Journal of Organometallic Chemistry 694 (2009) 161–166

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and structure of some *cis*-and *trans*-myrtanylstannanes

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ARTICLE INFO

Article history:
Received 13 August 2008
Received in revised form 1 October 2008
Accepted 6 October 2008
Available online 14 October 2008

Keywords:
Tin
Chirality

ABSTRACT

Enantiomerically pure *cis*- and *trans*-myrtanylstannanes *cis*-$MyrSnPh_3$ (**1**), *trans*-$MyrSnPh_3$ (**2**), *cis*-$MyrSnPh_2Cl$ (**3**), *trans*-$MyrSnPh_2Cl$ (**4**), *cis*-$MyrSnPhCl_2$ (**5**), *trans*-$MyrSnPhCl_2$ (**6**), *cis*-$MyrSnCl_3$ (**7**), *trans*-$MyrSnCl_3$ (**8**) were synthesized and fully characterized by ^1H, ^{13}C and ^{119}Sn NMR spectroscopy. The molecular structures of **1**, **3**, **6**, **7**, and [*trans*-$MyrSn(OH)Cl_2 \cdot H_2O]_2$ (**8a**) a hydrolysis product of **8**, were determined by X-ray crystallography.

1. Introduction

Chiral organotin compounds derived from menthol have received considerable attention in recent years [1]. For instance, menthyltin hydrides have found applications in diastereoselective hydrostannylation reactions [2] and as enantioselective reducing agents under free-radical conditions [3]. A noted shorting of menthylstannanes is their rather tedious synthesis usually involving the substitution of tin halides using the menthyl Grignard reagent, which consists of an epimeric mixture of menthylmagnesium chloride and neomenthylmagnesium chloride [4]. While chiral organotin compounds derived from other terpenes are rare [5], we have recently prepared two series of enantiomerically pure bis(myrtanyl)stannanes starting from β-pinene, which are sterically less encumbered than the related bis(menthyl)stannanes [6]. The Rh-catalyzed dehydropolymerisation of two of these compounds, namely *cis*-Myr_2SnH_2 and *trans*-Myr_2SnH_2 gave rise to the formation of the first chiral polystannanes. In continuation of this work we now report on the synthesis and structures of some enantiomerically pure *cis*- and *trans*-myrtanyltin compounds. It is noteworthy that a previous attempt at preparing a myrtanyltin compound by hydrostannylation of β-pinene failed due to radical ring-opening of the terpene skeleton [7].

2. Results and discussion

cis- and *trans*-Myrtanol were prepared according to modified literature procedures by oxidative hydroboration of (−)-β-pinene [8]. The diastereomeric purity of the crude alcohols was improved by recrystallization of the respective monophthalic esters. The pure *cis*-myrtanol (>98% de) and *trans*-myrtanol (>98% de) were then converted to *cis*- and *trans*-myrtanyl chloride using the Appel reagent (PPh_3/CCl_4) without affecting the stereochemical integrity of the chiral centers [9]. The reaction of triphenyltin chloride with one equivalent of the Grignard reagent prepared from *cis*- and *trans*-myrtanyl chloride and Mg, produced the enantiomerically pure myrtanyltriphenylstannanes *cis*-$MyrSnPh_3$ (**1**) and *trans*-$MyrSnPh_3$ (**2**) in high yields (Scheme 1). The stoichiometry controlled selective cleavage of one or two phenyl groups of **1** and **2** with iodine gave rise to the formation of myrtanyltin iodides, which were directly transferred into the corresponding myrtanyldiphenyltin chlorides *cis*-$MyrPh_2SnCl$ (**3**) and *trans*-$MyrPh_2SnCl$ (**4**) and myrtanylphenyltin dichlorides *cis*-$MyrPhSnCl_2$ (**5**) and *trans*-$MyrPhSnCl_2$ (**6**), respectively, in high overall yields by iodine-chlorine exchange using a conc. NH_4Cl solution (Scheme 1) [10]. Cleavage of all three phenyl groups was achieved by the reaction of **1** and **2** with refluxing conc. HCl solution and provided the myrtanyltin trichlorides *cis*-$MyrSnCl_3$ (**7**) and *trans*-$MyrSnCl_3$ (**8**) in very good yields (Scheme 1).

The myrtanyltin compounds were obtained also as colourless low-melting crystalline solids (**1**, **3**, **5**, **6**, **7**) or oils (**2**, **4**, **8**). In an attempt to grow crystals a hydrolysis product of **8** was isolated, namely [*trans*-$MyrSn(OH)Cl_2 \cdot H_2O]_2$ (**8a**). This substance is another example of the well established compound class $[RSn(OH)Cl_2 \cdot H_2O$ (R = Et, *n*-Bu, *i*-Pr, *i*-Bu)] [11]. The molecular structures of **1**, **3**, **6**, **7** and **8a** are shown in Figs. 1–5 and selected bond parameters collected in caption of the figures. The molecular structures confirm the relative and absolute (Flack parameters) configuration of the *cis*- and *trans*-myrtanyl residues. The unit cell of **1** contains two independent albeit similar conformers. The spatial arrangement around the Sn atoms is tetrahedral (**1**, **3**, **6**, **7**) and

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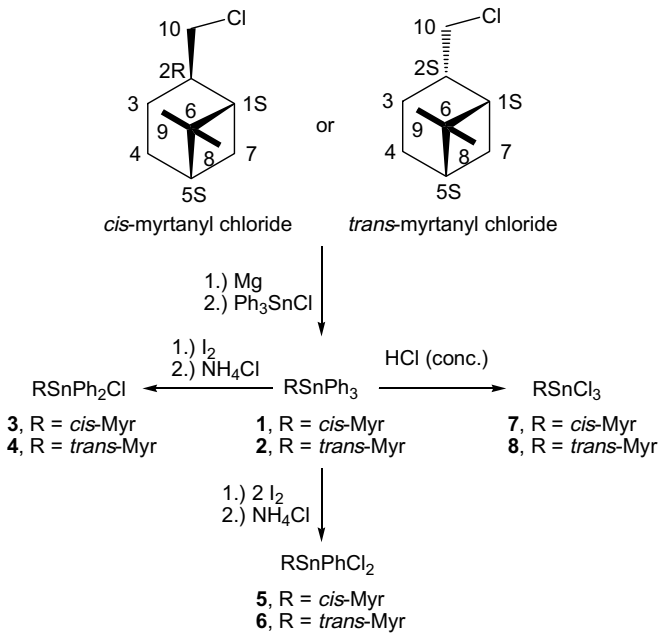
doi:10.1016/j.jorganchem.2008.10.013



Scheme 1.

