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Structural assignment of organotin hydrides containing the oxazoline ligand

Dobrochna Matkowska [a,b], Maciej Gola [a,b], Marcin Śnieżek [a,b], Piotr Cmoch [b,c,*], Krzysztof Staliński [b,*]

[a] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
[b] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
[c] Pharmaceutical Research Institute, Rydygiera 8, 01-793 Warsaw, Poland

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Abstract

A series of triorganotin hydrides and diorganotin dihydrides containing the optically active 2-(4-isopropyl-2-oxazolinyl)-5-phenyl ligand have been characterized by means of the multinuclear low-temperature NMR investigations, the results of which are discussed. In the corresponding organotin hydrides values of the $^{1}J(^{1}H–^{117/119}Sn)$ couplings appeared to be temperature dependent, supporting an axial/equatorial position of the hydrogen attached to the tin.

Keywords: Sn–N coordination; Tin hydrides; NMR spectroscopy

1. Introduction

The organotin hydrides with the potentially chelating ligands have been receiving increasing attention in recent years due to their ability for enantioselective quenching of trigonal sp^2 intermediates such as radicals [1–8].We have recently described the synthesis and NMR study of organotin hydrides **1**–**5** containing the chiral oxazoline moiety (Fig. 1) [9,10]. On the basis of the NMR results, especially the $J(^{15}N–^{117/119}Sn)$ coupling constants it appeared that the tin atom in the hydrides was weakly intramolecularly coordinated to the nitrogen atom from the oxazoline part. However, only in case of diastereomeric triorganotin hydrides **4**–**5** we were able to propose axial/equatorial positions of the hydrogen atom attached to the tin [11]. In connection with some free radical experiments done in our laboratory, it was of interest to estimate an exact position of the hydrogen atom in the investigated organotin hydrides. Herein we report our efforts along these lines based on the low-temperature NMR study of organotin hydrides **1**–**11**.

2. Synthesis

2.1. Methods and materials

The ^{1}H, ^{13}C, ^{117}Sn NMR spectra were measured in $CDCl_3$ at 303 K or in toluene-D_8 at 273 and 253 K on a Bruker DRX Avance 500 spectrometer equipped with a TBI 500SB H-C/BB-D-05 Z-G probehead, operating at 500.133, 125.773, and 186.501 MHz for ^{1}H, ^{13}C and ^{117}Sn, respectively. The assignment of the ^{1}H and ^{13}C NMR signals of all the compounds studied was made using results of 2D methods including $^{1}H–^{13}C$ gradient selected Heteronuclear Single Quantum Correlation (HSQC) and Heteronuclear Multiple Bond Correlation (HMBC). The ^{117}Sn NMR spectra were recorded using inverse gated decoupling sequence. The ^{1}H and ^{13}C NMR measurements in $CDCl_3$ and toluene-D_8 for all of the compounds studied were performed using internal tetramethylsilane as a standard, whereas for ^{117}Sn NMR external terminal tetramethyltin

* Corresponding authors. Tel.: +48 22 632 09 04; fax: +48 22 632 66 81.
E-mail addresses: piocmo@icho.edu.pl (P. Cmoch), stalinsk@icho.edu.pl (K. Staliński).

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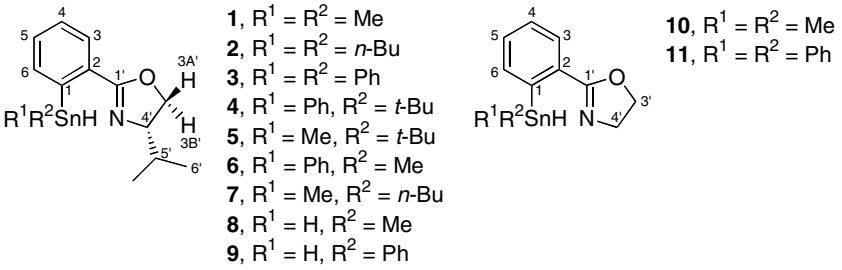


Fig. 1. The Sn–N coordinated organotin hydrides **1**–**11**.

was used. IR spectra were measured on a Perkin Elmer FT-IR spectrophotometer. EI, ESI and HRMS spectra were determined on an ADM 604 Inectra GmbH spectrometer. Thin layer chromatographies were run on silica gel (Merck 60 F_{254}) plates. HPLC analyses were run using a Merck-Hitachi apparatus and Kromasil SI 60/7 μm column.

