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Palladium-catalyzed stereoselective hydrostannation of substituted propargyl alcohols with trineophyltin hydride

María B. Faraoni [a], Darío C. Gerbino [a,b], Julio C. Podestá [a,b,*]

[a] *Instituto de Investigaciones en Química Orgánica, Departamento de Química, Universidad Nacional del Sur, Avenida Alem 1253, 8000 Bahía Blanca, Argentina*
[b] *CONICET, Rivadavia 1917, 1033 Buenos Aires, Argentina*

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Abstract

This paper reports results obtained in a study on the palladium-catalyzed hydrostannation of substituted propargyl alcohols with the bulky trineophyltin hydride (**1**). The reaction of **1** with 10 propargyl alcohols containing one up to three substituents, was carried out in THF at room temperature leading to the corresponding allylstannanes following in all cases a *syn* addition stereochemistry. These additions took place in good to excellent yields and, mostly, with a high degree of stereoselectivity. The results obtained suggest that the observed α/β regioselectivity might be ascribed to the steric bulk of the *proximal* substituents rather than to electronic effects. Full ^{1}H-, ^{13}C-, and ^{119}Sn NMR characteristics are included.

Keywords: Hydrostannation; Palladium catalyzed; Stereoselectivity; Propargyl alcohols; Stannylated allyl alcohols

1. Introduction

Vinylstannanes are very useful intermediates in organic synthesis and due to their great versatility as building blocks for synthesis, considerable effort has been devoted to their regio- and stereocontrolled synthesis. They can be condensed with a large array of electrophiles including carbonyl compounds, enones, acyl chlorides, vinyl, aryl, allyl, and benzyl halides or triflates [1]. The vinylstannanes are also valuable partners in Stille reactions, i.e., the palladium-catalyzed cross coupling reaction between organic halides and organostannanes, one of the more important methods used to make carbon–carbon bonds [2]. In total synthesis of natural products, the use of vinylstannanes enabled the stereoselective building of some unsaturated fragments [3].

The addition of organotin hydrides to alkynes is still the more simple, direct, and economical method for the preparation of vinylstannanes. Thus, palladium-catalyzed hydrostannation of propargylic alcohol derivatives with tri-*n*-butyltin hydride takes place with *syn* stereoselectivity leading to mixtures of the two possible stannylated allylic alcohols regioisomers in good to excellent yields [4]. It was observed that steric effects upon substitution at the propargylic position could change the regioselectivity of these reactions [5]. It should be noted that although the reported analytical yields of these hydrostannations were always nearly quantitative, we have found that the yields of the mixtures of adducts were substantially lower due to loss of material during chromatographic purification, and in most cases it was not possible to isolate a regioisomer in pure form.

In previous studies [6], we reported that hydrostannation of substituted alkynes with trineophyltin hydride (**1**) leads stereoselectively and in high yields to vinylstannanes which showed enhanced stability in comparison with that of the vinylstannanes resulting from the additions of the

* Corresponding author. Address: Instituto de Investigaciones en Química Orgánica, Departamento de Química, Universidad Nacional del Sur, Avenida Alem 1253, 8000 Bahía Blanca, Argentina. Tel.: +54 291 4595101; fax: +54 291 4595187.
E-mail address: jpodesta@uns.edu.ar (J.C. Podestá).

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more common triorganotin hydrides (Me, Bu, and Ph) [4,5]. Now, we considered it of interest to carry out a study on the palladium-catalyzed addition of trineophyltin hydride (**1**) to substituted propargyl alcohols in order to determine the effect of the bulk of the neophyl ligands attached to the tin atom combined with that of various substituents in the organic substrate on the regioselectivity of these reactions as well as on the stability of the new adducts.

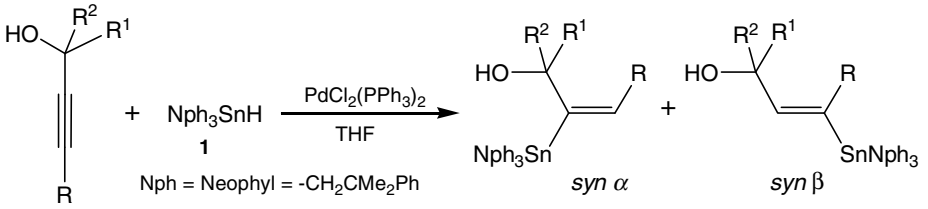
2. Results and discussion

The addition of trineophyltin hydride (**1**) to various mono-, di-, and trisubstituted propargyl alcohols, at r.t. in THF containing 2% of bis(triphenylphosphine) palladium(II) chloride led, after 30–120 min of reaction, in all cases to mixtures of adducts as shown in Scheme 1. The yields were in the range 60–90% and in all cases the regioisomers could be isolated in pure form.

The results obtained are summarized in Table 1.

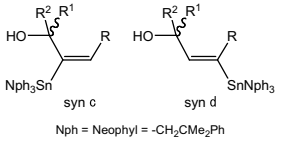
This Table shows that all the regioisomers formed were those resulting from a *syn* attack (Scheme 1, *syn* α and *syn* β). Full ^{1}H and ^{13}C NMR characteristics of compounds **2**–**21** are summarized in Tables 2 and 3.

The assignment of the stereochemistry of the new stannyl derivatives **2**–**21** was carried out making use of their NMR characteristics, especially $^{n}J(^{1}H,^{119}Sn)$ and $^{n}J(^{13}C,^{119}Sn)$ coupling constants. Thus, the ^{1}H NMR spectra of the adducts resulting from the α-*syn* attack, compounds **2**, **4**, **6**, **8**, **10**, **12**, **14**, **16**, **18**, and **20** (Table 2), show in all cases signals between 4.90 and 5.65 ppm corresponding to the proton attached to C(3) (H_A). The values of the $^{3}J(Sn,H)$ coupling constants range from 85 to 64 Hz indicating that this proton is *cis* with respect to the trineophyltin moiety attached to C(2). In the case of compounds **2**, **4**, **6**, **8**, and **10**, the ^{1}H NMR spectra also show that attached to C(3) there is another proton (H_B) with $^{3}J(Sn,H)$ coupling constants values of around 140 Hz, indicating a *trans* relationship between this proton and the triorganotin group attached to C(2). Similarly, the ^{1}H NMR spectra of the adducts resulting from the β-*syn* attack, compounds **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17**, **19**, and **21** (Table 3), also show in all cases signals between 5.10 and 6.20 ppm corresponding to the proton attached to C(2) (H_A) with $^{3}J(Sn,H)$ coupling constants values between 66 and 77 Hz indicating that this proton is *cis* with respect to the organotin substituent attached to C(3). Also, in the case of the adducts resulting from the hydrostannation of the terminal



Scheme 1. Palladium catalyzed hydrostannation of substituted propargyl alcohols.