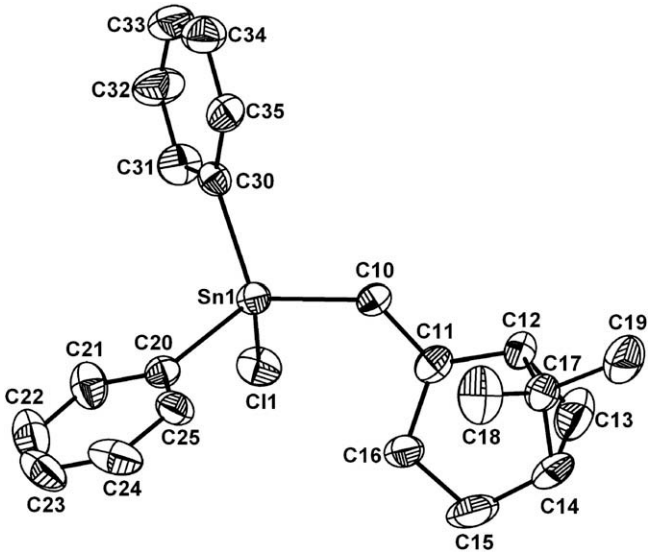


Fig. 2. Molecular structure of *cis*-MyrSnPh$_2$Cl (**3**). Selected bond parameters (Å, °): C10–Sn1 2.122(4), C20–Sn1 2.135(6), C30–Sn1 2.149(5), Cl1–Sn1 2.405(2), C10–Sn1–C20 119.9(2), C10–Sn1–C30 113.2(2), C20–Sn1–C30 115.3(2), C10–Sn1–Cl1 106.1(1), C20–Sn1–Cl1 98.1(2), C30–Sn1–Cl1 100.3(2).

distorted octahedral (**8a**). Unlike many other organotin chlorides [12], individual molecules of **3**, **6** and **7** are not associated by intermolecular Sn···Cl interactions. The (average) Sn–Cl bond length decreases when the number of chlorine atoms increases, e.g. **7** (2.295(1) Å), **6** (2.3477(7) Å) and **3** (2.405(2) Å). The distortion of the octahedral arrangement of **8a** is manifested by the Sn–O bond lengths ranging from 2.080(2) to 2.266(2) Å. The hydroxy group (O1, O2) and the water molecule (O3, O4) are involved in inter- and intramolecular hydrogen bonding with all chlorine atoms (Cl1– Cl4). The O···Cl donor acceptor distances vary between 3.082(3) and 3.325(7) Å.

In solution compounds **1**–**8** were fully characterized by ^{119}Sn, ^{13}C and ^{1}H NMR spectroscopy and the assigned resonances and $^{1}J(^{119}\text{Sn}-^{13}\text{C})$ couplings collected in Table 1. The ^{119}Sn chemical shifts of the *cis*- and *trans*-myrtanyltin series are equal within 2 ppm for the same substitution pattern, however, the ^{119}Sn NMR chemical shifts show no correlation with the number of phenyl groups and chlorine atoms. The $^{1}J(^{119}\text{Sn}-^{13}\text{C})$ couplings of the *cis*- and *trans*-myrtanyltin series are equal within 10 Hz and increase steadily when phenyl groups are replaced by more electronegative chlorine atoms, e.g. when going from MrySnPh$_3$ (approx. 400 Hz) to MyrSnCl$_3$ (approx. 600 Hz). The positions of the α-C atoms (C10) and the H atoms attached to it (H10) are shifted downfield when phenyl groups are replaced by chlorine atoms, whereas the remaining C-atoms (C1–C9) of the myrtanyl residues remain largely unaffected. Having established the synthesis and characterization of the *cis*- and *trans*-myrtanyltin compounds **1**–**8** as starting

