127. Glycosylidene Carbenes

Part 18

Insertion of Glycosylidene Carbenes into the Sn–H Bond of Tributyl- and Triphenylstannane: A Synthesis of Stannoglycosides

by **Peter Uhlmann, Daniel Nanz, Eva Bozó,** and **Andrea Vasella***

Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH–8092 Zürich

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Insertion of the glycosylidene carbenes, derived from the *gluco*- and the *manno*-diazirines **1** and **2**, into the Sn–H bond of R_3SnH (R = Bu or Ph) leads to the fully substituted stannoglycosides **3–8** (53–77%). The 1,2-*cis*-configurated products are formed preferentially (α-D/β-D ranges from 2.5:1 to 5.1:1 with **1**, and 1:1.3 to 1:4.2 with **2**). Relative to CH_2Cl_2, THF favors formation of the equatorial *Sn*-glycosides. The stannylated (benzyloxy)glucals **9** and **10** were isolated as side products. The reaction of **1** with $(Bu_3Sn)_2$ yielded **9** (17% in CH_2Cl_2; 36% in CCl_4) together with the azines **11** and the benzyloxyglucal **12**. NMR Data of the *Sn*-glycosides **3–8** show evidence for an anomeric effect, ^1J(C(1),H) being larger in the axial and ^1J(Sn,C(1)) larger in the equatorial anomers.

Introduction. – The formal insertion of glycosylidene carbenes into the OH group of phenols and alcohols proceeds essentially by protonation of the carbene, followed by combination of the ensuing ions to form glycosides [1–5]. The formal insertion of glycosylidene carbenes into the P–H bond of diphenylphosphine appears to proceed by nucleophilic attack of the phosphine to the carbene, followed by proton migration to form a glycosylphosphine [6]. The third possibility for the non-synchronous formal insertion into a X–H bond, *viz.* a nucleophilic attack of the carbene, followed by hydride migration, may conceivably be realized in the reaction of glycosylidene carbenes with stannanes[1]). We wondered if such a reaction leads (stereoselectively?) to glycosyl stannanes. Fully substituted *Sn*-glycosides[2]) are of interest as potential precursors of *C*-glycosides; we thus planned to find rapid access to these new glycosyl derivatives *via* carbenes while developing an alternative, ultimately more convenient method for their synthesis [17], a strategy which has proven successful for the synthesis of glycosyl phosphines [6] [18].

Insertion of carbenes into the Sn–H bond is well known. *Connor et al.* have investigated the insertion of [methoxy(phenyl)carbene]chromium complexes into the M–H bond of silanes, germanes, and stannanes (M = Si, M = Ge, M = Sn) [19–21]; the inser-

[1]) Stannanes are much less acidic than alcohols (Bu_3SnH: pK = 25.0; Ph_3SnH: p$K \approx 16$ [7]). An alternative mechanism, *viz.* a hydride transfer from Bu_3SnH to a (methoxycarbene)chromium complex leading diastereoselectively to an Sn,O-acetal has been reported by *Nakamura et al.* [8].

[2]) The known *Sn*-glycosides lack O- or N-substituents at C(2), see *e.g.* [9–16].

tion rate increased markedly from M = Si to M = Sn [21]. The reaction of chlorophenyldiazirine, a source of chlorophenylcarbene, with Bu_3SnH gave $Bu_3SnCHClPh$ in excellent yields [22] [23]. Similar kinetic constants have been reported for the reaction of chloro(phenyl)carbene with Bu_3SnH and tetramethylethylene [24].

We report on the reaction of the *gluco*- and *manno*-configurated diazirines **1** [25] and **2** [26] with Bu_3SnH, Ph_3SnH, and $(Bu_3Sn)_2$, and on the analysis of the NMR parameters of the insertion products.

Results and Discussion. – 1. *Reaction of the Diazirines* **1** *and* **2** *with* R_3SnH. The reaction of the diazirine **1** with 5 equiv. of Bu_3SnH in CH_2Cl_2 at room temperature gave a high yield of the anomeric *Sn*-glycosides **3** and **4** (α-D/β-D 5.1:1) and the stannylated (benzyloxy)glucal **9** (*Scheme 1* and *Table 1*). The isolated yields of the main products **3** (58%) and **4** (10%) do not correspond exactly to the ratio of the anomers **3** and **4** in the crude, probably due to some decomposition, mainly of **4**, during chromatography. The

Scheme 1

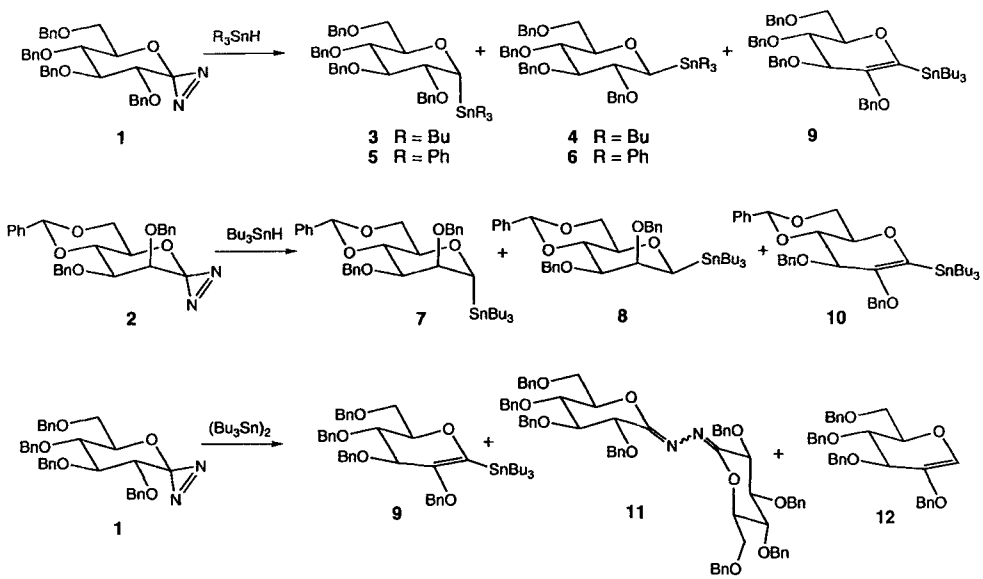


Table 1. *Reaction of the Diazirines* **1** *and* **2** *with* R_3SnH *and* $(Bu_3Sn)_2$

Diazirine	Substrate	Solvent	Products (Yield [%])[a]			Ratio α-D/β-D[b]
			α-D	β-D	(Benzyloxy)glucals	
1	Bu_3SnH	CH_2Cl_2	**3** (58)	**4** (10)	**9** (8)	5.1:1
1	Bu_3SnH	THF	**3** (54)	**4** (16)	**9** (3)	3.8:1
1	Ph_3SnH	CH_2Cl_2	**5** (63)	**6** (14)	–	3.5:1
1	Ph_3SnH	THF	**5** (53)	**6** (22)	–	2.5:1
2	Bu_3SnH	CH_2Cl_2	**7** (25)	**8** (28)	**10** (7)	1:1.3
2	Bu_3SnH	THF	**7** (13)	**8** (43)	–	1:4.2
1	$(Bu_3Sn)_2$	CH_2Cl_2	–	–	**9** (17)	–
1	$(Bu_3Sn)_2$	CCl_4	–	–	**9** (36)	–

[a]) After chromatography. [b]) Determined from the ^{1}H-NMR spectrum of the crude product.

analogous reaction in THF gave a similar yield of the *Sn*-glycosides (70%), but the ratio of the anomers was lowered to α-D/β-D 3.8:1.