2.1.1. General procedure for the preparation of tetraorganotin compounds *12*, *13*, *15*, *16*

A solution of the *o*-lithiophenyloxazole prepared by metallation of 2-(4-bromo-phenyl)-4-isopropyl-4,5-dihydro-oxazole (1.39 g, 5.0 mmoles) or 2-(4-bromo-phenyl)-4,5-dihydro-oxazole (1.13 g, 5.0 mmoles) with *n*-butyl lithium (3.15 ml, 5.0 mmoles, 1.6 M sln in hexane) was slowly added to a solution of R_3SnX (Ph_2SnMeI, *n*-$BuMe_2SnI$, Me_3SnCl, Ph_3SnCl, 5.0 mmoles) at −70 °C and the reaction mixture was stirred for an additional hour and quenched by water. After addition of diethyl ether the organic layer was worked up in the usual manner to give a crude product, which was purified by column chromatography (hexanes/ethyl acetate) to give tetraorganotin compounds **12**–**16**.

*2.1.1.1. 2-[(Methyldiphenylstannyl)-phenyl]-4-(S)-isopropyl-4,5-dihydro-oxazole (**12**).* White crystals, mp 61–63 °C, 89%. $[\alpha]_D = +8.5$ ($CHCl_3 c = 1$). IR cm^{-1} (film): 3061, 2959, 2928, 2903, 2873, 1648, 1480, 1427, 1354, 1086, 726, 699. ^1H NMR ($CDCl_3$) ppm: 7.95 (1H, dd, $J =$ 1.27 Hz, $J = 7.8$ Hz, $H_{arom.}$), 7.52–7.28 (13H, m, $H_{arom.}$), 4.35 (1H, dd, $J = 8.4$ Hz, $J = 9.8$ Hz, =NCHCH_2O–, C3A′), 4.00 (1H, *t*, $J = 8.8$ Hz, =NCHCH_2O, C3B′), 3.74 (1H, ddd, $J = 15.5$ Hz, $J = 9.4$ Hz $J = 6.2$ Hz, =NC*H*CH_2O–), 1.66-1.56 (1H, m, –C*H*Me_2), 0.74 (3H, d, $J = 6.8$ Hz, –CH*Me*$_2$), 0.73 [3H, s, ^2J(1H–$^{117/119}$Sn) = 59.2/61.9 Hz, –SnMe], 0.67 (3H, d, $J = 6.8$ Hz, –CH*Me*$_2$). ^{13}C NMR ($CDCl_3$) ppm: 165.1 [$J(^{13}C–^{117/119}Sn) = 12.3$ Hz, C1′], 144.0 [$J(^{13}C–^{117/119}Sn) = 485/507$ Hz], 143.7 [$J(^{13}C–^{117/119}Sn) = 491/513$ Hz], 142.8 [$J(^{13}C–^{117/119}Sn) = 533/558$ Hz], 138.1 [$J(^{13}C–^{117/119}Sn) =$ 40.3 Hz], 136.7 [$J(^{13}C–^{117/119}Sn) = 36.0$ Hz], 136.6 [$J(^{13}C–^{117/119}Sn) = 35.8$ Hz], 133.4 [$J(^{13}C–^{117/119}Sn) =$ 22.2 Hz], 130.8 [$J(^{13}C–^{117/119}Sn) = 53.2$ Hz], 128.7 [$J(^{13}C–^{117/119}Sn) = 10.2$ Hz], 128.1, 128.0, 127.9, 127.8, 127.7, 72.1 [$J(^{13}C–^{117/119}Sn) = 4.3$ Hz, C4′], 70.4 (C3′), 31.9 (C5′), 19.1 (C6′), 17.6 (C6′), −6.3 [$J(^{13}C–^{117/119}Sn) =$ 444/464 Hz, –SnMe]. ^{117}Sn NMR ($CDCl_3$) ppm: −117.7. MS (EI) *m*/*z*: 462 (M^+−Me, 29), 400 (100), 376 (8), 314 (16), 222 (6). Anal. Calcd for $C_{25}H_{27}N_1O_1Sn_1$: C, 63.06; H, 5.72; N, 2.94. Found: C, 63.08; H, 5.71; N, 2.94%.