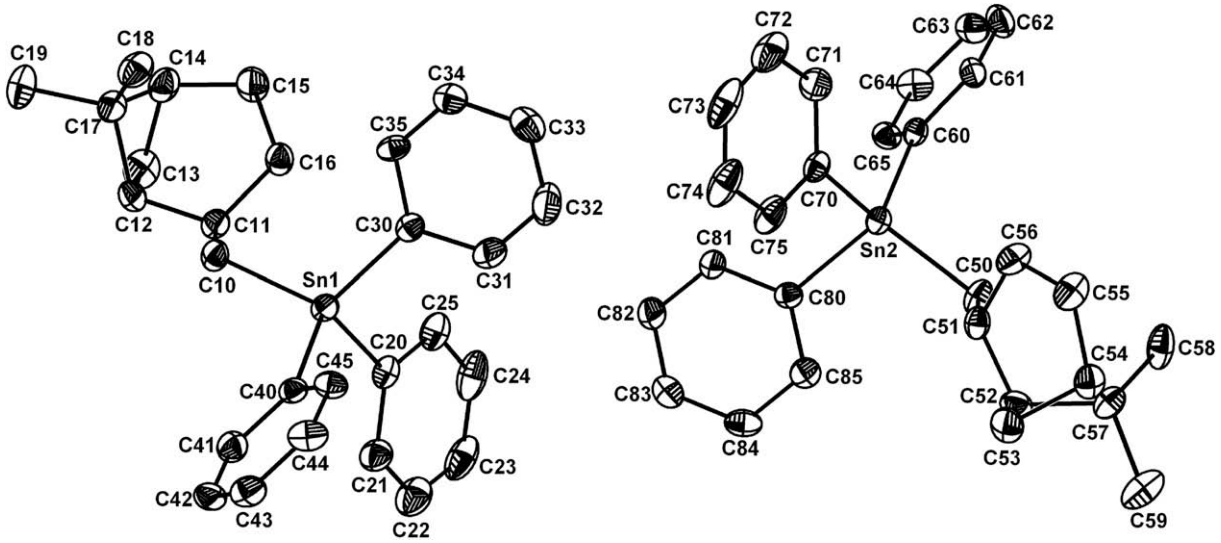


Fig. 1. Molecular structure of *cis*-MyrSnPh$_3$ (**1**). Selected bond parameters (Å, °): C10–Sn1 2.152(4), C20–Sn1 2.152(5), C30–Sn1 2.120(5), C40–Sn1 2.159(5), C50–Sn2 2.156(4), C60–Sn2 2.134(5), C70–Sn2 2.145(5), C80–Sn2 2.164(5), C10–Sn1–C20 111.0(2), C10–Sn1–C30 116.6(2), C10–Sn1–C40 107.3(2), C20–Sn1–C30 106.5(2), C20–Sn1–C40 109.2(2), C30–Sn1–C40 106.1(2), C50–Sn2–C60 110.8(2), C50–Sn2–C70 114.6(2), C50–Sn2, C80 107.6(2), C60–Sn2–C70 111.3 (2), C60–Sn2–C80 108.0(2), C70–Sn2–C80 104.1(2).

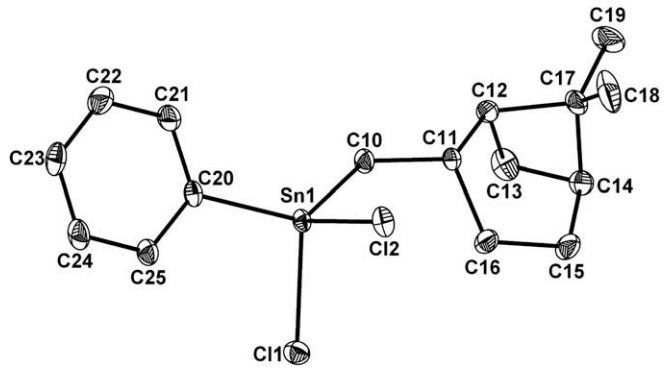


Fig. 3. Molecular structure of *trans*-MyrSnPhCl$_2$ (**6**). Selected bond parameters (Å, °): Sn1–C10 2.132(2), Sn1–C20 2.120(2), Sn1–Cl1 2.3477(7), Sn1–Cl2 2.3768(7), C10–Sn1–C20 129.20(7), C10–Sn1–Cl1 110.41(5),C20–Sn1–Cl1 105.24(5), C10–Sn1–Cl2 105.82(5), C20–Sn1–Cl2 102.01(5), Cl1–Sn1–Cl2 100.25(2).

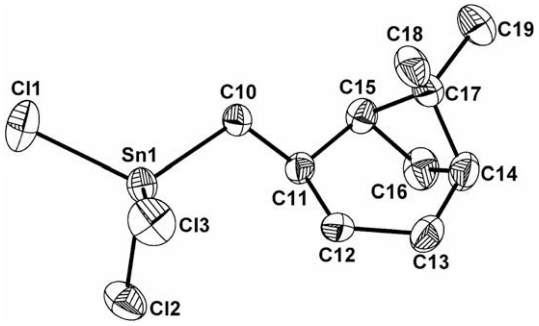


Fig. 4. Molecular structure of *cis*-MyrSnCl$_3$ (**7**). Selected bond parameters (Å, °): Sn1–C10 2.109(3), Sn1–Cl1 2.2968(1), Sn1–Cl3 2.304(1), Sn1–Cl2 2.313(1), C10–Sn1–Cl1 116.5(8), C10–Sn1–Cl3 114.7(1), Cl1–Sn1–Cl3 102.91(5), C10–Sn1–Cl2 112.7(1), Cl1–Sn1–Cl2 104.51(5), Cl2–Sn1–Cl3 104.28(4).

materials we are currently preparing new classes of chiral polystannanes [6].

4. Experimental

General. Triphenyltin chloride, (1S)-(−)-β-pinene (98%) and all reagents were purchased from commercial sources. ^{119}Sn, ^{13}C and ^{1}H NMR spectra were collected using a Jeol JNM-LA 400 FT spectrometer and Jeol Eclipse+ 500 FT spectrometer. Chemical shifts are referenced against Me_4Si and Me_4Sn. The assignment of the ^{13}C- and ^{1}H-resonances was achieved using standard 2D NMR techniques including ^{1}H–^{1}H COSY, ^{1}H–^{1}H-NOESY, ^{1}H–^{13}C-HSQC and ^{1}H–^{13}C-HMQC pulse programs. IR spectra were recorded with a Nicolet Nexus FT-IR spectrometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of cis-myrtanol. (1S)-(−)-β-pinene (182 g, 1.34 mol) and sodium borohydride (31.5 g, 0.83 mol) were added to THF (600 mL). While cooling the heavily stirred mixture on an ice bath dimethyl sulfate (104.1 g, 0.83 mol) was dropped in slowly so that the temperature was held between 20 and 30 °C. After the addition was completed the reaction mixture was stirred for 16 h at r.t. The mixture was cooled to 0 °C before the addition of water (200 mL), 3 M NaOH (200 mL) and 30% H_2O_2 (200 mL). The mixture was stirred for 1 h before Et_2O (400 mL) was added. The organic layer was washed with water (2 × 200 mL) and sat. NaCl solution (2 × 200 mL), and dried over Na_2SO_4. The solvent was removed *in vacuo* and fractional distillation afforded a colourless oil. The diastereomeric purity of the crude alcohol was 97% (estimated by ^{1}H NMR spectroscopy). To improve the diastereomeric purity, the alcohol was transformed into the mono phthalic ester. Therefore the crude *cis*-myrtanol (55.25 g, 360 mmol) and phthalic anhydride (53.35 g, 360 mmol) was heated in pyridine at 100 °C for 20 h. The mixture was allowed to cool to r.t. and was decanted in ice cold 10% HCl (200 mL). The organic layer was extracted with CH_2Cl_2 (200 mL), washed with water (3 × 100 mL) and dried over Na_2SO_4. The solvent was removed in vacuum and the resulting solid was recrystallized twice from CH_2Cl_2/hexane to yield the *cis*-myrtanyl phthalic