The *Sn*-glycosides **5** and **6** were obtained by treating **1** with Ph_3SnH (77% in CH_2Cl_2 and 75% in THF). The diastereoselectivity was lower than that observed in the reaction of **1** with Bu_3SnH (**5**/**6** 3.5:1 in CH_2Cl_2, *ca.* 2.5:1 in THF), but showed a similar solvent dependence. No stannylated (benzyloxy)glucal could be isolated. The constitution and configuration of the *Sn*-glycosides **3**–**6** were established by NMR spectroscopy (see *Table 5* and *Exper. Part*).

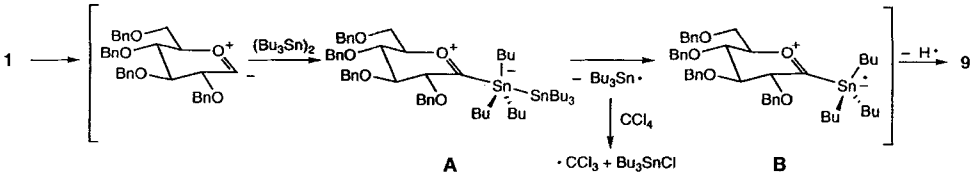
Thus, the *gluco*-diazirine **1** leads preferentially to the 1,2-*cis*-configurated α-D-*Sn*-glycosides. To check if the diastereoselectivity is due to a preferred formation of an α-D- or of a 1,2-*cis*-configurated *Sn*-glycoside, we treated the *manno*-diazirine **2** with Bu_3SnH in CH_2Cl_2 and THF (*Scheme 1* and *Table 1*). The *Sn*-mannosides **7** and **8** were formed in yields of 50–55% together with the stannylated (benzyloxy)glucal **10**. The ratio of anomers again depended upon the solvent: the slight preference for the β-D-anomer realized in CH_2Cl_2 (α-D/β-D 1:1.3) was improved significantly when the solvent was THF (α-D/β-D 1:4.2), clearly showing the preference for the formation of 1,2-*cis*-configurated *Sn*-glycosides.

These results are compatible with the above proposed mechanism[3]). Apparently, the migrating hydride avoids an electrostatic interaction with the C(2)-alkoxy substituent. Conceivably, this effect is accompanied by a favorable intramolecular interaction of the Sn center with this alkoxy group, similarly to the interaction which has been postulated for such alkoxy groups with a tetraligated phosphonium center [29]. An analogous intermolecular interaction with THF, increasing the bulk of the C(1)-substituent during hydride migration, and favoring the equatorial (= β-D) anomers may explain the solvent dependence of the diastereoselectivity.

2. *Reaction of* **1** *with* $(Bu_3Sn)_2$. The diazirine **1** was treated with 5 equiv. of $(Bu_3Sn)_2$ in CH_2Cl_2 at room temperature, to give the stannylated (benzyloxy)glucal **9** (17%), a mixture of azines **11** (60%), the (benzyloxy)glucal **12** (3%), and traces of Bu_3SnCl. Neither the 1,1-distannane nor *Sn*-glycosides could be isolated. The analogous reaction in CCl_4 doubled the yield of **9** (36%). Large amounts of Bu_3SnCl and traces of $CHCl_3$ were also formed (Bu_3SnCl/**9** *ca.* 5:1), besides **11** and small amounts of **12**.

Apparently, the nucleophilic attack of the carbene at $(Bu_3Sn)_2$ is not followed by migration of a Bu_3Sn moiety to C(1), but by homolytic cleavage of the Sn–Sn bond in the intermediate **A** [30] [31] (*Scheme 2*). This generates $Bu_3Sn^{\cdot}$ and a second radical species **B**;

Scheme 2



[3]) An electrophilic attack of the glycosylidene carbene on the Sn–H bond, as proposed for the interaction of dichlorocarbene [27] and an alkylidene carbene [28] with silanes, appears less likely for the nucleophilic to ambiphilic glycosylidene carbenes; there is no evidence for a free radical addition-dissociation-recombination sequence [19].

$Bu_3Sn^•$ reacts with CCl_4 to generate Bu_3SnCl, $^•CCl_3$, and ultimately $CHCl_3$; abstraction of $H^•$ from **B** leads to **9**.

3. *Conformation of the* Sn-*Glycosides.* The structure of the β-D-*Sn*-mannoside **8** was established by X-ray analysis (*Table 2*). Two conformers of **8** co-exist in the solid state at 85 K. The bond lengths correspond to standard values. The conformers differ in the orientation of the Bu moieties and in the conformation of the pyranose ring (slightly flattened $^4C_1$ in *Conformer A*, and $^4C_1$ in *Conformer B*, *Fig.* and *Table 3*).

In solution, the ^3J(H,H) constants $J(2,3)$, $J(3,4)$, and $J(4,5)$ imply a $^4C_1$ conformation for the pyranose ring of the *Sn*-glycosides **3**–**8** (*Table 5* in *Exper. Part*). However, the