Table 1
Hydrostannation of substituted propargyl alcohols with trineophyltin hydride (**1**)[a]



Entry number	Compound number	R	R^1	R^2	*syn* Adducts		Yield[b] (%)	Ratio β/α	^{119}Sn[c] (ppm)
					α (%)[b]	β (%)[b]			
1	**2** and **3**	H	H	Me	28 (**2**)	55 (**3**)	83	1.96	**2**: −84.2, **3**: −82.4
2	**4** and **5**	H	H	Ph	23 (**4**)	35 (**5**)	58	1.52	**4**: −79.1, **5**: −82.0
3	**6** and **7**	H	Me	Me	7 (**6**)	80 (**7**)	87	11.4	**6**: −82.8, **7**: −79.7
4	**8** and **9**	H	Me	Ph	24 (**8**)	60 (**9**)	84	2.5	**8**: −77.7, **9**: −79.3
5	**10** and **11**	H	Ph	Ph	38 (**10**)	44 (**11**)	82	1.15	**10**: −75.1, **11**: −78.6
6	**12** and **13**	Bu	H	H	59 (**12**)	19 (**13**)	78	0.32	**12**: −79.5, **13**: −74.4
7	**14** and **15**	Me	H	Me	8 (**14**)	55 (**15**)	63	6.88	**14**: −82.5, **15**: −73.4
8	**16** and **17**	Bu	H	Me	18 (**16**)	50 (**17**)	68	2.78	**16**: −80.7, **17**: −72.9
9	**18** and **19**	Bu	H	Ph	18 (**18**)	65 (**19**)	83	3.61	**18**: −77.4, **19**: −71.8
10	**20** and **21**	Bu	Me	Ph	8 (**20**)	48 (**21**)	56	5.87	**20**: −77.0, **21**: −70.4

[a] $PdCl_2(PPh_3)_2$ in dry THF; alkyne/hydride **1** ratio = 1.
[b] Yields of products isolated from column chromatography.
[c] In $CDCl_3$; in ppm with respect to Me_4Sn.

propargyl alcohols, i.e., compounds **3**, **5**, **7**, **9**, and **11**, the ^{1}H NMR spectra show signals corresponding to a proton attached to C(3) (H_B) with ^2J(Sn,H) coupling constants values between 76 and 72 Hz indicating that this proton and the organotin moiety are *geminal*. It should be noted that due to the multiplicity of the signals and the overlap between stannyl satellites and other signals, in many cases it was not possible the measurement of ^3J(Sn,H) coupling constants (see Tables 2 and 3).

The ^{13}C NMR chemical shifts (Tables 2 and 3) were assigned through the analysis of the multiplicity of the signals by means of DEPT experiments and taking into account the magnitude of $^nJ(^{13}C,^{119}Sn)$ coupling constants. Thus, the values of $^2J(^{13}C,^{119}Sn)_{geminal}$ coupling constants for adducts **12**, **14**, **16**, **18**, and **20** (see C(1), Table 2), within the range 31.7–22.7 Hz indicate that the configuration of these compounds is (*E*) [7]. The (*E*) configuration of these compounds is confirmed by the fact that the values of their $^3J(^{13}C,^{119}Sn)$ coupling constants lie between 61.2 and 54.8 Hz, indicating that the R substituent at C(3) is *trans* with respect to the the organotin moiety attached to C(2). Also, the $^2J(^{13}C,^{119}Sn)_{geminal}$ coupling constants with values ranging from 40.0 to 23.7 Hz for adducts **2**, **4**, **6**, **8**, and **10** (see C(1) in Table 2,) confirm that the vinyl groups are terminal. Similarly, $^3J(^{13}C,^{119}Sn)_{trans}$ coupling constant values of compounds **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17**, **19**, and **21** range from 67.8 to 60.2 Hz (see C(1) in Table 3) demonstrating the (*E*) stereochemistry of these adducts [7].

As shown in Table 1, the *syn* hydrostannation of substituted propargyl alcohols with trineophyltin hydride leads in all cases but one (Table 1, entry 6), to mixtures of regioisomers in which the β-isomer is always formed in higher proportion. These results could be explained [8] taking into account that, due to steric effects the reactions might take place through an intermediate complex **A** (Scheme 2) in which the palladium residue adopts the distal position to minimize the interaction between the metal and the R^1 and/or R^2, as shown in Scheme 2. In this way, the distal stannane is obtained even when an additional R substituent is attached to the C-γ position.

On the other hand, in the case of the hydrostannation of 2-heptyn-1-ol (Table 1, entry 6) with trineophyltin hydride (**1**) i.e., a compound in which the C-α is not substituted, the proximal stannylated derivative is obtained as the major regioisomer *via* the intermediate complex **B** (Scheme 2). This result together with the results reported previously [6a], clearly indicates that the proximal adduct will be the major isomer whenever the C-α is not substituted and whether or not the C-γ is substituted.

The chemical reactivity of the new stannylated allyl alcohols is similar to that of other vinyltriorganostannanes. Thus, the Stille reactions of vinylstannanes **9** and **11** with *p*-bromoanisole lead to the corresponding coupling products in 62 (**22**) and 65% (**23**) yield.

The major advantages of the hydrostannation of propargyl alcohols with trineophyltin hydride are not only the higher yields but the greater stability of the resulting adducts compared with that of their tributyl- and trimethylstannyl analogues [6b,9]. The stability of the trineophylstannyallyl alcohols enable their separation and purification by column chromatography using silica gel 60 (in most cases) as adsorbent, this resulting in a dramatic improvement of the yields of pure isolated compounds.

3. Experimental

3.1. General methods

NMR spectra were recorded on a Bruker ARX 300 instrument, using $CDCl_3$ as solvent; chemical shifts (δ) are reported in ppm with respect to TMS, ^{1}H and ^{13}C, and with respect to Me_4Sn in the case of ^{119}Sn NMR spectra. Mass spectra were obtained using a Finnigan MAT Incos 50 Galaxy System (DIP-MS) at Cologne University (Germany). Elemental analyses (C, H) were performed at Cologne University (Germany). High resolution mass spectra (HRMS) were recorded on a Finnigan Mat. 900 (HR-EI-MS). All the solvents and reagents used were analytical reagent grade. Trineophyltin hydride (**1**) was prepared as described [10]. 1-Phenyl-2-heptyn-1-ol was obtained by reduction of 1-phenyl-2-heptyn-1-one [11]. One experiment is described in detail in order to illustrate the methods used.

3.2. Addition of trineophyltin hydride (*1*) to substituted propargyl alcohols catalyzed by bis(triphenylphosphine)palladium(II) chloride

All the reactions were carried out following the same procedure. One experiment is described in detail in order to illustrate the methods used.