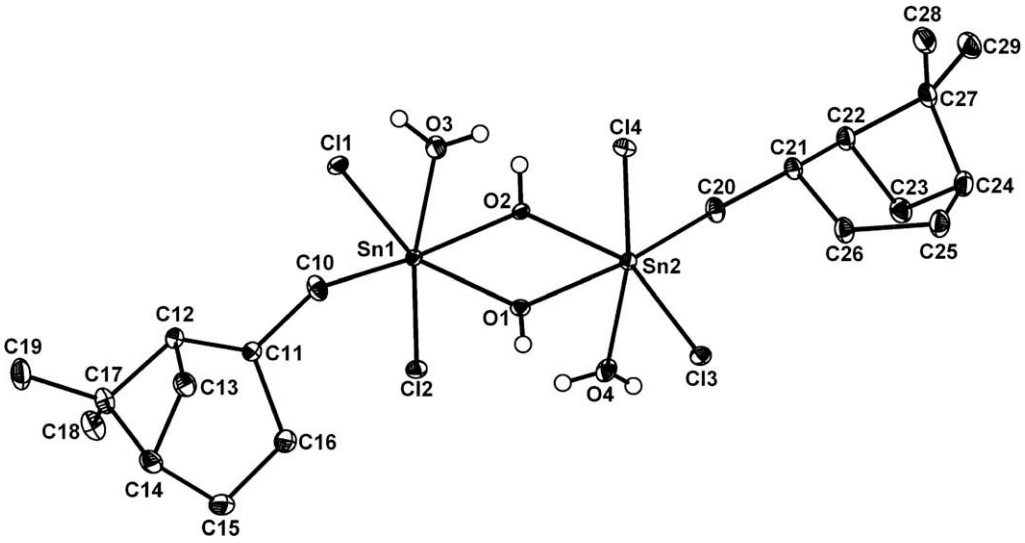


Fig. 5. Molecular structure of [*trans*-MyrSn(OH)Cl$_2$·H$_2$O]$_2$ (**8a**). Selected bond parameters (Å, °): Sn1–C10 2.139(3), Sn1–O1 2.159(2), Sn1–O2 2.080(2), Sn1–O3 2.266(2), Sn1–Cl1 2.434(1), Sn1–Cl2 2.4451(8), Sn2–O1 2.083(2), Sn2–C20 2.142(3), Sn2–O2 2.188(2), Sn2–O4 2.246(2), Sn2–Cl3 2.4272(9), Sn2–Cl4 2.4619(8), O2–Sn1–C10 164.17(9), O2–Sn1–O1 71.03(7), C10–Sn1–O1 100.8(1), O2–Sn1–O3 80.78(8), C10–Sn1–O3 84.81(9), O1–Sn1–O3 83.11(9), O2–Sn1–Cl1 86.58(6), C10–Sn1–Cl1 99.4(1), O1–Sn1–Cl1 156.87(5), O3–Sn1–Cl1 87.76(7), O2–Sn1–Cl2 87.81(6), C10–Sn1–Cl2 106.40(8), O1–Sn1–Cl2 92.21(6), O3–Sn1–Cl2 168.54(6), Cl1–Sn1–Cl2 92.66(3), O1–Sn2–C20 162.68(9), O1–Sn2–O2 70.41(7),C20–Sn2–O2 93.7(1), O1–Sn2–O4 80.58(9), C20–Sn2–O4 90.9(1), O2–Sn2–O4 82.53(8), O1–Sn2–Cl3 85.84(6), C20–Sn2–Cl3 108.97(9), O2–Sn2–Cl3 155.43(5), O4–Sn2–Cl3 87.56(7),O1–Sn2–Cl4 88.41(6), C20–Sn2–Cl4 99.13(8), O2–Sn2–Cl4 91.62(5), O4–Sn2–Cl4 168.74(7), Cl3–Sn2–Cl4 94.01(3), Sn2–O1–Sn1 109.78(9), Sn1–O2–Sn2 108.77(9).

Table 1
^{119}Sn NMR, ^{13}C NMR and ^{1}H NMR (in brackets) chemical shifts and $^{1}J(^{119}Sn–^{13}C)$ coupling constants (in brackets) of **1–8**.