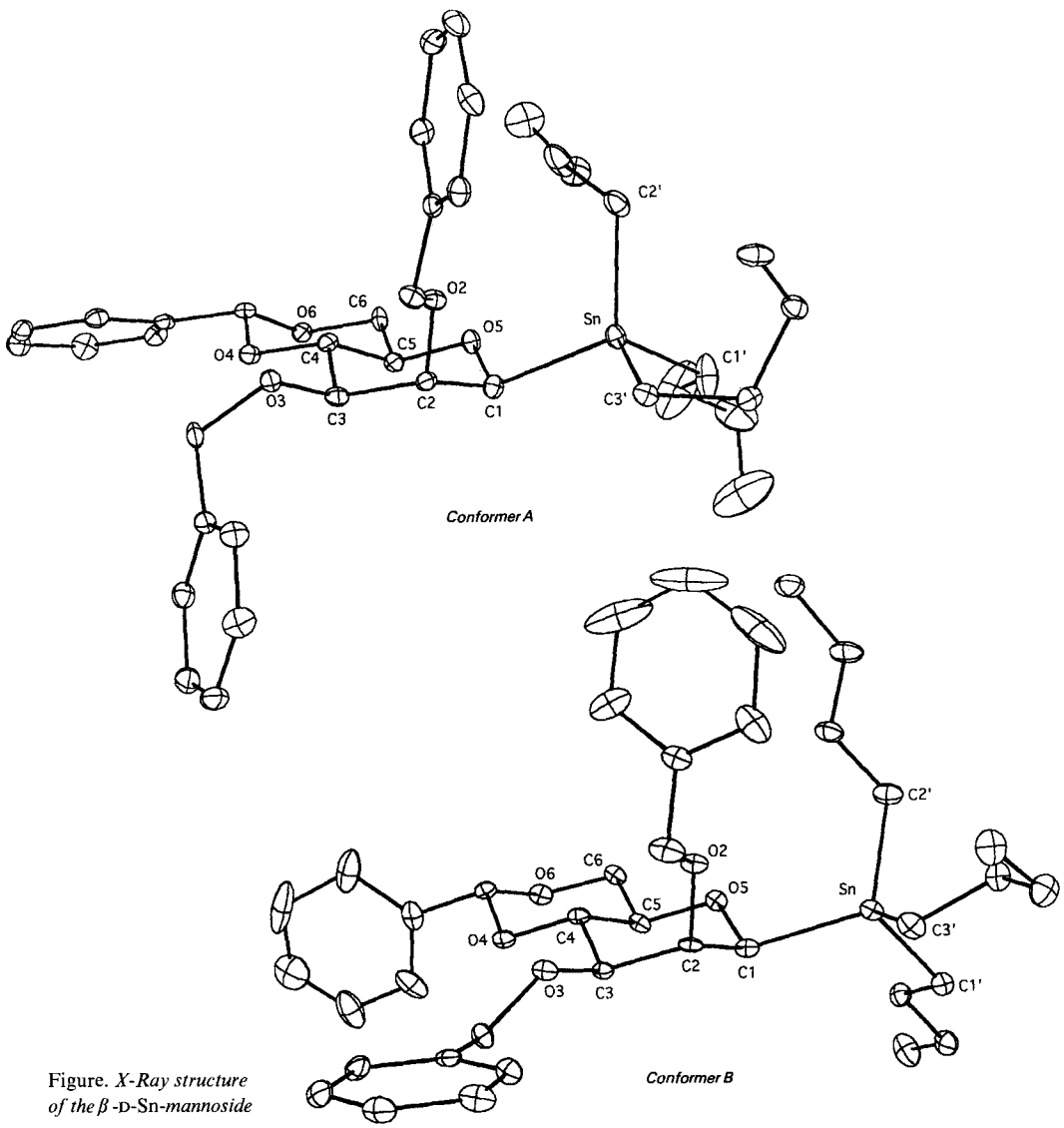


Figure. *X-Ray structure of the* β-D-Sn-*mannoside*

Table 2. *Crystal Data and Experimental Conditions for the X-Ray Analysis of* **8**

Molecular formula	$C_{39}H_{54}O_5Sn$	Calc. density [g/cm^3]	1.30
Formula weight	721.6	Temp. of data collection [K]	85
Crystal size [mm]	*ca.* 0.25 × 0.3 × 0.3	Radiation	MoK_α
Crystal structure	monoclinic	λ [Å] (graphite monochrom.)	0.7107
Space group	P2(1)	Diffractometer	*CAD4*
a [Å]	19.846 (8)	Θ_{max} [°]	26.0
b [Å]	9.058 (7)	No. of reflections measured	7663
c [Å]	20.447 (5)	Observed reflections [$I > 3\sigma(I)$]	6465
β [°]	90.97 (3)	$R(F)$	0.029
V [Å^3]	3675 (3)	$wR(F)$	0.035
Z	4	μ (MoK_α) [mm^{-1}]	0.74

Table 3. *Selected Atom Distances and Bond and Dihedral Angles of the X-Ray Structure of* **8**

Atom distances [Å]		Bond or dihedral angles [°]			
Conformer A					
Sn–C(1)	2.185 (5)	Sn–C(1)–O(5)	106.0 (3)	Sn–C(1)–C(2)–O(2)	43.6
Sn–C(1′)	2.157 (6)	Sn–C(1)–C(2)	109.7 (3)	Sn–C(1)–O(5)–C(5)	175.3
Sn–C(2′)	2.164 (5)	C(1)–Sn–C(1′)	107.9 (2)	C(1)–C(2)–C(3)–C(4)	–50.4
Sn–C(3′)	2.160 (5)	C(1)–Sn–C(2′)	113.4 (2)	C(2)–C(3)–C(4)–C(5)	59.0
C(1)–O(5)	1.445 (6)	C(1)–Sn–C(3′)	105.1 (2)	C(3)–C(4)–C(5)–C(6)	174.2
C(1)–C(2)	1.531 (6)	C(1′)–Sn–C(2′)	110.9 (3)	C(3)–C(4)–C(5)–C(6)	–66.0
C(2)–O(2)	1.441 (5)	C(1′)–Sn–C(3′)	108.8 (2)	C(4)–C(5)–O(5)–C(1)	62.9
		C(2′)–Sn–C(3′)	110.4 (2)	C(5)–O(5)–C(1)–C(2)	–54.9
		Sn–C(1)–C(2)–C(3)	166.6	O(5)–C(1)–C(2)–C(3)	48.3
Atom distances [Å]		Bond or dihedral angles [°]			
Conformer B					
Sn–C(1)	2.161 (5)	Sn–C(1)–O(5)	107.0 (3)	Sn–C(1)–C(2)–O(2)	55.0
Sn–C(1′)	2.166 (5)	Sn–C(1)–C(2)	113.3 (3)	Sn–C(1)–O(5)–C(5)	177.1
Sn–C(2′)	2.157 (6)	C(1)–Sn–C(1′)	105.3 (2)	C(1)–C(2)–C(3)–C(4)	–57.6
Sn–C(3′)	2.157 (6)	C(1)–Sn–C(2′)	111.4 (2)	C(2)–C(3)–C(4)–C(5)	58.0
C(1)–O(5)	1.443 (6)	C(1)–Sn–C(3′)	110.4 (2)	C(3)–C(4)–C(5)–C(6)	179.1
C(1)–C(2)	1.521 (6)	C(1′)–Sn–C(2′)	107.3 (2)	C(3)–C(4)–C(5)–O(5)	–61.0
C(2)–O(2)	1.431 (5)	C(1′)–Sn–C(3′)	110.4 (2)	C(4)–C(5)–O(5)–C(1)	60.8
		C(2′)–Sn–C(3′)	111.8 (2)	C(5)–O(5)–C(1)–C(2)	–58.8
		Sn–C(1)–C(2)–C(3)	178.2	O(5)–C(1)–C(2)–C(3)	57.8

Table 4. *NMR Spectroscopic Data*[a]) *of* α-D- *and* β-D-*Gluco-, and* α-D- *and* β-D-*Mannopyranosylstannanes* **3**–**8**

Compound (Configuration)	^1J		^2J		^3J			Chemical shifts [ppm]		
	C(1),H	Sn,C(1) [b])	Sn,*H*–C(1)	Sn,C(2)	Sn,*H*–C(2)	Sn,C(3) [b])	Sn,C(5) [b])	δ(*H*–C(1)) [c])	δ(C(1)) [c])	δ(Sn) [d])
3 (α-D-*gluco*)	*142.1*	353	24.8	< 5	95.9	10.5	14.7	4.81	76.55	–35.4
5 (α-D-*gluco*)	145.7	462	26.2	< 10	121.2	14.4	14.8	5.41	79.61	–142.0
4 (β-D-*gluco*)	134.2	394	15.0	7.2	30.8	51.6	46.3	3.68	75.24	–33.1
6 (β-D-*gluco*)	142.2	517	19.0	10.0	37.5	68.9	58.3	4.20	77.38	–138.9
7 (α-D-*manno*)	142.2	296	37.2	49.6	–	< 2	10.7	4.88	76.06	–36.1
8 (β-D-*manno*)	135.0	395	23.0	13.3	–	39.1	46.0	3.71	79.08	–41.2

[a]) In C_6D_6 at 300 K (the nuclei involved are ^{1}H, ^{13}C, and ^{119}Sn). [b]) Averaged values of the ^{119}Sn and ^{117}Sn coupling constants. [c]) With TMS as standard. [d]) With $SnMe_4$ as standard.