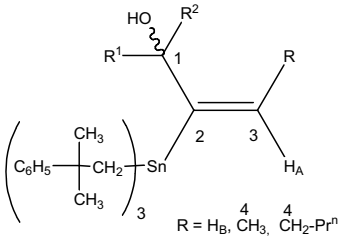
To a solution of 2-phenyl-3-butyn-2-ol (0.11 g, 0.77 mmol) and bis(triphenylphosphine) palladium(II) chloride (0.010 g, 0.015 mmol) in dry THF (3 mL) under argon was added trineophyltin hydride (0.40 g, 0.77 mmol), and the mixture was stirred at room temperature for 2 h. Then, the solvent was distilled off under reduced pressure. The ^{119}Sn NMR spectrum of the crude product showed a mixture of two compounds: α-2-trineophyltin-1-methyl-1-phenyl-2-propen-1-ol (**8**; 28%) and (*E*)-β-3-trineophyltin-1-methyl-1-phenyl-2-propen-1-ol (**9**; 72%). Column chromatography (silica gel 60) of the mixture afforded **8** (0.10 g, 0.16 mmol, 24%) and **9** (0.26 g, 0.39 mmol, 60%) in the fractions eluted with 98:2 and 96:4 hexane–diethyl ether, respectively.

3.3. Stille coupling reactions

All the reactions were carried out following the same procedure. One experiment is described in detail in order to illustrate the methods used.

To a mixture of 1-bromo-4-methoxybenzene (0.12 g, 0.74 mmol), $PdCl_2(PPh_3)_2$ (0.011 g, 2%), and some crystals of 2,6-di-*tert*-butyl-4-methylphenol under argon was added a solution of **9** (0.25 g, 0.37 mmol) in dry THF (2 mL) at

Table 2
^{1}H- and ^{13}C NMR spectra of compounds **2**, **4**, **6**, **8**, **10**, **12**, **14**, **16**, **18**, and **20**[a]



Compound number	**2**	**4**	**6**	**8**	**10**	**12**	**14**	**16**	**18**	**20**
R	H_B	H_B	H_B	H_B	H_B	*n*-Bu	Me	*n*-Bu	*n*-Bu	*n*-Bu
R^1	H	H	Me	Me	Ph	H	H	H	H	Me
R^2	Me	Ph	Me	Ph	Ph	H	Me	Me	Ph	Ph
δC_n [$^{n}J(^{119}Sn–^{13}C)$] $\delta H–C_n$ [$^{n}J(^{119}Sn–^{1}H)$] and [$^{n}J(^{1}H–^{1}H)$]	Compound **2**		Compound **4**		Compound **6**			Compound **8**	Compound **10**	
C_1 ($^{2}J_{Sn,C}$)	^{13}C: 73.38 (39.3)		^{13}C: 79.54 (40.0)		^{13}C: 75.49 (23.7)			^{13}C: 78.94 (24.1)	^{13}C: 85.36 (24.1)	
C_2 ($^{1}J_{Sn,C}$)	^{13}C: 161.69 (363.0)		^{13}C: 158.92 (354.9)		^{13}C: 166.84 (380.5)			^{13}C: 163.68 (382.0)	^{13}C: 164.23 (359.2)	
C_3 ($^{2}J_{Sn,C}$);	^{13}C: 123.40 (22.7)		^{13}C: 126.38 (23.7)		^{13}C: 122.26 (25.3)			^{13}C: 124.42 (25.5)	^{13}C: 128.39 (25.8)	
H_A: ($^{3}J_{Sn,H})_{cis}$ ($^{2}J_{H,H}$);	$^{1}H_A$: 4.91 (t) (67.6) (1.3)		$^{1}H_A$: 5.11 (t) (64.9) (1.6)		$^{1}H_A$: 4.91 (s) (72.0)			$^{1}H_A$: 5.11 (s) (70.0)	$^{1}H_A$: 5.65 (s) (64.8)	
H_B: ($^{3}J_{Sn,H})_{trans}$, ($^{2}J_{H,H}$)					$^{1}H_B$: 5.41 (s) (151.6)			$^{1}H_B$: 5.55 (s)(145.0)	$^{1}H_B$: 5.39 (s) (139.0)	
	$^{1}H_B$: 5.53 (t) (146.3) (1.3)		$^{1}H_B$: 5.49 (t) (140.3) (1.6)							
R^1	^{1}H: 3.92 (q, 1H) (42.3) (6.3)		^{1}H:4.81 (s, 1H) (34.7)					^{13}C: 31.02 (16.4)		
					^{13}C: 30.35 (9.7)			^{1}H: 1.24 (s, 3H)	^{13}C: 145.83 (12.0) (*ipso*)	
R^2	^{13}C: 23.63 (9.5)		^{13}C: 142.46 (10.5) (*ipso*)		^{1}H: 1.04 (s, 7H)[d]			^{13}C: 146.67 (NO) (*ipso*)		
	^{1}H: 1.01 (d, 3H) (6.3)									
Other signals	[b]		[c]		[e]			[f]	[g]	
	Compound **12**		Compound **14**		Compound **16**			Compound **18**	Compound **20**	
C_1 ($^{2}J_{C,Sn}$)	^{13}C: 62.73 (31.7)		^{13}C: 68.57 (23.1)		^{13}C: 68.84 (24.0)			^{13}C: 73.06 (22.7)	^{13}C: 78.47 (26.5)	
C_2 ($^{1}J_{C,Sn}$)	^{13}C: 145.93 (404.6)		^{13}C: 153.12 (411.2)		^{13}C: 152.14 (406.9)			^{13}C: 149.01 (NO)	^{13}C: 155.88 (NO)	
C_3 ($^{2}J_{Sn,C}$);	^{13}C: 142.02 (22.5);		^{13}C: 133.19 (26.1);		^{13}C: 139.64 (21.4);			^{13}C: 142.44 (21.8);	^{13}C: 140.35 (24.2)	
H_A: ($^{3}J_{Sn,H})_{cis}$ ($^{4}J_{H,H}$);	$^{1}H_A$: 5.35 (tt) (74.7) (6.7) (1.5)		$^{1}H_A$: 5.17 (dq) (75.7) (6.7) (1.5)		$^{1}H_A$: 5.20 (dt) (77.8) (6.7) (1.5)			$^{1}H_A$: 5.47 (t) (73.8) (6.8)	$^{1}H_A$: 5.39 (t) (85.3) (7.2)	
C_4 ($^{3}J_{Sn,C}$); H ($^{3}J_{H,H}$)	^{13}C: 28.94 (54.8);		^{13}C: 15.00 (61.2);		^{13}C: 29.13 (56.4)			^{13}C: 31.46 (NO)	^{13}C: 30.61 (NO);	
	^{1}H: 1.86 (dd) (13.5)		^{1}H: 1.33–1.51 (m,4H)[i]		^{1}H: below neophyl			^{1}H: 1.16–1.37 (m,3H)[l]	^{1}H: below neophyl	
R^1			^{1}H:4.13 (m, 1H) (64.4)		^{1}H:4.16 (q, 1H) (65.2) (6.3)			^{1}H: 5.23 (m, 1H) (68.6)	^{13}C: 29.62 (9.9);	
	^{1}H: 3.76 (s, 2H) (44.8)								^{1}H: 1.54 (s, 3H)	
R^2			^{13}C: 22.71 (NO); ^{1}H: below neophyl		^{13}C: 13.99 (13.90); ^{1}H: below neophyl			^{13}C: 142.89 (NO) (*ipso*)	^{13}C: 148.15 (10.2) (*ipso*)	
Other signals	[h]		[j]		[k]			[m]	[n]	