	Sn	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	Ph
1	−104.0 (390 Hz)	49.8 (1.83–1.80)	39.2 (2.42–2.36)	26.5 (1.94–1.85)	26.5 (1.48–1.38) (1.79–1.77)	41.2 (1.67–1.59) (1.77–1.73)	38.7	33.8 (2.18–2.13) (0.69)	28.0 (0.98)	23.4 (1.00)	21.6 (1.67–1.65)	139.5, 137.0, 128.7, 128.4 (7.44–7.43), (7.25–7.24)
3	12.2 (417 Hz)	49.6 (1.82–1.80)	38.4 (2.51–2.43)	25.8 (2.05–1.95)	(1.49–1.39) (1.88–1.85)	40.9 (1.76–1.66) (1.82–1.80)	38.7	33.7 (2.25–2.20) (0.78)	27.9 (1.05)	23.4 (1.00)	27.8 (1.89–1.87)	139.5, 135.7, 130.0, 128.9 (7.53–7.51), (7.35–7.33)
5	40.2 (479 Hz)	49.5 (1.97–1.90)	37.7 (2.69–2.61)	25.3 (2.23–2.16)	(1.59–1.51) (2.03–1.96)	40.8 (1.91–1.85) (1.97–1.90)	38.8	33.6 (2.42–2.37) (0.95)	27.8 (1.21)	23.4 (1.01)	35.4 (2.26–2.23)	139.9, 134.5, 131.3, 129.5 (7.67–7.64), (7.53–7.49)
7	−2.6 (609 Hz)	49.1 (1.94–1.93)	37.7 (2.69–2.62)	24.6 (2.27–2.19)	(1.58–1.50) (2.05–1.98)	40.5 (1.94–1.88) (2.00–1.96)	38.8	33.4 (2.45–2.40) (0.98)	27.7 (1.24)	23.3 (1.08)	41.9 (2.57–2.55)	
2	−103.5 (395 Hz)	49.3 (1.79–1.76)	32.7 (2.45–2.37)	26.7 (1.74–1.70)	(1.44–1.32)	40.7 (1.74–1.70) (1.90–1.86)	39.7	22.8 (2.10–2.04) (1.49)	26.7 (1.12)	19.7 (0.67)	19.8 (1.66–1.53)	139.6, 137.0, 128.7, 128.4 (7.60–7.57), (7.41–7.39)
4	13.3 (423 Hz)	49.2 (1.65–1.62)	32.2 (2.43–2.35)	26.1 (1.73–1.60)	(1.73–1.60)	24.3 (1.80–1.75)	39.9	22.9 (1.99–1.93) (1.31)	26.7 (1.05)	19.8 (0.64)	26.5 (1.73–1.60)	139.5, 135.7, 129.9, 128.9 (7.50–7.48), (7.31–7.29)
6	41.9 (486 Hz)	48.8 (1.67–1.60)	32.0 (2.50–2.42)	25.5 (1.74–1.70)	(1.23–1.15)	24.1 (1.67–1.60) 40.4 (1.80–1.75)	40.0	22.9 (2.00–1.94) (1.25)	26.6 (1.07)	19.9 (0.70)	34.5 (1.96–1.83)	140.0, 134.4, 131.3, 129.4 (7.52–7.50), (7.38–7.34)
8	−1.2 (613 Hz)	48.3 (1.71–1.68)	32.4 (2.58–2.50)	24.8 (1.86–1.83)	(1.33–1.25)	23.9 40.3 (1.91–1.87)	40.2	22.8 (2.12–2.07) (1.33)	26.6 (1.17)	19.9 (0.79)	41.3 (2.36–2.24)	

ester 101.20 g (335 mmol; d.e. >99%). For the base hydrolysis the mono phthalic ester (101.00 g, 334 mmol) was refluxed in 3 M NaOH (300 ml) for 16 h. The product was extracted with Et_2O (200 mL) and the organic layer was washed with water (2 × 100 mL) and dried over Na_2SO_4. After the solvent was removed *in vacuo* distillation yielded *cis*-myrtanol (51.14 g, 331 mmol, 97%; b.p. 101 °C/11 mbar; d.e. >99%) as a viscous colourless oil.

cis-Myrtanyl phthalic ester. Yield 101 g, 335 mmol. M.p. 128–129 °C. (Lit. m.p. 124.5–125.5 °C) [13] $[\alpha]_D$: −3.7 (c = 0.6, $CHCl_3$). ^{1}H NMR: δ = 12.53 (1H, s; O-*H*), 7.88 (1H, dd; H-3′), 7.67 (1H, dd; H-6′), 7.57 (1H, dt; H-5′), 7.53 (1H, dt; H-4′), 4.28 (2H, dd; ^3J(2–10) = 7.9 Hz; H-10), 2.54–2.47 (1H, m; H-2), 2.36–2.31 (1H, m; Hs(e)-7), 2.02–2.0 (1H, m; H-1), 1.96–1.81 (3H, m; H-4, Hs(e)-3), 1.89–1.81 (1H, m; H-5), 1.58–1.50 (1H, m; Ha(a)-3), 1.17 (3H, s; H-8), 1.02 (3H, s; H-9), 0.92 (1H, d, $^2J(^1H–^1H)$ = 10 Hz; Ha(a)-7). ^{13}C-{^{1}H} NMR: δ = 172.7 (C-8′), 168.0 (C-7′), 133.5 (C-1′), 132.0 (C-5′), 130.6 (C-4′), 129.8 (C-2′), 129.6 (C-3′), 128.6 (C-6′), 70.3 (C-10), 43.0 (C-1), 41.1 (C-5), 39.9 (C-2), 38.4 (C-6), 32.8 (C-7), 27.7 (C-8), 25.7 (C-4), 23.1 (C-9), 18.5 (C-3). Anal. Calc. for $C_{18}H_{22}O_4$ (302.37): C, 71.50; H, 7.33. Found: C, 71.34; H, 7.21%.

cis-Myrtanol. Yield 51 g, 332 mmol. $[\alpha]_D$: −19.8 (c = 1.77 $CHCl_3$). ^{1}H NMR: δ = 4.19 (1H, s; O-*H*), 3.35–3.26 (2H, m; H-10), 2.21–2.15 (1H, m; Hs(e)-7), 2.08–2.00 (1H, m; H-2), 1.86–1.83 (1H, m; H-1), 1.79–1.65 (4H, m; H-4, Ha(e)-3, H-5), 1.31–1.25 (1H, m; Hs(a)-3), 1.01 (3H, s; H-8), 0.80 (3H, s; H-9), 0.75 (1H, d, $^2J(^1H–^1H)$ = 10 Hz; Ha(a)-7). ^{13}C-{^{1}H} NMR: δ = 66.7 (C-10), 43.7 (C-2), 42.6 (C-1), 41.1 (C-5), 38.1 (C-6), 32.8 (C-7), 27.6 (C-8), 25.6 (C-4), 22.9 (C-9), 18.5 (C-3) [14].