*2.1.1.2. 2-[(Dimethyl-n-butylstannyl)-phenyl]-4-(S)-isopropyl-4,5-dihydro-oxazole (**13**).* Yellowish oil, 85%. IR cm^{-1} (film): 3055, 2958, 2920, 2872, 2854, 1648, 1464, 1351, 1084, 1043, 727. ^1H NMR ($CDCl_3$) ppm: 7.91 (1H, dd, $J = 7.5$ Hz, $J = 1.1$ Hz, $H_{arom.}$), 7.63 (1H, dd, $J = 7.2$ Hz, $J = 1.2$ Hz, $H_{arom.}$), 7.41 (1H, dt, $J = 7.3$ Hz, $J = 1.3$ Hz, $H_{arom.}$), 7.34 (1H, dt, $J = 7.5$ Hz, $J = 1.4$ Hz, $H_{arom.}$), 4.40 (1H, dd, $J = 8.9$ Hz, $J = 7.5$ Hz, =NCHCH_2O–), 4.10–4.00 (2H, m, =NCHCH_2O–), 1.93–1.83 (1H, m, –C*H*Me_2), 1.52–1.44 (2H, m, –CH_2CH_2CH_2CH_3), 1.33–1.25 (2H, m, –CH_2CH_2CH_2CH_3), 1.06–1.01 (2H, m, –CH_2CH_2CH_2CH_3), 1.03 (2H, d, $J = 6.8$ Hz, –CH*Me*$_2$), 0.91 (3H, d, $J = 6.8$ Hz, –CH*Me*$_2$), 0.86 (3H, *t*, $J = 7.3$ Hz, –CH_2CH_2CH_2CH_3), 0.22 [3H, s, $^2J(^1H–^{117/119}Sn) = 50.2/52.3$ Hz, –SnMe$_2$], 0.20 [3H, s, $^2J(^1H–^{117/119}Sn) = 49.6/51.7$ Hz, –SnMe$_2$]. ^{13}C NMR ($CDCl_3$) ppm: 164.9 [$J(^{13}C–^{117/119}Sn) = 9.4$ Hz, C1′], 145.3 [$J(^{13}C–^{117/119}Sn) = 440/460$ Hz, C1], 136.6 [$J(^{13}C–^{117/119}Sn) = 33.7$ Hz], 133.4 [$J(^{13}C–^{117/119}Sn) =$ 19.3 Hz], 130.2 [$J(^{13}C–^{117/119}Sn) = 44.8$ Hz], 128.0 [$J(^{13}C–^{117/119}Sn) = 31.0$ Hz], 127.9 [$J(^{13}C–^{117/119}Sn) =$ 9.3 Hz], 72.8 (C3′), 70.0 [$J(^{13}C–^{117/119}Sn) = 33.0$ Hz, C4′], 32.3 (C5′), 29.0 [$J(^{13}C–^{117/119}Sn) = 19.9$ Hz, –CH_2CH_2CH_2CH_3], 27.1 [$J(^{13}C–^{117/119}Sn) = 61.0/63.3$ Hz, –CH_2CH_2CH_2CH_3], 19.4 (C6′), 18.0 (C6′), 13.9 [$J(^{13}C–^{117/119}Sn) = 410/429$ Hz, –CH_2CH_2CH_2CH_3], 13.7 (–CH_2CH_2CH_2CH_3), −7.3 [$J(^{13}C–^{117/119}Sn) = 335/350$ Hz, –SnMe$_2$], −7.5 [$J(^{13}C–^{117/119}Sn) = 330/345$ Hz, –SnMe$_2$]. ^{117}Sn NMR ($CDCl_3$) ppm: −49.6. MS (EI) *m*/*z*: 380 (M^+−Me, 95), 338 (100), 308 (28), 252 (32), 238 (19), 222 (38). Anal. Calcd for $C_{18}H_{29}N_1O_1Sn_1$: C, 54.86; H, 7.42; N, 3.55. Found: C, 54.79; H, 7.49; N, 3.45%.