[a] In $CDCl_3$ solution; chemical shifts, δ, in ppm with respect to TMS; $^{n}J(^{119}Sn,^{1}H)$ coupling constants in Hz (in brackets); multiplicity (in brackets): d = doublet, dd = double doublet, t = triplet, dt = double triplet, tt = triple triplet, q = quartet, dq = double quartet, m = multiplet; NO = not observed.

[b] Neophyl: ^{13}C: 31.50 (328.7), 33.23 (36.7), 33.42 (36.7), 38.22 (19.5), 125.43, 125.63, 127.97, 151.31 (19.0); ^{1}H: 1.03 (s, 3H, $^{2}J_{Sn,H} = 50.0$), 1.04 (s, 3H, $^{2}J_{Sn,H} = 50.0$), 1.13 (s, 18H), 7.05–7.20 (m, 15H). OH: 0.66 (s, 1H).

[c] Neophyl: ^{13}C: 31.48 (328.2), 33.25 (35.7), 38.15 (19.0), 125.42, 125.61,127.97, 151.41 (19.6); ^{1}H: 0.92 (s, 6H, $^{2}J_{Sn,H} = 50.3$), 1.08 (s, 19H) (includes OH proton), 6.97–7.27 (m, 20H); Phenyl: ^{13}C: 127.15, 127.25, 128.11; ^{1}H: below neophyl.

[d] Probably includes the OH proton.

[e] Neophyl: ^{13}C: 32.25 (326.7), 33.36 (36.2), 38.42 (19.2), 125.40, 125.71, 128.01, 151.63 (19.4); ^{1}H: 1.08 (s, 6H, $^{2}J_{Sn,H} = 49.9$), 1.14 (s, 18H), 6.90–7.20 (m, 15H).

room temperature, and this mixture was stirred for 24 h under reflux, with monitoring by TLC. Column chromatography on silica gel 60 of the crude product gave compound **23** (0.061 g, 0.24 mmol, 65%) in the fraction eluted with 97:3 hexane–diethyl ether.

3.4. Mass spectra, and elemental analyses of the new compounds

3.4.1. α-3-Trineophyltin-3-buten-2-ol (**2**)

MS (*m*/*z*, relative intensity): 590 (M^+, Sn-pattern); 519 (40%, $[SnNph_3]^+$); 457 (10%, $[M-Nph]^+$, Sn-pattern); 403 (15%, Sn-pattern); 253 (7%, $[SnNph]^+$); 197 (20%, Sn-pattern); 133 (15%, $[Nph]^+$); 118 (10%, $[Sn]^+$); 105 (11%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (18%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{34}H_{46}OSn$ 590.2571, found 590.2563. Anal. Calc. for $C_{34}H_{46}OSn$: C, 69.28; H, 7.87. Found: C, 69.39; H, 7.74%.

3.4.2. (E)-β-4-Trineophyltin-3-buten-2-ol (**3**)

MS (*m*/*z*, relative intensity): 590 (M^+, Sn-pattern); 519 (30%, $[SnNph_3]^+$); 457 (35%, $[M-Nph]^+$, Sn-pattern); 253 (4%, $[SnNph]^+$); 197 (18%, Sn-pattern); 133 (14%, $[Nph]^+$); 118 (10%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (20%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{34}H_{46}OSn$ 590.2571, found 590.2565. Anal. Calc. for $C_{34}H_{46}OSn$: C, 69.28; H, 7.87. Found: C, 69.37; H, 7.76%.

3.4.3. α-2-Trineophyltin-1-phenyl-2-propen-1-ol (**4**)

MS (*m*/*z*, relative intensity): 652 (M^+, Sn-pattern); 519 (45%, $[SnNph_3]^+$); 403 (37%, Sn-pattern); 253 (8%, $[SnNph]^+$); 197 (22%, Sn-pattern); 133 (16%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (21%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{39}H_{48}OSn$ 652.2727, found 652.2735. Anal. Calc. for $C_{39}H_{48}OSn$: C, 71.90; H, 7.43. Found: C, 71.81; H, 7.54%.

3.4.4. (E)-3-Trineophyltin-1-phenyl-2-propen-1-ol (**5**)

MS (*m*/*z*, relative intensity): 652 (M^+, Sn-pattern); 519 (45%, $[SnNph_3]^+$); 403 (37%, Sn-pattern); 253 (8%, $[SnNph]^+$); 197 (22%, Sn-pattern); 133 (16%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (21%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{39}H_{48}OSn$ 652.2727, found 652.2738. Anal. Calc. for $C_{39}H_{48}OSn$: C, 71.90; H, 7.43. Found: C, 71.79; H, 7.35%.

3.4.5. α-3-Trineophyltin-2-methyl-3-buten-2-ol (**6**)

MS (*m*/*z*, relative intensity): 604 (M^+, Sn-pattern); 519 (54%, $[SnNph_3]^+$); 403 (32%, Sn-pattern); 253 (9%, $[SnNph]^+$); 197 (20%, Sn-pattern); 133 (16%, $[Nph]^+$); 118 (10%, $[Sn]^+$); 105 (13%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (23%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{35}H_{48}OSn$ 604.2727, found 604.2737. Anal. Calc. for $C_{35}H_{48}OSn$: C, 69.66; H, 8.02. Found: C, 69.74; H, 8.10%.

[f] Neophyl: ^{13}C: 31.92 (326.0), 33.06 (35.8), 33.54 (35.8), 38.26 (19.3), 125.34, 125.70, 127.94, 151.49 (19.8); ^1H: 0.69–1.10 (m, 25 H) (probably includes OH proton), 6.97–7.32 (m, 20H); Phenyl: ^{13}C: 125.63, 126.48, 127.82; ^1H: below neophyl.