Synthesis of trans-myrtanol. trans-Myrtanol was prepared in the same manner as described above in the first instance. Before performing the hydrolysis/oxidation step isomeric xylenes (300 mL) were added to the reaction mixture. After the complete removal of the THF *in vacuo* the reaction mixture was refluxed at 140 °C for 20 h. The mixture was allowed to cool to r.t. and the removed THF re-added, followed by hydrolysis/oxidation and purification steps described before. Crude *trans*-myrtanol was obtained in a diastereomeric purity of 74% (97.58 g, 48% yield). Synthesis and repeated recrystallization of the *trans*-myrtanyl phthalic ester from 55.25 g (360 mmol) crude *trans*-myrtanol gave 68.15 g (63% yield) of 97% diastereomeric purity. Base hydrolysis of this amount afforded *trans*-myrtanol (33.6 g, 218 mmol, 97%, d.e. 97%) as a viscous colourless oil (99–100 °C/11 mbar).

trans-Myrtanyl phthalic ester. Yield 68 g, 225 mmol. M.p. 107–108 °C. (Lit. m.p. 108.5–109 °C) [13] $[\alpha]_D$: −19.2 (c = 0.64, $CHCl_3$). ^{1}H NMR: δ = 11.77 (1H, s; O-*H*), 7.89 (1H, dd; H-3′), 7.67 (1H, dd; H-6′), 7.58 (1H, dt; H-5′), 7.53 (1H, dt; H-4′), 4.14 (2H, d; ^3J(2–10) = 7.2 Hz; H-10), 2.45–2.38 (1H, m; H-2), 2.09–2.04 (1H, m; Hs(e)-7), 1.88–1.83 (1H, m; H-5), 1.88–1.85 (1H, m; H-1), 1.81–1.65 (3H, m; H-4, Hs(e)-3), 1.41–1.32 (1H, m; Ha(a)-3), 1.36 (1H, d, ^2J = 10.2 Hz; Ha(a)-7), 1.18 (3H, s; H-8), 0.81 (3H, s; H-9). ^{13}C-{^{1}H} NMR: δ = 172.5 (C-8′), 168.2 (C-7′), 133.6 (C-1′), 132.0 (C-5′), 130.6 (C-4′), 129.9 (C-2′), 129.6 (C-3′), 128.6 (C-6′), 69.6 (C-10), 42.4 (C-1), 40.7 (C-5), 39.1 (C-6), 34.0 (C-2), 26.5 (C-8), 23.9 (C-4), 23.3 (C-7), 20.0 (C-9), 18.2 (C-3). Anal. Calc. for $C_{18}H_{22}O_4$ (302.37): C, 71.50; H, 7.33. Found: C, 71.38; H, 7.19%.

trans-Myrtanol. Yield 33 g, 218 mmol. $[\alpha]_D$: −27.2 (c = 4.6, $CHCl_3$). ^{1}H NMR: δ = 3.40 (1H, s; O-*H*), 3.29–3.27 (2H, m; H-10), 2.10–2.02 (1H, m; H-2), 1.98–1.93 (1H, m; Hs(e)-7), 1.84–1.79 (2H, m; H-1, H-5), 1.77–1.73 (1H, m; Hs(a)-4), 1.71–1.66 (1H, m; Ha(e)-4), 1.57–1.49 (1H, m; Hs(e)-3), 1.23 (1H, d, $^2J(^1H–^1H)$ = 10 Hz; Ha(a)-7), 1.19–1.10 (1H, m; Ha(a)-3), 1.14 (3H, s; H-8), 0.78 (3H, s; H-9). ^{13}C-{^{1}H} NMR: δ = 66.1 (C-10), 42.0 (C-1), 40.8 (C-5), 38.9 (C-6), 37.3 (C-2), 27.8 (C-8), 24.0 (C-4), 23.2 (C-7), 20.0 (C-9), 18.1 (C-3) [14].

Synthesis of cis- and trans-Myrtanyl chloride. A solution of the appropriate myrtanol (25.0 g, 162 mmol) and triphenylphosphine (90.0 g, 343 mmol) in carbon tetrachloride (450 mL) was refluxed

Table 2
Crystal data and structure refinement for **1**, **3**, **6**, **7** and **8a**.

	1	**3**	**6**	**7**	**8a**
Formula	$C_{28}H_{32}Sn$	$C_{22}H_{27}ClSn$	$C_{16}H_{22}Cl_2Sn$	$C_{10}H_{17}Cl_3Sn$	$C_{20}H_{40}Cl_4O_4Sn_2$
Formula weight (g mol^{-1})	487.23	445.58	403.93	362.28	723.70
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Crystal size (mm)	0.80 × 0.35 × 0.28	0.40 × 0.15 × 0.15	0.40 × 0.30 × 0.18	0.40 × 0.40 × 0.40	0.50 × 0.25 × 0.20
Space group	*P*1	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a (Å)	10.433(3)	10.078(2)	9.889(3)	6.6915(4)	11.128(3)
b (Å)	10.902(3)	10.950(2)	10.779(3)	9.6701(6)	6.5827(17)
c (Å)	11.554(3)	19.136(4)	15.762(5)	21.6218(14)	18.191(5)
α (°)	77.234(5)	90	90	90	90
β (°)	68.671(5)	90	90	90	95.561(5)
γ (°)	79.775(7)	90	90	90	90
V (Å^3)	1187.0(6)	2111.7(7)	1680.2(9)	1399.09(15)	1326.3(6)
Z	2	4	4	4	2
$D_{calcd.}$ (mg m^{-3})	1.363	1.402	1.597	1.720	1.812
Temperature (K)	153	293	173	293	133
μ (mm^{-1})	1.087	1.337	1.824	2.364	2.310
F(000)	500	904	808	712	720
θ range (°)	1.9–30.5	2.1–28.4	2.3–30.5	1.9–27.5	1.0–30.5
Index ranges	$-12 \leqslant h \leqslant 14$	$-12 \leqslant h \leqslant 2$	$-14 \leqslant h \leqslant 13$	$-7 \leqslant h \leqslant 8$	$-21 \leqslant h \leqslant 19$
	$-12 \leqslant k \leqslant 15$	$-14 \leqslant k \leqslant 13$	$-15 \leqslant k \leqslant 14$	$-12 \leqslant k \leqslant 12$	$-17 \leqslant k \leqslant 17$
	$-16 \leqslant l \leqslant 16$	$-22 \leqslant l \leqslant 23$	$-22 \leqslant l \leqslant 22$	$-19 \leqslant l \leqslant 28$	$-34 \leqslant l \leqslant 34$
No. of reflections collected	14775	5917	20986	8733	16600
Completeness to θ_{max} (%)	97.2	95.3	99.6	99.5	99.8
No. of independent reflections [$R_{(int)}$]	9864	3634	5124	3178	7725
No. of reflections observed with ($I > 2\sigma(I)$)	9344	2254	4892	2815	7348
No. of refined parameters	523	217	172	127	293
Goodness-of-fit (GOF) (F^2)	1.045	0.844	1.087	1.006	1.134
R_1 (F) ($I > 2\sigma(I)$)	0.0250	0.0396	0.0163	0.0289	0.0192
wR_2 (F^2) (all data)	0.0673	0.0578	0.0366	0.0626	0.0555
$(\Delta/\sigma)_{max}$	<0.001	<0.001	<0.001	<0.001	<0.001
Flack parameter	0.000(5)	0.000(1)	0.000(1)	0.00(2)	0.002(1)
Largest difference peak/hole (e Å^{-3})	1.908/−0.611	0.972/−0.769	0.290/−0.561	0.471/−0.245	1.124/−0.759

