ^4J = 1.6)	—	0.93 (t, 3H, CH_3, ^3J = 7.2), 1.25–1.48 (m, 4H, CH_2), 2.13–2.50 (m, 2H, CH_2)
31c	0.49/68.2	6.54 (s)	—	1.65 (m, 4H, CH_2), 2.00 (m, 4H, CH_2), 5.60 (s, 1H, CH)
31d	0.47/70.5	6.05 (t, ^4J = 1.5)	3.85 (d, ^4J = 1.5)	4.60 (s, 2H, CH_2), 7.38 (m, 5H, $H_{aromat.}$)
31e	0.60/68.2	6.74 (t, ^4J = 1.5)	4.43 (dd, ^2J = 11.9, ^4J = 1.5), 4.73 (dd, ^2J = 11.9, ^4J = 1.5)	1.62 (m, 6H, CH_2), 3.88 (m, 1H, CH_2), 3.93 (m, 1H, CH_2), 5.38 (t, 1H, CH, ^4J = 7.2)
31f	0.36/74.8	7.08 (t, ^4J = 1.6)	4.33 (d, ^4J = 1.6)	0.08 (s, 9H, $SiMe_3$)
31g	0.52/66.0	7.29 (t, ^4J = 1.6)	3.74 (d, ^4J = 1.6)	2.31 (s, 6H, CH_3)
31h	0.57/68.3	5.80 (t, ^4J = 1.5)	3.11 (d, ^4J = 1.5)	2.58 (m, 4H, NCH_2), 3.65 (m, 4H, OCH_2)
31i	0.79/68.3	5.62 (t, ^4J = 1.6)	4.32 (d, ^4J = 1.6)	1.96 (s, 3H, CH_3)
31j	0.67/69.8	7.34 (s)	—	3.75 (s, 3H, CH_3)
31k [a]	0.61/107.7	6.38 (t, ^4J = 1.6)	4.10 (d, ^4J = 1.6)	—
35	0.70/67.6	5.58 (t, ^4J = 1.6)	4.33 (d, ^4J = 1.6)	−0.01 (s, 9H, $SiMe_3$)

[a] In D_2O.

31d. IR: $\nu = 500\ cm^{-1}$ (νSn–O), 557 (νSn–C), 689 (νC–S), 759 (νS–O), 1054 (νSO_3), 1115 (νC–O–C), 1175 (νS=O), 1650 (νC=C), 2920 (νCH), 3000 (νCH).

31e. IR: $\nu = 521\ cm^{-1}$ (νSn–O), 554 (νSnC), 683 (νC–S), 774 (νS–O), 1066 (νSO_3), 1096 (νC–O–C), 1196 (νS=O), 1637 (νC=C), 2955 (νCH).

31f. IR: $\nu = 541\ cm^{-1}$ (νSn–O), 559 (νSn–C), 669 (νC–S), 782 (νS–O), 1043 (SO_3), 1217 (νS=O), 1655 (νC=C), 2930 (νCH).

31g. IR: $\nu = 506\ cm^{-1}$ (νSn–O), 559 (νSnC), 658 (νC–S), 784 (νS–O), 1053 (νSO_3), 1245 (νS=O), 1655 (νC=C), 2830 (νCH), 2925 (νCH).

31h. IR: $\nu = 500\ cm^{-1}$ (νSn–O), 557 (νSn–C), 689 (νC–S), 782 (νS–O), 1054 (νSO_3), 1195 (νS=O), 1655 (νC=C), 2930 (νCH).

31i. IR: $\nu = 417\ cm^{-1}$ (νSn–O), 426 (νSn–C), 650 (νC–S), 773 (νS–O), 1096 (νSO_3), 1687 (νC=C), 1707 (νC=O), 2920 (νCH), 2970 (νCH).

31j. IR: $\nu = 546\ cm^{-1}$ (νSn–O), 558 (νSn–C), 650 (νC–S), 786 (νS–O), 1075 (νSO_3), 1198 (νS=O), 1647 (νC=C), 1723 (νC=O), 2930 (νCH).

31k. IR: $\nu = 511\ cm^{-1}$ (νSn–O), 560 (νSn–C), 694 (νC–S), 785 (νS–O), 1045 (νSO_3), 1195 (νS=O), 1641 (νC=C), 2920 (νCH).

32. IR: $\nu = 512\ cm^{-1}$ (νSnO), 553 (νSnC), 687 (νC–S), 773 (νSO), 1194 (νSO), 1658 (νC=C), 2925 (νCH), 3005 (νCH).

33. ^{1}H NMR($CDCl_3$): $\delta = 0.04$ (s, 9H, $SnMe_3$, $^2J_{SnH} = 53.1$ Hz), 0.64 (s, 9H, $SnMe_3$, $^2J_{SnH} = 67.6$ Hz), 3.34 (s, 3H, CH_3), 3.84 (d, 2H, CH_2, $^4J_{HH} = 1.4$ Hz), 6.28 (t, 1H, CH, $^4J_{HH} = 1.4$ Hz). ^{13}C NMR($CDCl_3$): $\delta = -5.8$ ($SnMe_3$, $^1J_{SnC} = 377$ Hz) 0.9 ($SnMe_3$, $^1J_{SnC} = 498$ Hz), 58.8 (CH_3), 73.2 (CH_2, $^2J_{SnC} = 63$ Hz), 142.9 (CH, $^2J_{SnC}$ = n.d.), 160.1 (C_q, $^1J_{SnC} = 411$ Hz). ^{119}Sn NMR($CDCl_3$): $\delta = -18.2$ ($SnMe_3C$), 84.4 ($SnMe_3SO_3$). IR: $\nu = 528\ cm^{-1}$ (νSn–O), 560 (νSn–C), 684 (νC–S), 781 (νS–O), 1047 (νSO_3), 1188 (νS=O), 1655 (νC=C), 2965 (νCH).

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