[g] Neophyl: ^{13}C: 32.03 (326.3), 33.30 (35.8), 38.22 (19.2), 125.33, 127.69, 127.94, 151.58 (22.0); ^1H: 1.30 (s, 7H, $^2J_{Sn,H} = 50.5$) (probably includes OH proton), 1.52 (s, 18H), 7.30–7.80 (m, 25H); Phenyl: ^{13}C: 125.57, 126.89; ^1H: below neophyl.

[h] Neophyl: ^{13}C: 31.60 (325.5), 33.25 (36.7), 38.18 (18.0), 125.38, 125.57, 127.94, 151.54 (19.1); ^1H: 1.03 (s, 7H, $^2J_{Sn,H} = NO$) (probably includes OH proton), 1.13 (s, 18H), 6.90–7.30 (m, 15H). *n*-Bu: ^{13}C: 13.95, 22.39, 31.57; ^1H: 0.83 (t, 3H, $^3J_{H,H} = 7.1$), 1.18–1.27 (m, 4H).

[i] Probably includes the OH proton.

[j] Neophyl: ^{13}C: 32.14 (325.7), 32.42 (31.0), 34.22 (41.1), 38.42 (18.4), 125.38, 125.82, 127.85, 151.53 (18.1); ^1H: 0.84–1.00 (m, 6H), 1.05–1.30 (m, 21H), 6.85–7.40 (m, 15H).

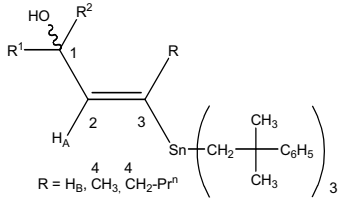
[k] Neophyl: ^{13}C: 32.11 (324.9), 32.50 (31.6), 34.13 (42.1), 38.40 (18.8), 125.37, 125.78, 127.86, 151.56 (18.6); ^1H: 0.77–0.99 (m, 10H), 1.03–1.32 (m, 25H), 6.95–7.00 (m, 15H). *n*-Bu: ^{13}C: 22.58, 23.22, 31.58; ^1H: 1.68–1.96 (m, 2H), other signals together with neophyl signals.

[l] Probably includes the OH proton.

[m] Neophyl: ^{13}C: 32.02 (326.0), 32.98 (34.8), 33.56 (38.3), 38.29 (18.0), 125.33, 125.72, 127.86, 151.56 (19.2); ^1H: 0.71–1.04 (m, 11H), 1.09 (s, 18H), 7.00–7.28 (m, 20H). *n*-Bu: ^{13}C: 13.96, 22.58, 29.75; ^1H: 1.71–2.00 (m, 2H), other signals together with neophyl signals. Phenyl: ^{13}C: 126.49, 126.71, 128.00; ^1H: together with neophyl signals.

[n] Neophyl: ^{13}C: 32.10 (324.5), 33.28 (34.3), 33.41 (35.8), 38.42 (18.5), 125.25, 125.65, 127.95, 152.03 (20.1); ^1H: 0.95–1.09 (m, 11H) (probably includes the OH proton.), 1.14 (s, 18H), 6.97–7.43 (m, 20H). *n*-Bu: ^{13}C: 13.86, 22.39, 31.42; ^1H: 0.68 (t, 3H, $^3J_{H,H} = 6.8$), 1.25–1.70 (m, 2H), other signals together with neophyl signals. Phenyl: ^{13}C: 126.25, 126.83, 128.08; ^1H: together with neophyl signals.

Table 3
^{1}H- and ^{13}C NMR spectra of compounds **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17**, **19**, and **21**[a]



Compound number	**3**	**5**	**7**	**9**	**11**	**13**	**15**	**17**	**19**	**21**
R	H_B	H_B	H_B	H_B	H_B	*n*-Bu	Me	*n*-Bu	*n*-Bu	*n*-Bu
R^1	H	H	Me	Me	Ph	H	H	H	H	Me
R^2	Me	Ph	Me	Ph	Ph	H	Me	Me	Ph	Ph
δC_n [$^nJ(^{119}Sn–^{13}C)$] $\delta H–C_n$ [$^nJ(^{119}Sn–^1H)$] and [$^nJ(^1H–^1H)$]	Compound 3		Compound **5**			Compound **7**	Compound **9**		Compound **11**	
C_1 ($^3J_{Sn,C}$)	^{13}C: 70.72 (65.1)		^{13}C: 77.23 (67.8)			^{13}C: 71.89 (62.3)	^{13}C: 75.56 (60.4)		^{13}C: 80.30 (60.6)	
C_2 ($^2J_{Sn,C}$);	^{13}C: 149.47 (NO);		^{13}C: 147.22 (NO);			^{13}C: 152.92 (NO);	^{13}C: 151.39 (NO);		^{13}C: 149.74 (NO);	
H_A: ($^3J_{Sn,H})_{cis}$ ($^3J_{H,H}$)	^1H_A: 5.51 (dd) (68.6) (18.6) (5.2)		^1H_A: 5.64 (dd) (66.4) (18.7) (5.2)			^1H_A: 6.00 (d) (71.3) (19.0)	^1H_A: 6.21 (d) (67.6) (19.0)		^1H_A: 6.16 (d) (69.6) (19.0)	
C_3 ($^1J_{Sn,C}$);	^{13}C: 128.75 (388.0);		^{13}C: 130.71 (369.0);			^{13}C: 124.98 (393.0);	^{13}C: 126.72 (382.2);		^{13}C: 128.57 (373.3);	
H_B: ($^2J_{Sn,H})_{gem}$; ($^3J_{H,H}$)	^1H_B: 5.19 (d) (75.3) (18.6)		^1H_B: 5.37 (dd) (74.1) (18.7) (1.4)			^1H_B: 5.54 (d) (76.3) (19.0)	^1H_B: 5.71 (d) (73.8) (19.0)		^1H_B: 5.34 (d) (72.2) (19.0)	
R^1	^{1}H: 3.83 (qui, 1H) (5.9)		^{1}H: 4.77 (d, 1 H) (5.2)				^{13}C: 28.91;			
R^2	^{13}C: 22.39; ^{1}H: 1.01 (d, 3H) (6.2)		^{13}C: 142.58 (*ipso*)			^{13}C: 28.91; ^{1}H: 1.45 (s, 7H)[d]	^{1}H: 1.78 (s, 3H) ^{13}C: 146.65 (*ipso*)		^{13}C: 145.93 (*ipso*)	
Other signals	[b]		[c]			[e]	[f]		[g]	
	Compound **13**		Compound **15**			Compound **17**	Compound **19**		Compound **21**	
C_1 ($^3J_{Sn,C}$)	^{13}C: 59.04 (64.9)		^{13}C: 63.52 (61.1)			^{13}C: 63.41 (63.3)	^{13}C: 69.28 (60.2)		^{13}C: 75.09 (65.7)	
C_2 ($^2J_{Sn,C}$); H_A:	^{13}C: 140.16 (28.2);		^{13}C: 144.63 (23.6) ^1H_A:			^{13}C: 144.95 (25.0); ^1H_A:	^{13}C: 142.65 (27.6);		^{13}C: 147.26 (27.0);	
($^3J_{Sn,H})_{cis}$, ($^3J_{H,H}$)	^1H_A: 5.14(t)(73.1) (6.2)		5.24 (d) (72.5) (7.9)			5.12 (d) (73.3) (8.4)	^1H_A: 5.31 (s) (72.1)		^1H_A: 5.63 (s) (77.3)	
C_3 ($^1J_{Sn,C}$)	^{13}C: 148.51 (NO)		^{13}C: 141.54(399.1)			^{13}C: 147.00 (NO)	^{13}C: 148.29(380.9)		^{13}C: 150.94 (388.8)	
C_4 ($^3J_{Sn,C}$); H: ($^3J_{Sn,H}$) ($^3J_{H,H}$)	^{13}C: 32.80 (37.9) H: 1.94 (t, 2H) (30.3) (7.9)		^{13}C: 18.65 (41.9); ^{1}H: 1.42 (s, 3H) (46.6)			^{13}C: 32.83 (NO) ^{1}H: 1.96 (m, 2H)	^{13}C: 32.84 (NO); ^{1}H: 2.09 (t, 2H) (60.1) (8.1)		^{13}C: 33.46(NO); ^{1}H: see other signals	
R^1	^{1}H: 3.90 (d,2H) (6.2)		^{1}H: 4.42 (qui, 1H) (6.6)			^{1}H: 4.40 (m, 1H)	^{1}H: 7.24 (s, 1H)		^{13}C: 32.89; ^{1}H: 1.47 (s, 3H)	
R^2			^{13}C: 22.70; ^{1}H: 1.06 (d, 3H) (6.3)			^{13}C: 23.04; ^{1}H: below neophyl	^{13}C: 143.63 (*ipso*)		^{13}C: 148.95 (*ipso*)	
Other signals	[h]		[i]			[j]	[k]		[l]	