$J(1,2)$ values differ markedly from the corresponding values of *O*-glycosides. This is either due to the presence of the electropositive Sn-substituent at C(1), or to a distortion of the chair conformation. To clarify this point, we calculated the $J(1,2)$ values as a function of the dihedral angle H–C(1)–C(2)–H according to *Haasnoot et al.* [32] [33], and found 4.1 Hz (60°) for **3** and **5**, 11.0 Hz (180°) for **4** and **6**, 2.9 Hz (60°) for **7**, and 1.3 Hz (60°) for **8**. The values observed for the β-D-glucosides (**4**: 11.1 Hz, **6**: 11.0 Hz) and the β-D-mannoside (**8**: 1.2 Hz) are in agreement with those calculated for the $^4C_1$-conformation. The α-D-glucosides (**3**: 7.0 Hz, **5**: 6.8 Hz) show larger and the α-D-mannoside (**7**: < 0.5 Hz) shows a smaller $J(1,2)$ value than what was calculated, probably due to a slight deviation of SnR_3 from the axial position[4]).

The $^3J(^{119}Sn,^{13}C)$ values display a typical *Karplus*-type dependence on the dihedral angle [35] [36]. The large values of $J(Sn,C(3))$ and $J(Sn,C(5))$ in the β-D-anomers and the corresponding small values in the α-D-anomers confirm the configuration of the α-D- and β-D-*Sn*-glycosides, and their $^4C_1$-conformation (*Table 4*). This interpretation is supported by the large $^3J(Sn,H-C(2))$ values for the α-D-anomers and the small ones for the β-D-anomers.

With this information, we investigated the NMR-spectroscopic evidence for an anomeric effect in *Sn*-glycosides. Typically, one expects $^1J(C,H)$ and $\delta(H-C(1))$ to be larger for the axial anomer [37]. A difference of *ca.* 10 Hz in the one-bond coupling constant ($^1J(C(1),H)$) between pairs of anomers is usually observed [38–40]. Higher $^1J(C(1),H)$ values are found for glycosyl derivatives with more strongly electronegative C(1)-substituents (F, Cl); conversely, lower values are typical for more strongly electropositive substituents (NHPh) [39]. The electronegativity does not affect the difference of the coupling constants of *ca.* 10 Hz between the two anomers. Quantitatively, the same relations are found for the $SnPh_3$ and $SnBu_3$ glycosides, although the difference between the $^1J(C(1),H)$ values for the anomeric $SnPh_3$ glucosides **5** and **6** amounts to only 2.5% of the smaller coupling constant[5]) (5.9% for the $SnBu_3$ glucosides **3** and **4**, and 5.3% for $SnBu_3$ mannosides **7** and **8**; *Table 4*). The relatively small $^1J(C(1),H)$ values are a consequence of the electropositive Sn-substituent at C(1), in agreement with expectations.

The $^1J(Sn,C(1))$ constants follow the same rules, *i.e.*, α-D-glycosides display smaller coupling constants than β-D-glycosides. The differences between the $^1J(Sn,C)$ constants (11.6% for the $SnBu_3$ glucosides **3** and **4**, 11.9% for the $SnPh_3$ glucosides **5** and **6**, and 36.2% for the $SnBu_3$ mannosides **7** and **8**) appear significant, when they are compared to the parameters of analogous cyclohexane derivatives which show very small differences between the $^1J(Sn,C)$ values for equatorial and axial Sn-substituents. In some cases, there are even differences of opposite sign [41]. In contrast to the one-bond coupling constants, the differences between the $\delta(^{119}Sn)$ values for the α-D- and β-D-anomers are rather small and similar to the shift changes found in the cyclohexane analogs, where differences of opposite sign have again been found [41].

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[4]) α-D-Isomers necessarily contain bulky axial substituents in a $^4C_1$ conformation. The tabulated *A* values for trialkyl- and triaryltin substituents range between 1.06 and 1.44 kcal/mol [34].

[5]) For the anomeric pentaacetylated glucopyranosides, the difference is 7.3% of the smaller coupling constant (177 *vs.* 165 Hz [39]).

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Experimental Part

General. Solvents were freshly distilled. Reagents were from *Fluka* or *Aldrich*, and used as received. Powdered 4-Å molecular sieves (*Union Carbide*) were dried *i.v.* for 6 h at 280° and stored under Ar. Anal. TLC: *Merck* precoated silica gel *60 F-254* plates; detection by treatment with a soln. of 5% $(NH_4)_6Mo_7O_{26}\cdot 4\ H_2O$ and 0.1% $Ce(SO_4)_2\cdot 4\ H_2O$. Flash chromatography (FC): silica gel *Merck 60* (40–63 μm). M.p.: uncorrected. Optical rotations: in a 1-dm cell at 25° at 365, 436, 546, 578, and 589 nm; values at 589 nm obtained from a regression curve. IR Spectra: 2–3% $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR Spectra: at 300, 400, and 600 MHz (^{1}H) and at 50, 75, and 100 MHz (^{13}C); chemical shifts δ are given in ppm relative to TMS. Coupling constants J are in Hz; in ambiguous cases, ^{1}H-NMR signals were assigned by selective homonuclear decoupling experiments; ^{13}C-assignments by ^{1}H,^{13}C-HMQC (^{1}H 400 MHz).

^{119}Sn-NMR Spectroscopy. Sn,C-Coupling constants are taken from the ^{1}H-decoupled ^{13}C-NMR (100 MHz). For sensitivity reasons, only the chemical shifts and coupling constants of the most abundant isotope ^{119}Sn were determined. The ^{119}Sn{^{1}H} spectra were obtained from refocused ^{1}H,^{119}Sn-INEPT experiments [42]. The defocusing delay was optimised for an active coupling constant of 90 Hz, whereas the two refocusing delays were set to 1 ms. ^{119}Sn,^{1}H-Coupling constants were determined using the sequence $\pi/2$(H)-1/[4J(Sn,H)]-π(H),π(Sn)-1/[4J(Sn,H)]-3 μs-$\pi/2$(Sn)-Acq.(H) with appropriate phase cycling of the tin pulses [43]. The ^{119}Sn carrier frequency was set on resonance with the resonance frequency of the compounds. The delays were generally optimised for an active coupling of 90 Hz. The spectra obtained only display the ^{119}Sn-satellite signals of the ^{1}H-NMR, the active coupling being in antiphase. Whereas the δ(H) evolution during the pulse sequence is refocused, homonuclear ^{1}H,^{1}H couplings of similar size as the active coupling induce phase distortions in the *multiplets* of the H–C(1) response. Nevertheless, the Sn,H-coupling constants were extracted with no major effort. ^{119}Sn,^{13}C-Coupling constants were obtained from the ^{13}C{^{1}H} spectra. The ^{117}Sn (natural abundance 7.6%) and the ^{119}Sn (8.6%) satellites could only be resolved for one-bond coupling interactions. The tabulated long-range coupling constants, therefore, represent an average of the ^{117}Sn,^{13}C and ^{119}Sn,^{13}C constants. The ^1J constants of ^{117}Sn correspond – within experimental error – to values calculated from $^1J(^{119}Sn,^{13}C)$ constants and the ratio of the γ values ($\gamma(^{117}Sn)/\gamma(^{119}Sn)$ 0.956:1 [44]). ^{13}C,^{1}H-Coupling constants and the assignments of the ^{13}C-resonances were obtained from refocused, phase sensitive ^{1}H,^{13}C-HMQC experiments [45] which yielded spectra displaying the active coupling in the F_2 domain.

Reaction of Bu_3SnH with **1**. Under Ar, solid **1** (110 mg, 0.2 mmol) was added to a mixture of Bu_3SnH (0.27 ml, 1 mmol) and 4-Å molecular sieves in CH_2Cl_2 (1 ml). The mixture was stirred for 16 h at 24° and filtered through *Celite*. The filtrate was concentrated, and filtered through a short column of SiO_2 (7 g). Excess Bu_3SnH was eluted with hexane. Further elution with hexane/CH_2Cl_2 1:9 gave 153 mg (94%) of **3**/**4**/**9** (**3**/**4** 5.1:1). FC (pentane/CH_2Cl_2 3:2) gave 95 mg (58%) of **3**, 17 mg (10%) of **4**, and 13 mg (8%) of **9**.