*2.1.1.3. 2-[(Trimethylstannyl)-phenyl]-4,5-dihydro-oxazole (**15**).* Yellowish crystals mp 90–93 °C, 35%. IR cm^{-1} (film): 3064, 3042, 2977, 2959, 2935, 2902, 2879, 1658, 1359, 1329, 1264, 1126, 1086, 1044, 943, 777, 708. ^1H NMR ppm ($CDCl_3$): 7.92 (1H, dd, $J = 7.6$ Hz $J = 0.8$ Hz, $H_{arom.}$), 7.67 (1H, dd, $J = 7.3$ Hz, $J = 0.9$ Hz, $H_{arom.}$), 7.45 (1H, dt, $J = 7.3$ Hz, $J = 1.3$ Hz, $H_{arom.}$), 7.38 (1H,

dt, $J = 7.6$ Hz $J = 1.4$ Hz, $H_{arom.}$), 4.45 (2H, *t*, $J = 9.5$ Hz, $=NCH_2CH_2O-$), 4.00 (2H, *t*, $J = 9.5$ Hz, $=NCH_2CH_2$-O–), 0.25 [9H, s, $^2J(^1H-^{117/119}Sn) = 53.0/54.3$ Hz, $-SnMe_3$]. ^{13}C NMR ppm ($CDCl_3$): 165.9 [$J(^{13}C-^{117/119}Sn) = 10.2$ Hz, C1′], 145.7 [$J(^{13}C-^{117/119}Sn) = 473/495$ Hz, C1], 136.4 [$J(^{13}C-^{117/119}Sn) = 36.4$ Hz], 133.0 [$J(^{13}C-^{117/119}Sn) = 19.5$ Hz], 130.2 [$J(^{13}C-^{117/119}Sn) = 47.2$ Hz], 128.0 [$J(^{13}C-117/119Sn) = 9.6$ Hz], 127.6 [$J(^{13}C-^{117/119}Sn) = 31.9$ Hz], 67.9 (C3′), 54.1 (C4′), −6.2 [$J(^{13}C-^{117/119}Sn) = 364/381$ Hz, $-SnMe_3$]. ^{117}Sn NMR ppm ($CDCl_3$): −53.2. MS (EI) *m/z*: 296 (M^+-Me, 100), 266 (36), 252 (9), 222 (12). Anal. Calcd for $C_{12}H_{17}N_1O_1Sn_1$: C, 46.50; H, 5.53; N, 4.52 Found: C, 46.57; H, 5.63; N, 4.53%.