[a] In $CDCl_3$ solution; chemical shifts, δ, in ppm with respect to TMS; $^nJ(^{119}Sn,^1H)$ coupling constants in Hz (in brackets); multiplicity (in brackets): d = doublet, dd = double doublet, t = triplet, dt = double triplet, tt = triple triplet, q = quartet, dq = double quartet, qui = quintet, m = multiplet; NO = not observed.

[b] Neophyl: ^{13}C: 31.24 (339.1), 33.05 (35.5), 33.14 (36.5), 38.03 (18.7), 125.32, 125.36, 127.94, 151.24 (19.8); ^{1}H: 0.94 (s, 6H, $^2J_{H,Sn} = 50.0$), 1.13 (m, 19H) (probably includes OH proton), 6.90–7.30 (m, 15H).

[c] Neophyl: ^{13}C: 31.33 (340.3), 33.03 (35.2), 33.16 (36.5), 38.07 (18.9), 125.42, 128.02, 151.26 (19.9); ^{1}H: 0.93 (s, 6H, $^2J_{H,Sn} = 50.1$), 1.10 (s, 18H), 6.80–7.40 (m, 20H). OH: 1.50 (s, 1H). Phenyl: ^{13}C: 126.28, 127.32, 128.27; ^{1}H: below neophyl.

[d] Probably includes the OH proton.

[e] Neophyl: ^{13}C: 31.25 (339.1), 33.14 (35.4), 38.09 (18.5), 125.35, 125.40, 127.99, 151.32 (19.9); ^{1}H: 1.38 (s, 6H, $^2J_{H,Sn} = 50.1$), 1.56 (s, 18H), 7.30–7.70 (m, 15H).

[f] Neophyl: ^{13}C: 31.24 (340.0), 33.07 (36.0), 33.16 (36.0), 38.04 (19.8), 125.36, 127.99, 151.19 (19.2); ^{1}H: 1.39 (s, 6H, $^2J_{H,Sn} = 50.0$), 1.56 (s, 18H), 7.40–7.80 (m, 20H). OH: 1.88 (s, 1H). Phenyl: ^{13}C: 125.15, 126.51, 127.88; ^{1}H: below neophyl.

[g] Neophyl: ^{13}C: 31.33 (339.6), 33.07 (35.6), 38.03 (18.8), 125.37, 125.40, 128.04, 151.17 (19.9); ^{1}H: 0.92 (s, 6H, $^2J_{H,Sn} = 49.8$), 1.08 (s, 18H), 6.90–7.30 (m, 25H). OH: 1.83 (s, 1H). Phenyl: ^{13}C: 126.89,

127.00, 127.85; ^{1}H: below neophyl.

[h] Neophyl: ^{13}C: 31.02 (317.9), 33.36 (35.2), 38.10 (18.9), 125.37, 125.52, 127.99, 151.41 (18.0); ^{1}H: 0.97 (s, 3H, $^2J_{H,Sn}$ = 49.6), 1.00–1.40 (m, 26H), 6.95–7.30 (m, 15H). *n*-Bu: ^{13}C: 13.98, 22.86, 32.81; ^{1}H: 0.84 (t, 3H, $^3J_{H,H}$ = 7.2), other signals below neophyl.

[i] Neophyl: ^{13}C: 30.79 (322.8), 33.19 (36.0), 33.32 (37.5), 37.97(18.4), 125.36, 125.43, 127.95, 151.31 (18.2); ^{1}H: 0.95 (s, 6H, $^2J_{H,Sn}$ = 49.4), 1.11 (s, 19H) (includes OH proton), 6.75–7.50 (m, 15H).

[j] Neophyl: ^{13}C: 30.90 (318.1), 33.33 (35.3), 38.08 (18.1), 125.38, 125.47, 127.99, 151.42 (18.4); ^{1}H: 0.88–1.30 (m, 32H), 6.75–7.30 (m, 15H). *n*-Bu: ^{13}C: 14.00, 22.96, 33.15; ^{1}H: 0.85 (t, 3H, $^3J_{H,H}$ = 6.9), other signals below neophyl.