Similarly, but in THF (1 ml) instead of CH_2Cl_2, 136 mg (84%) of **3**/**4**/**9** (**3**/**4** 3.8:1) were obtained and separated: 88 mg (54%) of **3**, 26 mg (16%) of **4**, and 5 mg (3%) of **9**.

*Tributyl(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)stannane* (**3**). R_f (hexane/CH_2Cl_2 1:9) 0.40. $[\alpha]_D^{25} = +59.0$ (c = 2.74, $CHCl_3$). IR: 3060*w*, 3000*m*, 2960*s*, 2920*s*, 2870*s*, 1495*m*, 1465*m* (sh), 1455*s*, 1420*w*, 1375*m*, 1360*m*, 1320*w*, 1290*w*, 1185*w*, 1145*m*, 1090*s* (br.), 1070*s* (sh), 1030*s*, 1000*m* (sh), 960*w* (sh), 910*w*, 865*w*, 700*s*, 660*w*. ^{1}H-NMR (400 MHz, C_6D_6; see also *Table 5*): 7.38–7.05 (*m*, 20 arom. H); 5.09 (*d*, J = 11.3, 1 H, PhCH_2); 5.02 (*d*, J = 11.3, 1 H, PhCH_2); 4.94 (*d*, J = 11.3, 1 H, PhCH_2); 4.81 (*d*, J = 7.0, J(Sn,H) = 24.8, H–C(1)); 4.66 (*d*, J = 11.3, 1 H, PhCH_2); 4.59 (*d*, J = 11.7, 1 H, PhCH_2); 4.49 (*d*, J = 11.0, 1 H, PhCH_2); 4.46 (*d*, J = 11.3, 1 H, PhCH_2); 4.40 (*d*, J = 12.2, 1 H, PhCH_2); 4.04 (*dd*, J = 7.0, 8.6, J(Sn,H) = 95.9, H–C(2)); 3.83 (*t*, J = 8.8, H–C(3)); 3.79 (*d*, J = 3.5, 2 H–C(6)); 3.76 (*t*, $J \approx$ 8.9, H–C(4)); 3.48 (*td*, J = 3.3, 9.5, H–C(5)); 1.69–1.60 (*m*, J(Sn,H) = 42.4, 6 H–C(2′)); 1.43–1.34 (*m*, 6 H–C(3′)); 1.13–1.07 (*m*, J(Sn,H) = 49.9, 6 H–C(1′)); 0.95–0.91 (*m*, 9 H–C(4′)). ^{13}C-NMR (100 MHz, C_6D_6): 139.64 (*s*); 139.40 (*s*); 139.18 (*s*); 138.92 (*s*); 128.61–127.66 (*m*); 86.86 (*d*, J(Sn,C) = 10.5, C(3)); 82.16 (*d*, J(Sn,C) < 5, C(2)); 80.59 (*d*, J(Sn,C) = 14.7, C(5)); 79.02 (*d*, C(4)); 76.55 (*d*, J(Sn,C) = 353, C(1)); 75.56 (*t*, PhCH_2); 75.19 (*t*, PhCH_2); 73.86 (*t*, PhCH_2); 73.77 (*t*, PhCH_2); 70.24 (*t*, C(6)); 29.71 (3*t*, J(Sn,C) = 19.8, C(2′)); 28.06 (3*t*, J(Sn,C) = 57.7, C(3′)); 14.07 (3*q*, C(4′)); 11.06 (3*t*, J(Sn,C) = 303, C(1′)). ^{119}Sn-NMR: −35.35. FAB-MS: 757 (4.2, [M − Bu]$^+$), 756 (2.4), 755 (3.7), 341 (30, [BnOSnBu$_2$]$^+$), 340 (13),

Table 5. *Selected Coupling Constants* [Hz] *of the Stannanes* **3**–**8**

	3	**4**	**5**	**6**	**7**	**8**
$J(1,2)$	7.0	11.1	6.8	11.0	< 0.5	1.2
$J(2,3)$	8.6	8.4	8.8	8.2	3.2	3.1
$J(3,4)$	8.8	9.3	8.6	9.1	8.6	9.8
$J(4,5)$	9.5	9.6	–	9.5	9.5	9.0
$J(5,6_A)$	3.3	2.0	–	3.0	4.9	4.9
$J(5,6_B)$	3.3	3.8	–	3.0	10.0	10.3
$J(6_A,6_B)$	–	9.6	–	–	10.4	10.3

339 (23), 338 (10), 337 (15), 291 (31, $[SnBu_3]^+$), 290 (13), 289 (25), 288 (11), 287 (16), 235 (26, $[SnBu_2 + 1]^+$), 234 (11), 233 (22), 232 (10), 231 (16), 181 (41), 179 (52, $[SnBu + 2]^+$), 178 (22), 177 (49), 176 (22), 175 (36), 91 (100). Anal. calc. for $C_{46}H_{62}O_5Sn$ (813.68): C 67.90, H 7.68; found: C 67.71, H 7.76.

*Tributyl(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)stannane* (**4**). R_f (hexane/CH_2Cl_2 9:1) 0.58. $[\alpha]_D^{25} = -2.8$ (c = 1.95, $CHCl_3$). IR: 3060*w*, 3000*m*, 2960*s*, 2920*s*, 2870*s*, 1495*m*, 1465*m* (sh), 1455*m*, 1375*m*, 1360*m*, 1345*m* (sh), 1315*w*, 1280*w* (br.), 1170*m* (sh), 1120*s*, 1095*s*, 1065*s* (br.), 1030*m*, 1000*m*, 960*w*, 910*s*, 865*w*, 835*w* (br.), 700*s*, 670*m*, 650*m*. ^{1}H-NMR (400 MHz, C_6D_6): 7.37–7.05 (*m*, 20 arom. H); 5.20 (*d*, J = 11.5, 1 H, PhCH_2); 4.97 (*d*, J = 11.2, 1 H, PhCH_2); 4.89 (*d*, J = 11.3, 1 H, PhCH_2); 4.81 (*d*, J = 11.2, 1 H, PhCH_2); 4.68 (*d*, J = 11.5, 2 H, PhCH_2); 4.53 (*d*, J = 12.3, 1 H, PhCH_2); 4.45 (*d*, J = 12.3, 1 H, PhCH_2); 3.88 (*dd*, J = 8.4, 11.1, J(Sn,H) = 30.8, H–C(2)); 3.82 (*t*, $J \approx 9.3$, H–C(4)); 3.74–3.68 (*m*, H–C(3), 2 H–C(6)); 3.68 (*d*, J = 11.1, J(Sn,H) = 15.0, H–C(1)); 3.34 (*ddd*, J = 2.0, 3.8, 9.6, H–C(5)); 1.71–1.58 (*m*, J(Sn,H) = 47.6, 6 H–C(2′)); 1.42–1.33 (*m*, 6 H–C(3′)); 1.17–1.01 (*m*, J(Sn,H) = 51.7, 6 H–C(1′)); 0.94–0.91 (*m*, 9 H–C(4′)). ^{13}C-NMR (100 MHz, C_6D_6): 139.45 (*s*); 139.35 (2*s*); 139.29 (*s*); 128.76–127.41 (*m*); 89.93 (*d*, J(Sn,C) = 51.6, C(3)); 83.80 (*d*, J(Sn,C) = 46.3, C(5)); 81.98 (*d*, J(Sn,C) = 7.2, C(2)); 79.59 (*d*, C(4)); 75.33 (*t*, PhCH_2); 75.24 (*d*, J(Sn,C) = 394, C(1)); 75.02 (*t*, PhCH_2); 74.39 (*t*, PhCH_2); 73.61 (*t*, PhCH_2); 69.85 (*t*, C(6)); 29.59 (3*t*, J(Sn,C) = 20.2, C(2′)); 27.84 (3*t*, J(Sn,C) = 55.2, C(3′)); 13.95 (3*q*, C(4′)); 9.51 (3*t*, J(Sn,C) = 323, C(1′)). ^{119}Sn-NMR: –33.10. FAB-MS: 758 (14), 757 (30, $[M - Bu]^+$), 756 (18), 755 (24), 754 (13), 753 (13), 341 (15, $[BnOSnBu_2]^+$), 340 (7), 339 (12), 338 (5), 337 (8), 291 (31, $[SnBu_3]^+$), 290 (14), 289 (26), 288 (11), 287 (17), 235 (22, $[SnBu_2 + 1]^+$), 234 (10), 233 (20), 232 (9), 231 (15), 181 (38), 179 (44, $[SnBu + 2]^+$), 178 (19), 177 (42), 176 (19), 175 (30), 91 (100).