*2.1.1.4. 2-[(Triphenylstannyl)-phenyl]-4,5-dihydro-oxazole (**16**).* White crystals, mp 163-165 °C, 40%. IR cm^{-1} (KBr): 3058, 3004, 2983, 2877, 1654, 1578, 1560, 1479, 1426, 1363, 1330, 1264, 1192, 1124, 1084, 1069, 1041, 1022, 997, 936. ^1H NMR ppm ($CDCl_3$): 8.05 (1H, dd, $J = 1.4$ Hz, $J = 1.1$ Hz, $H_{arom.}$), 7.75–7.63 (7H, m, $H_{arom.}$), 7.53–7.47 (2H, m, $H_{arom.}$), 7.45–7.38 (9H, m, $H_{arom.}$), 4.37 (2H, *t*, $J = 9.5$ Hz, $=NCH_2CH_2O-$), 3.60 (2H, *t*, $J = 9.5$ Hz, $=NCH_2CH_2O-$). ^{13}C NMR ppm ($CDCl_3$): 166.4 [$J(^{13}C-^{117/119}Sn) = 15.5$ Hz, C1′], 143.2 [$J(^{13}C-^{117/119}Sn) = 571/598$ Hz, C1], 142.9 [$J(^{13}C-^{117/119}Sn) = 560/573$ Hz, C_{Ph}], 138.3 [$J(^{13}C-^{117/119}Sn) = 43.3$ Hz], 137.1 [$J(^{13}C-^{117/119}Sn) = 37.1$ Hz], 132.9 [$J(^{13}C-^{117/119}Sn) = 21.4$ Hz], 131.3 [$J(^{13}C-^{117/119}Sn) = 56.6$ Hz], 129.0 [$J(^{13}C-^{117/119}Sn) = 10.4$ Hz], 128.1 [$J(^{13}C-^{117/119}Sn) = 52.6$ Hz], 128.0 [$J(^{13}C-^{117/119}Sn) = 11.3$ Hz], 127.4 [$J(^{13}C-^{117/119}Sn) = 37.1$ Hz], 68.1 (C3′), 52.6 [$J(^{13}C-^{117/119}Sn) = 5.8$ Hz, C4′]. ^{117}Sn NMR ($CDCl_3$) ppm: −167.4. MS (EI) *m/z*: 496 (M^+-H, 4), 469 (10), 420 (M^+-Ph, 100), 376 (4), 299 (4), 266 (4). Anal. Calcd for $C_{27}H_{23}N_1O_1Sn_1$: C, 65.36; H, 4.67; N, 2.82 Found: C, 65.33; H, 4.80; N, 2.69%.

*2.1.2. General procedure for the preparation of triorganotin iodides **17–20***

A solution of teraorganotin compounds **12** (2.0 mmoles), **13**, **15** and **16** (4.0 mmoles) and I_2 (520 mg, 4.1 mmoles) in THF (20 mL) was stirred at ambient temperature. The mixture was then evaporated and the crude product was recrystalized (if possible) from hexane/CH_2Cl_2 to give the corresponding triorganotin iodides **17–20**.

*2.1.2.1. 2-[(2-Iodo-methyl-phenylstannyl)-phenyl]-4-(S)-isopropyl-4,5-dihydro-oxazole (**17**).* Mixture of diastereoisomers 1.28/1.0, yellowish crystals mp 159–162 °C, 97%. $[\alpha]_D = +15.8$ ($CHCl_3 c = 1$). IR cm^{-1} (film): 3063, 3049, 2961, 2928, 2910, 2873, 1634, 1559, 1480, 1430, 1384, 1137, 1099, 950. MS (EI) *m/z*: 512 (M^+-Me, 2), 450 (3), 400 (100), 314 (31), 222 (20). Anal. Calcd for $C_{19}H_{22}I_1N_1O_1Sn_1$: C, 43.39; H, 4.22; N, 2.66; I, 24.13. Found: C, 43.42; H, 4.26; N, 2.68; I, 22.88%.

Major diastereoisomer **17a**: ^1H NMR ($CDCl_3$) ppm: 8.63 (1H, d, $J = 7.4$ Hz, $H_{arom.}$), 7.90–7.00 (8H, m, $H_{arom.}$), 4.56 (1H, *t*, $J = 9.5$ Hz, $=NCHCH_2O-$, C3A′), 4.36 (1H, *t*, $J = 8.8$ Hz, $=NCHCH_2O-$, C3B′), 4.07–4.00 (1H, m, $=NCHCH_2O-$), 1.55–1.48 (1 H, m, $-CHMe_2$), 1.30 [3H, s, $^2J(^1H-^{117/119}Sn) = 69.9/73.1$ Hz, –SnMe], 0.88 (3H, d, $J = 6.8$ Hz, $-CHMe_2$), 0.82 (3H, d, $J = 6.8$ Hz, $-CHMe_2$). ^{13}C NMR ($CDCl_3$) ppm: 170.4 [$J(^{13}C-^{117/119}Sn) = 17.5$ Hz, C1′], 143.2 [$J(^{13}C-^{117/119}Sn) = 740/774$ Hz], 142.8 [$J(^{13}C-^{117/119}Sn) = 669/701$ Hz], 139.4 [$J(^{13}C-^{117/119}Sn) = 43.5$ Hz], 134.9, 133.0 [$J(^{13}C-^{117/119}Sn) = 33.0$ Hz], 130.0, 129.7, 129.3, 127.2, 126.5, 71.7 (C3′), 68.5 [$J(^{13}C-^{117/119}Sn) = 11.1$ Hz, C4′], 30.3 (C5′), 19.3 (C6′), 15.6 (C6′), 7.0 [$J(^{13}C-^{117/119}Sn) = 544/569$ Hz, –SnMe]. ^{117}Sn NMR ($CDCl_3$) ppm: −178.5.