for 30 h. After cooling to r.t., about 300 mL of hexane were added, and the white precipitate of triphenylphosphine oxide was removed by filtration with a Büchner funnel. In order to remove the residual triphenylphosphine oxide the filtrate was filtered through a silica gel filled column (hexane was used as eluent). After evaporation of the solvent, fractional distillation afforded the desired chloride.

cis-Myrtanyl chloride. Yield 19.9 g, 115 mmol, 71%. B.p. 93–94 °C/16 mbar. $[\alpha]_D$: −25.6 (c = 0.18, $CHCl_3$). ^{1}H NMR: δ = 3.49 (1H, dd, ^2J = 10.6 Hz, ^3J(2–10) = 7.8 Hz; H-10), 3.46 (1H, dd, ^2J = 10.4 Hz, ^3J(2–10′) = 8.4 Hz; H-10′), 2.40–2.33 (2H, m; H-2, Hs(e)-7), 2.08–2.06 (1H, m; H-5), 2.05–1.98 (1H, m; Ha(e)-3), 1.98–1.92 (1H, m; Hs(e)-4), 1.93–1.89 (1H, m; H-1), 1.88–1.83 (1H, m; Ha(a)-4), 1.53–1.45 (1H, m; Hs(a)-3), 1.18 (3H, s; H-8), 0.96 (3H, s; H-9), 0.91 (1H, d, ^2J(^{1}H–^{1}H) = 9.8 Hz; Ha(a)-7). ^{13}C-{^{1}H} NMR: δ = 49.8 (C-10), 43.9 (C-5), 43.9 (C-2), 41.1 (C-1), 38.4 (C-6), 32.8 (C-7), 27.7 (C-8), 25.7 (C-4), 23.1 (C-9), 20.3 (C-3). Anal. Calc. for $C_{10}H_{17}Cl$ (172.70): C, 69.55; H, 9.92. Found: C, 69.62; H, 9.96%.

trans-Myrtanyl chloride. Yield 23.4 g, 135 mmol, 84%. B.p. 93–94 °C/17 mbar. $[\alpha]_D$: −25.0 (c = 0.20, $CHCl_3$). ^{1}H NMR: δ = 3.32–3.31 (1H, m; H-10), 3.30–3.29 (1H, m; H-10′), 2.30–2.22 (1H, m; H-2), 2.08–2.02 (1H, m; Hs(e)-7), 1.94–1.91 (1H, m; H-1), 1.89–1.84 (1H, m; H-5), 1.82–1.69 (3H, m; H-4, Hs(e)-3), 1.33–1.23 (1H, m; Ha(a)-3), 1.28 (1H, d, ^2J(^{1}H–^{1}H) = 10 Hz; Ha(a)-7), 1.21 (3H, s; H-8), 0.82 (3H, s; H-9). ^{13}C-{^{1}H} NMR: δ = 49.2 (C-10), 43.3 (C-1), 40.7 (C-5), 39.3 (C-6), 37.8 (C-2), 26.5 (C-8), 23.9 (C-4), 23.2 (C-7), 20.2 (C-3), 19.9 (C-9). Anal. Calc. for $C_{10}H_{17}Cl$ (172.70): C, 69.55; H, 9.92. Found: C, 69.67; H, 10.03%.

*Synthesis of cis-myrtanyltriphenyltin (**1**) and trans-myrtanyltriphenyltin (**2**).* Mg turnings (1.86 g, 76.5 mmol) covered with dry THF (8 mL) were activated by addition of 1,2-dibromoethane (150 μL). To this suspension the appropriate myrtanyl chloride (10.85 g, 62.8 mmol) dissolved in THF (60 mL) was slowly added. The mixture was refluxed for 17 h. After cooling to room temperature the Grignard reagent was decanted from the excess Mg and added dropwise to a solution of triphenyltin chloride (24.20 g, 62.8 mmol) in THF (130 mL). The mixture was stirred for 18 h at room temperature before *n*-pentane (50 mL) and water (80 mL) were added. The organic layer was washed with water (2 × 80 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure, the remaining oil dissolved in Et_2O (50 mL) and stirred with a saturated solution of KF (40 mL) for 2 h. The organic layer was washed with water (3 × 30 mL) and dried over Na_2SO_4. The solvent and organic by-products were removed under reduced pressure to yield the desired product.