*1,5-Anhydro-2,3,4,6-tetra-*O*-benzyl-1-(tributylstannyl)-*D*-arabino-hex-1-enitol* (**9**). R_f (hexane/CH_2Cl_2 1:9) 0.63. $[\alpha]_D^{25} = -8.2$ (c = 2.26, $CHCl_3$). IR: 3090*w*, 3070*w*, 3010*m*, 2960*s*, 2930*s*, 2880*s*, 2860*s* (sh), 1495*w*, 1465*m* (sh), 1455*s*, 1380*m*, 1365*m*, 1310*w*, 1285*w*, 1260*m*, 1185*m* (sh), 1120*s* (sh), 1100*s*, 1070*s* (sh), 1030*s*, 965*m*, 910*m*, 870*w*, 695*s*, 660*m* (sh). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.34–7.25 (*m*, 20 arom. H); 4.87 (*d*, J = 11.4, 1 H, PhCH_2); 4.80 (*d*, J = 11.6, 1 H, PhCH_2); 4.71 (*d*, J = 11.6, 1 H, PhCH_2); 4.60 (*d*, $J \approx 5$, H–C(3)); 4.59 (*s*, 2 H, PhCH_2); 4.57 (*d*, $J \approx 13.1$, 1 H, PhCH_2); 4.55 (*d*, J = 11.3, 1 H, PhCH_2); 4.47 (*d*, J = 11.1, 1 H, PhCH_2); 4.08 (*dd*, J = 5.2, 7.6, H–C(4)); 3.99 (*td*, $J \approx 4.1$, 7.8, H–C(5)); 3.83 (*dd*, J = 4.7, 10.8, H_A–C(6)); 3.79 (*dd*, J = 3.7, 10.8, H_B–C(6)); 1.56–1.41 (*m*, 6 H–C(2′)); 1.31–1.22 (*m*, 6 H–C(3′)); 1.05–0.82 (*m*, 6 H–C(1′), 9 H–C(4′)). ^{13}C-NMR (50 MHz, C_6D_6): 154.52 (*s*); 143.82 (*s*); 139.23 (*s*); 139.13 (2*s*); 138.67 (*s*); 129.30–125.66 (*m*); 77.31 (*d*); 74.89 (*d*); 73.62 (*t*); 73.58 (*t*); 73.31 (*d*); 72.55 (*t*); 69.33 (*t*); 69.16 (*t*); 29.56 (3*t*); 27.69 (3*t*); 13.98 (3*q*); 10.57 (3*t*). ^{119}Sn-NMR: –57.69.

Reaction of Ph_3SnH with **1**. As described for **3**/**4**/**9**, with Ph_3SnH (351 mg, 0.1 mmol) instead of Bu_3SnH (16 h at 27°). Evaporation of the CH_2Cl_2 or THF and FC (pentane/CH_2Cl_2 1:4) gave 110 mg (63%) of **5** and 25 mg (14%) of **6**, or 93 mg (53%) of **5** and 39 mg (22%) of **6**, respectively.

*Triphenyl(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)stannane* (**5**). R_f (hexane/CH_2Cl_2 1:9) 0.38. $[\alpha]_D^{25} = +60.7$ (c = 2.20, $CHCl_3$). IR: 3060*m*, 3040*m*, 3000*m*, 2920*m*, 2870*m*, 1498*m*, 1480*w*, 1455*m*, 1430*m*, 1360*m*, 1320*w*, 1290*w*, 1260*w*, 1185*w*, 1145*m*, 1090*s*, 1075*s*, 1030*s*, 995*m*, 910*w*, 865*w*, 700*s*, 655*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.84–7.70 (*m*, J(Sn,H) ≈ 46, 15 arom. H); 7.30–6.95 (*m*, 20 arom. H); 5.41 (*d*, J = 6.8, J(Sn,H) = 26.2, H–C(1)); 4.78 (*d*, J = 11.5, 1 H, PhCH_2); 4.70 (*d*, J = 11.4, 1 H, PhCH_2); 4.62 (*d*, J = 11.4, 1 H, PhCH_2); 4.55 (*d*, J = 11.5, 1 H, PhCH_2); 4.50 (*d*, J = 11.3, 1 H, PhCH_2); 4.41 (*d*, J = 12.1, 1 H, PhCH_2); 4.37 (*d*, J = 11.3, 1 H, PhCH_2); 4.31 (*d*, J = 12.0, 1 H, PhCH_2); 4.06 (*dd*, J = 6.8, 8.8, J(Sn,H) = 121.2, H–C(2)); 3.92 (*t*, J = 8.7, H–C(3)); 3.82–3.75 (*m*, H–C(4), H–C(5)); 3.69 (*s*, 2 H–C(6)). ^{13}C-NMR (100 MHz, C_6D_6): 139.70 (3*s*, J(Sn,C) = 471); 139.01 (*s*); 138.72 (*s*); 138.44 (*s*); 137.74 (*s*); 137.40 (6*d*, J(Sn,C) = 36); 128.80–127.01 (*m*); 85.29 (*d*, J(Sn,C) = 14.4, C(3)); 80.88 (*d*, J(Sn,C) < 10, C(2)); 80.31 (*d*, J(Sn,C) = 14.8, C(5)); 79.61 (*d*, J(Sn,C) = 462, C(1)); 77.90 (*d*, C(4)); 74.80

(*t*, PhCH$_2$); 74.05 (*t*, PhCH$_2$); 73.71 (*t*, PhCH$_2$); 73.07 (*t*, PhCH$_2$); 69.12 (*t*, C(6)). ^{119}Sn-NMR: −142.00. FAB-MS: 798 (1.7), 797 (3.7, $[M - Ph]^+$), 796 (2.2), 795 (3.1), 794 (1.5), 793 (1.6), 351 (60, $[SnPh_3]^+$), 350 (31), 349 (50), 348 (25), 347 (33), 275 (23, $[SnPh_2 + 1]^+$), 274 (11), 273 (20), 272 (9), 271 (13), 197 (19, $[SnPh]^+$), 196 (7), 195 (15), 194 (6), 193 (9), 91 (100). Anal. calc. for $C_{52}H_{50}O_5Sn$ (873.67): C 71.49, H 5.77; found: C 71.20, H 5.74.