[k] Neophyl: ^{13}C: 30.96 (319.1), 33.26 (36.1), 38.00 (18.4), 125.37, 125.44, 127.98, 151.32 (19.2); ^{1}H: 0.91 (s, 6H, $^2J_{H,Sn}$ = 49.0), 1.00–1.60 (m, 21H) (includes OH proton), 6.90–7.35 (m, 20H). *n*-Bu: ^{13}C: 14.00, 23.03, 32.98; ^{1}H: 0.85 (t, 3H, $^3J_{H,H}$ = 7.1), 1.90–2.30 (m, 2H), other signals below neophyl. Phenyl: ^{13}C: 125.96, 127.07, 128.22; ^{1}H: together with neophyl signals.

[l] Neophyl: ^{13}C: 31.24 (NO), 33.29 (NO), 33.47 (NO), 38.14 (18.7), 125.43, 125.50, 128.05, 151.49 (19.8); ^{1}H: 0.93 (s, 6H, $^2J_{H,Sn}$ = 49.1), 1.11–1.12 (split signal, 19H) (includes OH proton), 6.90–7.50 (m, 20H). *n*-Bu: ^{13}C: 13.82, 23.08, 33.68; ^{1}H: 0.66 (t, 3H, $^3J_{H,H}$ = 7.6), 1.52–2.24 (m, 6H). Phenyl: ^{13}C: 125.13, 126.25, 127.85; ^{1}H: together with neophyl signals.

3.4.6. (*E*)-4-Trineophyltin-2-methyl-3-buten-2-ol (**7**)

MS (*m*/*z*, relative intensity): 604 (M^+, Sn-pattern); 519 (54%, $[SnNph_3]^+$); 403 (32%, Sn-pattern); 253 (9%, $[SnNph]^+$); 197 (20%, Sn-pattern); 133 (16%, $[Nph]^+$); 118 (10%, $[Sn]^+$); 105 (13%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (23%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{35}H_{48}OSn$ 604.2727, found 604.2734. Anal. Calc. for $C_{35}H_{48}OSn$: C, 69.66; H, 8.02. Found: C, 69.72; H, 8.08%.

3.4.7. α-3-Trineophyltin-2-phenyl-3-buten-2-ol (**8**)

MS (*m*/*z*, relative intensity): 666 (M^+, Sn-pattern); 519 (54%, $[SnNph_3]^+$); 403 (40%, Sn-pattern); 385 (9%, $[SnNph_2]^+$); 253 (8%, $[SnNph]^+$); 197 (24%, Sn-pattern); 133 (17%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (10%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (19%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{40}H_{50}OSn$ 666.2884, found 666.2875. Anal. Calc. for $C_{40}H_{50}OSn$: C, 72.19; H, 7.57. Found: C, 72.25; H, 7.51%.

3.4.8. (*E*)-4-Trineophyltin-2-phenyl-3-buten-2-ol (**9**)

MS (*m*/*z*, relative intensity): 666 (M^+, Sn-pattern); 533 (25%, $[M-Nph]^+$, Sn-pattern); 253 (6%, $[SnNph]^+$); 197 (25%, Sn-pattern); 133 (14%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (18%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{40}H_{50}OSn$ 666.2884, found 666.2878. Anal. Calc. for $C_{40}H_{50}OSn$: C, 72.19; H, 7.57. Found: C, 72.22; H, 7.50%.

3.4.9. α-2-Trineophyltin-1,1-diphenyl-2-propen-1-ol (**10**)

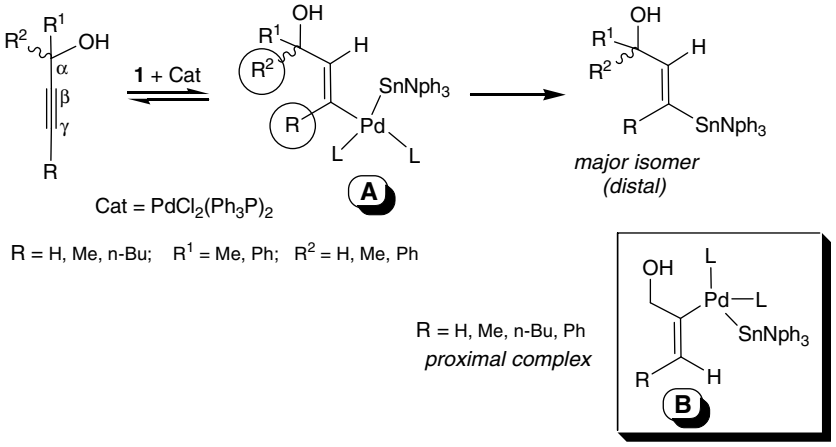
MS (*m*/*z*, relative intensity): 728 (M^+, Sn-pattern); 519 (31%, $[SnNph_3]^+$); 253 (8%, $[SnNph]^+$); 197 (23%, Sn-pattern); 133 (12%, $[Nph]^+$); 118 (10%, $[Sn]^+$); 105 (13%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (17%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{45}H_{52}OSn$ 728.3040, found 728.3031. Anal. Calc. for $C_{45}H_{52}OSn$: C, 74.28; H, 7.20. Found: C, 74.21; H, 7.30%.

3.4.10. (*E*)-3-Trineophyltin-1,1-diphenyl-2-propen-1-ol (**11**)

MS (*m*/*z*, relative intensity): 728 (M^+, Sn-pattern); 595 (22%, $[M-Nph]^+$, Sn-pattern); 253 (10%, $[SnNph]^+$); 197 (21%, Sn-pattern); 133 (13%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (15%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{45}H_{52}OSn$ 728.3040, found 728.3033. Anal. Calc. for $C_{45}H_{52}OSn$: C, 74.28; H, 7.20. Found: C, 74.20; H, 7.27%.

3.4.11. (*E*)-2-Trineophyltin-2-hepten-1-ol (**12**)

MS (*m*/*z*, relative intensity): 632 (M^+, Sn-pattern); 519 (13%, $[SnNph_3]^+$); 403 (28%, Sn-pattern); 253 (9%, $[SnNph]^+$); 197 (20%, Sn-pattern); 133 (15%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (13%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (18%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{37}H_{52}OSn$ 632.3040, found 632.3031. Anal. Calc. for $C_{37}H_{52}OSn$: C, 70.37; H, 8.30. Found: C, 70.29; H, 8.21%.



Scheme 2. Palladium catalyzed addition of trineophyltin hydride (**1**) to substituted propargyl alcohols.

*3.4.12. (E)-3-Trineophyltin-2-hepten-1-ol (**13**)*

MS (*m*/*z*, relative intensity): 632 (M^+, Sn-pattern); 519 (19%, $[SnNph_3]^+$); 403 (24%, Sn-pattern); 253 (8%, $[SnNph]^+$); 197 (22%, Sn-pattern); 133 (13%, $[Nph]^+$); 118 (10%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (15%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{37}H_{52}OSn$ 632.3040, found 632.3032. Anal. Calc. for $C_{37}H_{52}OSn$: C, 70.37; H, 8.30. Found: C, 70.30; H, 8.19%.