1. Recrystallization from hot methanol gave colourless crystals. Yield 21.34 g, 43.8 mmol, 70%. M.p. 76 °C. $[\alpha]_D$: −16.7 (c = 2.65, $CHCl_3$). Anal. Calc. for $C_{28}H_{32}Sn$ (487.27): C, 69.02; H, 6.62. Found: C, 69.05; H, 6.40%.

2. The product is a colourless oil. Yield 23.87 g, 49.0 mmol, 78%. $[\alpha]_D$: −4.8 (c = 1.33, $CHCl_3$). Anal. Calc. for $C_{28}H_{32}Sn$ (487.27): C, 69.02; H, 6.62. Found: C, 69.07; H, 6.78%.

*Synthesis of cis-myrtanyldiphenyltin chloride (**3**) and trans-myrtanyldiphenyltin chloride (**4**).* A solution of the appropriate myrtanyltriphenyltin (19.92 g, 40.9 mmol) in CH_2Cl_2 (130 mL) was cooled at 0 °C and iodine (20.40 g, 80.4 mmol) added in small portions. The solvent and iodobenzene were removed under reduced pressure. The remainder was dissolved in Et_2O (90 mL) and stirred with a saturated solution of NH_4Cl (3 × 60 mL) for 1 h. The organic layer was washed with water (3 × 50 mL) and dried over Na_2SO_4. The removal of the solvent provided the desired product.

3. Recrystallization from CH_2Cl_2/hexane afforded colourless crystals. Yield 15.81 g, 35.5 mmol, 87%. M.p. 98 °C. $[\alpha]_D$: −17.2 (c = 1.07, $CHCl_3$). Anal. Calc. for $C_{22}H_{27}ClSn$ (445.62): C, 59.30; H, 6.11. Found: C, 59.17; H, 5.85%.

4. The product is a colourless oil. Yield 13.85 g, 31.1 mmol, 76%. $[\alpha]_D$: −2.4 (c = 0.84, $CHCl_3$). Anal. Calc. for $C_{22}H_{27}ClSn$ (445.62): C, 59.30; H, 6.11. Found: C, 59.49; H, 6.01%.

*Synthesis of cis-myrtanylphenyltin dichloride (**5**) and trans-myrtanylphenyltin dichloride (**6**).* A solution of the appropriate myrtanyltriphenyltin (15.00 g, 30.8 mmol) in CH_2Cl_2 (100 mL) was cooled at 0 °C and iodine (15.31 g, 60.3 mmol) added in small portions. The solvent and iodobenzene were removed under reduced pressure. The remainder was dissolved in Et_2O (70 mL) and stirred with a saturated solution of NH_4Cl (3 × 40 mL) for 1 h. The organic layer was washed with water (3 × 50 mL) and dried over Na_2SO_4. The removal of the solvent provided the desired product that was subject to Kugelrohr distillation (200 °C/10^{-2} mbar).

5. Recrystallization from CH_2Cl_2/hexane gave a colourless solid. Yield 10.49 g, 26.0 mmol, 84%. M.p. 59 °C. $[\alpha]_D$: −23.1 (c = 1.00, $CHCl_3$). Anal. Calc. for $C_{16}H_{22}Cl_2Sn$ (403.97): C, 47.57; H, 5.49. Found: C, 47.00; H, 5.46%.

6. Colourless crystals from the melt. Yield 9.91 g, 24.5 mmol, 80%. M.p. 47 °C. $[\alpha]_D$: −0.6 (c = 1.73, $CHCl_3$). Anal. Calc. for $C_{16}H_{22}Cl_2Sn$ (403.97): C, 47.57; H, 5.49. Found: C, 47.21; H, 5.19%.

*Synthesis of cis-myrtanyltin trichloride (**7**) and trans-myrtanyltin trichloride (**8**).* The appropriate myrtanyltriphenyltin (5.00 g, 10.3 mmol) was suspended in conc. HCl (100 mL) and refluxed for 48 h. The crude product was extracted with CH_2Cl_2 (70 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure.

7. Recrystallization from hexane gave colourless crystals. Yield 3.42 g, 9.4 mmol, 92%. M.p. 88 °C. $[\alpha]_D$: −31.5 (c = 0.71, $CHCl_3$). Anal. Calc. for $C_{10}H_{17}Cl_3Sn$ (362.31): C, 33.15; H, 4.73. Found: C, 33.07; H, 4.79%.

8. The product is a colourless oil. Yield 3.15 g, 8.7 mmol, 85%. $[\alpha]_D$: +5.9 (c = 1.73, $CHCl_3$). Anal. Calc. for $C_{10}H_{17}Cl_3Sn$ (362.31): C, 33.15; H, 4.73. Found: C, 32.95; H, 4.73%.

8a. The colourless crystalline hydrolysis product [*trans*-MyrSn(OH)$Cl_2 \cdot H_2O]_2$ was obtained in an attempt to recrystallize **8** from hexane at aerobic conditions. M.p. 83 °C. $[\alpha]_D$: +7.2 (c = 0.85, $CHCl_3$). IR (KBr): ν(OH): 3473shd, 3381vs cm^{-1}. Anal. Calc. for $C_{20}H_{40}Cl_4O_4Sn_2$ (723.77): C, 33.19; H, 7.77. Found: C, 32.79; H, 5.09%.

X-ray crystallography. Intensity data were collected on a Bruker SMART 1000 area detector with graphite-monochromated Mo Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS [15]. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WINGX 2002 [16]. Full-matrix least-squares refinements on F^2, using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically. For **8a**, the hydrogen atoms attached to oxygen atoms was located during the refinement and was also refined isotropically. Crystal and refinement details are collected in Table 2. Figures were created using DIAMOND [17].

Supplementary material

CCDC 702006, 702007, 702008, 702009 and 702010 contain the supplementary crystallographic data for **1**, **3**, **6**, **7** and **8a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Mrs. Irene Brüdgam (Freie Universität Berlin) is thanked for the X-ray data collection. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

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