Minor diastereoisomer **17b**: ^1H NMR ($CDCl_3$) ppm: 8.59 (1 H, d, $J = 7.4$ Hz, $H_{arom.}$), 7.90–7.00 (8H, m, $H_{arom.}$), 4.65 (1H, *t*, $J = 9.4$ Hz, $=NCHCH_2O-$, C3A′), 4.43 (1H, *t*, $J = 8.7$ Hz, $=NCHCH_2O-$, C3B′), 3.92–3.86 (1H, m, $=NCHCH_2O-$), 2.06–2.00 (1H, m, $-CHMe_2$), 1.20 [3H, s, $^2J(^1H-^{117/119}Sn) = 71.9/74.8$ Hz, –SnMe], 0.67 (3H, d, $J = 6.8$ Hz, $-CHMe_2$), 0.44 (3H, d, $J = 6.8$ Hz, $-CHMe_2$). ^{13}C NMR ($CDCl_3$) ppm: 170.3 [$J(^{13}C-^{117/119}Sn) = 18.1$ Hz], 143.9 [$J(^{13}C-^{117/119}Sn) = 708/740$ Hz], 142.1 [$J(^{13}C-^{117/119}Sn) = 672/704$ Hz], 139.6 [$J(^{13}C-^{117/119}Sn) = 42.8$ Hz], 134.9, 133.1 [$J(^{13}C-^{117/119}Sn) = 32.8$ Hz], 130.0, 129.8, 129.4, 127.3, 126.5, 72.6 (C3′), 69.7 [$J(^{13}C-^{117/119}Sn) = 10.7$ Hz, C4′], 30.8 (C5′), 19.1 (C6′), 16.2 (C6′), 6.2 [$J(^{13}C-^{117/119}Sn) = 572/598$ Hz, –SnMe]. ^{117}Sn NMR ($CDCl_3$) ppm: −181.9.

*2.1.2.2. 2-[(2-Iodo-n-butyl-methylstannyl)-phenyl]-4-(S)-isopropyl-4,5-dihydro-oxazole (**18**).* Mixture of diastereoisomers 1.33/1.0, yellowish oil, 97%. IR cm^{-1} (film): 3050, 2958, 2922, 2871, 2855, 1634, 1559, 1382, 1135, 1096, 951, 730. MS (EI) *m/z*: 400 (M^+-Me, 2), 450 (10), 380 (100), 308 (21), 238 (7), 222 (11). Anal. Calcd for $C_{17}H_{26}I_1N_1O_1Sn_1$: C, 40.35; H, 5.18; N, 2.77; I, 25.08. Found: C, 40.42; H, 5.20; N, 2.76; I, 23.78%.