*Triphenyl(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)stannane* (**6**). R_f (hexane/CH_2Cl_2 1:9) 0.50. $[\alpha]_D^{25} = +1.3$ ($c = 2.38$, $CHCl_3$). IR: 3060*m*, 3000*m*, 2900*m*, 2860*m*, 1495*m*, 1480*w*, 1455*m*, 1430*m*, 1395*w*, 1360*m*, 1315*w*, 1265*w*, 1170*m* (sh), 1120*s*, 1090*s*, 1075*s*, 1060*s* (sh), 1030*m*, 995*m*, 910*w*, 700*s*, 660*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.82–7.68 (*m*, J(Sn,H) ≈ 47, 15 arom. H); 7.31–6.99 (*m*, 20 arom. H); 4.98 (*d*, J = 11.1, 1 H, PhCH_2); 4.93 (*d*, J = 11.3, 1 H, PhCH_2); 4.83 (*d*, J = 11.3, 1 H, PhCH_2); 4.78 (*d*, J = 11.3, 1 H, PhCH_2); 4.62 (*d*, J = 11.3, 1 H, PhCH_2); 4.47 (*d*, J = 12.3, 1 H, PhCH_2); 4.40 (*d*, J = 12.3, 1 H, PhCH_2); 4.20 (*d*, J = 11.0, J(Sn,H) = 19.0, H–C(1)); 4.18 (*d*, J = 11.2, 1 H, PhCH_2); 4.06 (*dd*, J = 8.2, 11.0, J(Sn,H) = 37.5, H–C(2)); 3.78 (*t*, J ≈ 9.3, H–C(4)); 3.73–3.69 (*m*, H–C(3), 2 H–C(6)); 3.40 (*td*, J = 3.0, 9.5, H–C(5)). ^{13}C-NMR (100 MHz, C_6D_6): 138.92 (3*s*, J(Sn,C) = 507, C(1′)); 138.84 (*s*); 138.59 (*s*); 138.31 (*s*); 137.72 (6*d*, J(Sn,C) = 35.0, C(2′)); 137.54 (*s*); 128.99–127.07 (*m*); 89.54 (*d*, J(Sn,C) = 68.9, C(3)); 83.49 (*d*, J(Sn,C) = 58.3, C(5)); 80.70 (*d*, J(Sn,C) = 10.0, C(2)); 79.03 (*d*, C(4)); 77.38 (*d*, J(Sn,C) = 517, C(1)); 75.06 (*t*, PhCH_2); 74.83 (*t*, PhCH_2); 73.90 (*t*, PhCH_2); 73.42 (*t*, PhCH_2); 69.40 (*t*, C(6)). ^{119}Sn-NMR: −138.94. FAB-MS: 798 (7), 797 (14, $[M - Ph]^+$), 796 (7), 795 (11), 794 (6), 793 (6), 351 (56, $[SnPh_3]^+$), 350 (31), 349 (47), 348 (25), 347 (31), 275 (12, $[SnPh_2 + 1]^+$), 274 (6), 273 (12), 272 (6), 271 (8), 197 (22, $[SnPh]^+$), 196 (8), 195 (17), 194 (7), 193 (12), 91 (100). Anal. calc. for $C_{52}H_{50}O_5Sn$ (873.67): C 71.49, H 5.77; found: C 71.18, H 5.93.

Reaction of Bu_3SnH with **2**. Under Ar, a mixture of **2** (46 mg, 0.1 mmol) and 4-Å molecular sieves in CH_2Cl_2 (1.5 ml) was treated at 0° with Bu_3SnH (0.13 ml, 0.5 mmol), allowed to reach 24°, and stirred for 16 h. The mixture was filtered through *Celite* and concentrated. Excess Bu_3SnH was eluted with pentane from a short column of SiO_2 (5 g). Further elution with pentane/AcOEt 4:1 gave 54 mg (74%) of **7**/**8**/**10** (**7**/**8** 1:1.3). FC (30 g of SiO_2, 150 ml of pentane/CH_2Cl_2 1:1, 100 ml of hexane/AcOEt 6:1) gave 18 mg (25%) of **7**, 20 mg (28%) of **8**, and 5 mg (7%) of **10**.

Similarly, but in THF (1.5 ml) instead of CH_2Cl_2, 52 mg (72%) of **7**/**8**/**10** (**7**/**8** 1:4.2) were obtained and separated: 9 mg (13%) of **7**, and 31 mg (43%) of **8**.

*Tributyl(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-*D*-mannopyranosyl)stannane* (**7**). R_f (hexane/CH_2Cl_2 1:9) 0.20. $[\alpha]_D^{25} = +54.2$ ($c = 0.95$, $CHCl_3$). IR: 3067*w*, 3043*w*, 2959*m*, 2930*s*, 2872*m*, 1496*w*, 1454*m*, 1412*w*, 1378*m*, 1312*w*, 1290*w*, 1271*w*, 1139*m*, 1096*s*, 1028*m*, 962*w*, 913*w*, 864*w*, 645*w*, 594*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.66–7.08 (*m*, 15 arom. H); 5.44 (*s*, PhCH); 4.93 (*d*, J = 12.7, 1 H, PhCH_2); 4.88 (*s*, J(Sn,H) = 37.2, H–C(1)); 4.83 (*d*, J ≈ 12.4, 2 H, PhCH_2); 4.76 (*d*, J = 12.3, 1 H, PhCH_2); 4.61 (*t*, J ≈ 9.0, H–C(4)); 4.29 (*dd*, J = 4.9, 10.4, H_{eq}–C(6)); 3.96–3.92 (*m*, H–C(2), H–C(3)); 3.75 (*t*, J ≈ 10.2, H_{ax}–C(6)); 3.42 (*dt*, J ≈ 4.8, 9.5, H–C(5)); 1.51–1.38 (*m*, 6 H–C(2′)); 1.32–1.22 (*m*, 6 H–C(3′)); 0.91–0.80 (*m*, 6 H–C(1′), 9 H–C(4′)). ^{13}C-NMR (100 MHz, C_6D_6): 139.50 (*s*); 139.41 (*s*); 138.82 (*s*); 128.84–127.71 (*m*); 101.91 (*d*, PhCH); 80.41 (*d*, C(4)); 80.39 (*d*, J(Sn,C) = 49.6, C(2)); 78.42 (*d*, J(Sn,C) < 2, C(3)); 76.06 (*d*, J(Sn,C) = 296, C(1)); 73.39 (*d*, J(Sn,C) = 10.7, C(5)); 72.63 (*t*, PhCH_2); 72.11 (*t*, PhCH_2); 69.05 (*t*, C(6)); 29.42 (3*t*, J(Sn,C) = 20.6, C(2′)); 27.70 (3*t*, J(Sn,C) = 55.0, C(3′)); 13.90 (3*q*, C(4′)); 10.20 (3*t*, J(Sn,C) = 303, C(1′)). ^{119}Sn-NMR: −36.07. FAB-MS: 665 (2.0, $[M - Bu]^+$), 664 (1.1), 663 (1.6), 662 (1.2), 661 (1.1), 341 (5.2, $[BnOSnBu_2]^+$), 340 (2.1), 339 (4.3), 338 (1.8), 337 (2.6), 291 (27, $[SnBu_3]^+$), 290 (10), 289 (21), 288 (8), 287 (12), 235 (17, $[SnBu_2 + 1]^+$), 234 (6), 233 (14), 232 (6), 231 (10), 181 (10), 179 (40, $[SnBu + 2]^+$), 178 (13), 177 (37), 176 (14), 175 (25), 91 (100). Anal. calc. for $C_{39}H_{54}O_5Sn$ (721.56): C 64.92, H 7.54; found: C 65.18, H 7.33.