*3.4.13. (E)-3-Trineophyltin-3-penten-2-ol (**14**)*

MS (*m*/*z*, relative intensity): 604 (M^+, Sn-pattern); 519 (23%, $[SnNph_3]^+$); 471 (12%, $[M-Nph]^+$); (24%, Sn-pattern); 403 (27%, Sn-pattern); 253 (10%, $[SnNph]^+$); 197 (19%, Sn-pattern); 133 (16%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (13%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (18%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{35}H_{48}OSn$ 604.2727, found 604.2719. Anal. Calc. for $C_{35}H_{48}OSn$: C, 69.66; H, 8.02. Found: C, 69.59; H, 8.10%.

*3.4.14. (E)-4-Trineophyltin-3-penten-2-ol (**15**)*

MS (*m*/*z*, relative intensity): 604 (M^+, Sn-pattern); 519 (5%, $[SnNph_3]^+$); 471 (45%, $[M-Nph]^+$); (24%, Sn-pattern); 253 (7%, $[SnNph]^+$); 197 (27%, Sn-pattern); 133 (15%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (22%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{35}H_{48}OSn$ 604.2727, found 604.2720. Anal. Calc. for $C_{35}H_{48}OSn$: C, 69.66; H, 8.02. Found: C, 69.57; H, 8.13%.

*3.4.15. (E)-3-Trineophyltin-3-octen-2-ol (**16**)*

MS (*m*/*z*, relative intensity): 646 (M^+, Sn-pattern); 519 (6%, $[SnNph_3]^+$); 403 (18%, Sn-pattern); 253 (6%, $[SnNph]^+$); 197 (18%, Sn-pattern); 133 (14%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (11%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (18%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{38}H_{54}OSn$ 646.3197, found 646.3192. Anal. Calc. for $C_{38}H_{54}OSn$: C, 70.70; H, 8.43. Found: C, 70.78; H, 8.37%.

*3.4.16. (E)-4-Trineophyltin-3-octen-2-ol (**17**)*

MS (*m*/*z*, relative intensity): 646 (M^+, Sn-pattern); 519 (35%, $[SnNph_3]^+$); 253 (6%, $[SnNph]^+$); 197 (32%, Sn-pattern); 133 (18%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (27%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{38}H_{54}OSn$ 646.3197, found 646.3192. Anal. Calc. for $C_{38}H_{54}OSn$: C, 70.70; H, 8.43. Found: C, 70.78; H, 8.37%.

*3.4.17. (E)-2-Trineophyltin-1-phenyl-2-hepten-1-ol (**18**)*

MS (*m*/*z*, relative intensity): 708 (M^+, Sn-pattern); 575 (18%, $[M-Nph]^+$); 519 (35%, $[SnNph_3]^+$); 253 (6%, $[SnNph]^+$); 197 (32%, Sn-pattern); 133 (18%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (12%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (27%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{43}H_{56}OSn$ 708.3353, found 708.3345. Anal. Calc. for $C_{43}H_{56}OSn$: C, 72.99; H, 7.98. Found: C, 72.87; H, 7.90%.

*3.4.18. (E)-2-Trineophyltin-1-phenyl-2-hepten-1-ol (**19**)*

MS (*m*/*z*, relative intensity): 708 (M^+, Sn-pattern); 575 (27%, $[M-Nph]^+$); 519 (7%, $[SnNph_3]^+$); 253 (7%, $[SnNph]^+$); 197 (30%, Sn-pattern); 133 (11%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (10%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (21%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{43}H_{56}OSn$ 708.3353, found 708.3351. Anal. Calc. for $C_{43}H_{56}OSn$: C, 72.99; H, 7.98. Found: C, 72.89; H, 7.91%.

*3.4.19. (E)-3-Trineophyltin-3-octen-2-ol (**20**)*

MS (*m*/*z*, relative intensity): 722 (M^+, Sn-pattern); 519 (7%, $[SnNph_3]^+$); 403 (26%, Sn-pattern); 253 (8%, $[SnNph]^+$); 197 (21%, Sn-pattern); 133 (15%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (11%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (18%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for $C_{44}H_{58}OSn$ 722.3510, found 722.3519. Anal. Calc. for $C_{44}H_{58}OSn$: C, 73.23; H, 8.10. Found: C, 73.29; H, 8.17%.

*3.4.20. (E)-4-Trineophyltin-3-octen-2-ol (**21**)*

MS (*m*/*z*, relative intensity): 722 (M^+, Sn-pattern); 589 (30%, $[M-Nph]^+$); 519 (6%, $[SnNph_3]^+$); 253 (7%, $[SnNph]^+$); 197 (35%, Sn-pattern); 133 (14%, $[Nph]^+$); 118 (11%, $[Sn]^+$); 105 (15%, $[C_8H_9]^+$); 91 (100%, $[C_7H_7]^+$); 55 (20%, $[C_3H_3O]^+$). HR-MS (ESI) calcd for

$C_{44}H_{58}OSn$ 722.3510, found 722.3517. Anal. Calc. for $C_{44}H_{58}OSn$: C, 73.23; H, 8.10. Found: C, 73.27; H, 8.19%.

*3.4.21. (E)-3-(4-Methoxyphenyl)-1,1-diphenyl-2-propen-1-ol (**22**)*

^{1}H NMR ($CDCl_3$)δ 189 (s, 1H); 3.85 (s, 3H); 6.63 (d, 1H, ^3J(H, H) 16.1 Hz); 6.89–7.23 (m, 14H); 7.28 (d, 1H, ^3J(H,H) 16.1 Hz). ^{13}C NMR ($CDCl_3$) δ 54.84; 78.82; 113.03; 125.90; 127.20; 127.35; 128.01; 129.07; 129.95; 133.65; 148.01; 160.59. HR-MS (ESI) calcd for $C_{22}H_{20}O_2$ 316.1463, found 316.1453.

*3.4.22. (E)-4-(4-Methoxyphenyl)-2-phenyl-3-buten-2-ol (**23**)*

^{1}H NMR ($CDCl_3$)δ 1.17 (s, 3H); 2.02 (s, 1H); 3.83 (s, 3H); 6.50 (d, 1H, ^3J(H,H) 16.1 Hz); 7.12 (d, 1H, ^3J(H,H) 16.1 Hz); 7.15–7.45 (m, 9H). ^{13}C NMR ($CDCl_3$)δ 30.78; 54.85; 74.77; 113.41; 123.05; 125.66; 127.39; 127.65; 127.72; 129.73; 135.01; 148.04; 160.49. HR-MS (ESI) calcd for $C_{17}H_{18}O_2$ 254.1307, found 254.1301.

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