*Tributyl(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-*D*-mannopyranosyl)stannane* (**8**). R_f (hexane/CH_2Cl_2 1:9) 0.58. $[\alpha]_D^{25} = -58.7$ ($c = 1.12$, $CHCl_3$). IR: 3090*w*, 3067*w*, 2957*m*, 2926*m*, 2871*m*, 1497*w*, 1454*m*, 1377*m*, 1342*w*, 1292*w*, 1269*w*, 1104*s*, 1086*s*, 1027*m*, 962*w*, 914*w*, 885*w*, 640*w*, 593*w*. ^{1}H-NMR (600 MHz, C_6D_6): 7.50–7.07 (*m*, 15 arom. H); 5.39 (*s*, PhCH); 5.38 (*d*, J ≈ 11.1, 1 H, PhCH_2); 4.87 (*d*, J = 12.3, 1 H, PhCH_2); 4.64 (*d*, J = 12.3, 1 H, PhCH_2); 4.50 (*d*, J = 10.8, 1 H, PhCH_2); 4.26 (*t*, J ≈ 9.4, H–C(4)); 4.11 (*dd*, J = 4.9, 10.3, H_{eq}–C(6)); 3.71 (*d*, J = 1.2, J(Sn,H) = 23.0, H–C(1)); 3.70 (*dd*, J = 1.3, 3.1, H–C(2)); 3.67 (*dd*, J = 3.1, 9.8, H–C(3)); 3.55 (*t*, J ≈ 10.3, H_{ax}–C(6)); 3.20 (*dt*, J ≈ 4.9, 9.6, H–C(5)); 1.51–1.43 (*m*, J(Sn,H) = 48.6, 6 H–C(2′)); 1.30–1.23 (*m*, 6 H–C(3′)); 0.94–0.81 (*m*, J(Sn,H) = 55.2, H–C(1′), H–C(4′)). ^{13}C-NMR (100 MHz, C_6D_6): 139.62 (2*s*); 138.94 (*s*); 129.22–127.69 (*m*); 101.67 (*d*, PhCH); 82.33 (*d*, J(Sn,C) = 39.1, C(3)); 81.00 (*d*, J(Sn,C) = 13.3, C(2)); 80.68 (*d*, C(4)); 79.08 (*d*, J(Sn,C) ≈ 395, C(1)); 76.07 (*d*, J(Sn,C) = 46.0, C(5)); 75.12 (*t*, PhCH_2); 73.83 (*t*, PhCH_2); 68.91 (*t*, C(6)); 29.41 (3*t*, J(Sn,C) = 20.1, C(2′)); 27.72 (3*t*, J(Sn,C) = 55.5, C(3′)); 13.91 (3*q*, C(4′)); 9.89 (3*t*, J(Sn,C) = 314, C(1′)). ^{119}Sn-NMR: −41.2. FAB-MS: 341 (24, $[BnOSnBu_2]^+$), 340 (9), 339 (19), 338 (7), 337 (11), 291 (23, $[SnBu_3]^+$), 290 (10), 289 (18), 288 (7), 287 (11), 235 (32, $[SnBu_2 + 1]^+$), 234 (11), 233 (27), 232 (10), 231 (18), 197 (47), 179 (70, $[SnBu + 2]^+$), 178 (25), 177 (66), 176 (26), 175 (46), 91 (100). Anal. calc. for $C_{39}H_{54}O_5Sn$ (721.56): C 64.92, H 7.54; found: C 65.17, H 7.43.

*1,5-Anhydro-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-(tributylstannyl)-*D*-arabino-hex-1-enitol* (**10**). R_f (hexane/CH_2Cl_2 1:9) 0.67. $[\alpha]_D^{25} \approx 0$ (c = 1.31, $CHCl_3$). IR: 3067*w*, 3042*w*, 2958*m*, 2924*m*, 2872*m*, 1497*w*, 1455*m*, 1376*m*, 1341*w*, 1278*w*, 1262*w*, 1154*m*, 1093*s*, 1056*m*, 1028*m*, 913*w*, 875*w*, 650*w*, 600*w*, 545*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.71–7.09 (*m*, 15 arom. H); 5.34 (*s*, PhC*H*); 5.02 (*d*, J = 12.0, 1 H, PhCH_2); 4.93 (*d*, J = 11.2, 1 H, PhCH_2); 4.82 (*d*, J = 7.3, H–C(3)); 4.79 (*d*, $J \approx 11.9$, 1 H, PhCH_2); 4.46 (*d*, J = 11.2, 1 H, PhCH_2); 4.33 (*dd*, J = 5.1, 10.3, H_{eq}–C(6)); 4.19 (*dd*, J = 7.3, 10.2, H–C(4)); 3.85 (*dt*, $J \approx 5.1$, 10.2, H–C(5)); 3.67 (*t*, $J \approx 10.3$, H_{ax}–C(6)); 1.82–1.57 (*m*, 6 H–C(2′)); 1.50–1.37 (*m*, 6 H–C(3′)); 1.30–1.07 (*m*, J(Sn,H) ≈ 52.8, 6 H–C(1′)); 1.02–0.97 (*m*, 9 H–C(4′)). ^{13}C-NMR (75 MHz, $CDCl_3$): 154.90 (*s*); 143.18 (*s*); 138.29 (*s*); 137.35 (*s*); 137.12 (*s*); 128.72–125.83 (*m*); 100.72 (*d*); 79.32 (*d*); 72.88 (*d*, J(Sn,C) ≈ 19.8); 72.59 (*t*); 70.53 (*t*); 69.10 (*d*, J(Sn,C) = 19.2); 68.48 (*t*); 28.73 (3*t*, J(Sn,C) = 20.3); 26.89 (3*t*, J(Sn,C) = 59.3); 13.43 (4*q*); 9.82 (3*t*, J(Sn,C) ≈ 353.6). FAB-MS: 663 (21, $[M - Bu]^+$), 662 (11), 661 (16), 660 (7), 659 (8), 291 (9, $[SnBu_3]^+$), 290 (4), 289 (7), 288 (3), 287 (4), 235 (12, $[SnBu_2 + 1]^+$), 234 (5), 233 (10), 232 (4), 231 (8), 181 (12), 179 (37, $[SnBu + 2]^+$), 178 (12), 177 (36), 176 (13), 175 (24), 91 (100). Anal. calc. for $C_{39}H_{52}O_5Sn$ (719.55): C 65.10, H 7.28; found: C 65.10, H 7.42.

Reaction of $(Bu_3Sn)_2$ *with* **1**. Under Ar, solid **1** (40 mg, 0.07 mmol) was added to a mixture of $(Bu_3Sn)_2$ (210 mg, 0.36 mmol) and 4-Å molecular sieves in CH_2Cl_2 (0.35 ml). The mixture was stirred for 6 h at 24° and filtered through *Celite*. The filtrate was concentrated, and filtered through a short column of SiO_2 (7 g). Excess $(Bu_3Sn)_2$ was eluted with hexane. Further elution with hexane/CH_2Cl_2 1:9 gave 10 mg (17%) of **9** and 24 mg of a mixture of **11**/**12** [26] *ca.* 15:1.

Similarly, in CCl_4 (0.35 ml) instead of CH_2Cl_2, 36% of **9** were obtained.

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