Major diastereoisomer **18a**: ^1H NMR ($CDCl_3$) ppm: 8.54 (1H, d, $J = 7.2$ Hz, $H_{arom.}$), 7.83–7.46 (3H, m, $H_{arom.}$), 4.68 (1H, *t*, $J = 9.7$ Hz, $=NCHCH_2O-$, C3A′), 4.47 (1H, *t*, $J = 8.7$ Hz, $=NCHCH_2O-$, C3B′), 4.20–4.11 (1H, m, $=NCHCH_2O-$), 2.11–2.02 (1H, m, $-CHMe_2$), 1.72–1.56 (4H, m), 1.37–1.25 (2H, m), 1.06–1.00 (6H, m), 0.92–0.83 (6H, m). ^{13}C NMR ($CDCl_3$) ppm: 170.5 [$J(^{13}C-^{117/119}Sn) = 11.9$ Hz, C1′], 144.6 [$J(^{13}C-^{117/119}Sn) = 583/609$ Hz, C1], 139.1 [$J(^{13}C-^{117/119}Sn) = 38.6$ Hz], 132.8 [$J(^{13}C-^{117/119}Sn) = 57.6$ Hz], 129.5, 128.9 [$J(^{13}C-^{117/119}Sn) = 28.4$ Hz], 126.6 [$J(^{13}C-^{117/119}Sn) = 38.8$ Hz], 71.7 (C3′), 68.7 (C4′), 30.6 (C5′), 28.4 [$J(^{13}C-^{117/119}Sn) = 33.7$ Hz, $-CH_2CH_2CH_2CH_3$], 26.2 [$J(^{13}C-^{117/119}Sn) = 101$ Hz, $-CH_2CH_2CH_2CH_3$], 24.1 [$J(^{13}C-^{117/119}Sn) = 550/572$ Hz, $-CH_2CH_2CH_2CH_3$], 19.4 (C6′), 15.6 (C6′), 13.7 ($-CH_2CH_2CH_2CH_3$), 6.0 [$J(^{13}C-^{117/119}Sn) = 478/500$ Hz]. ^{117}Sn NMR ($CDCl_3$) ppm: −111.2.

Minor diastereoisomer **18b**: ^1H NMR ($CDCl_3$) ppm: 8.54 (1 H, d, $J = 7.6$ Hz, $H_{arom.}$), 7.83–7.46 (3H, m, $H_{arom.}$), 4.68 (1H, *t*, $J = 9.7$ Hz, $=NCHCH_2O-$, C3A′),

4.45 (1H, *t*, $J = 9.4$ Hz, =NCHCH_2O–, C3B′), 4.20–4.11 (1H, m, =NCHCH_2O–), 2.11–2.02 (1H, m, –CHMe$_2$), 1.72–1.56 (4H, m), 1.37–1.25 (2H, m), 1.06–1.00 (6H, m), 0.92–0.83 (6H, m). ^{13}C NMR ($CDCl_3$) ppm: 170.5 [J(^{13}C–$^{117/119}$Sn) = 11.9 Hz, C1′], 144.3 [J(^{13}C–$^{117/119}$Sn) = 584/611 Hz, C1], 139.1 [J(^{13}C–$^{117/119}$Sn) = 38.6 Hz], 132.8 [J(^{13}C–$^{117/119}$Sn) = 57.4 Hz], 129.5, 129.0 [J(^{13}C–$^{117/119}$Sn) = 29.0 Hz], 126.6 [J(^{13}C–$^{117/119}$Sn) = 38.8 Hz], 71.8 (C3′), 68.7 (C4′), 30.6 (C5′), 28.2 [J(^{13}C–$^{117/119}$Sn) = 32.7 Hz, –$CH_2CH_2CH_2CH_3$], 26.1 [J(^{13}C–$^{117/119}$Sn) = 94.9 Hz, –$CH_2CH_2CH_2CH_3$], 23.4 [J(^{13}C–$^{117/119}$Sn) = 522/547 Hz, –$CH_2CH_2CH_2CH_3$], 19.6 (C6′), 15.8 (C6′), 13.5 (–CH_2-$CH_2CH_2CH_3$), 6.0 [J(^{13}C–$^{117/119}$Sn) = 507/528 Hz, –SnMe]. ^{117}Sn NMR ($CDCl_3$) ppm: −107.4.

*2.1.2.3. 2-[(2-Iodo-dimethylstannyl)-phenyl]-4,5-dihydro-oxazole (**19**).* Yellowish oil, 99%. IR cm^{-1} (KBr): 3053, 2968, 2927, 2867, 1637, 1559, 1475, 1391, 1344, 1281, 1211, 1137, 1105, 1044, 927. ^{1}H NMR ppm ($CDCl_3$): 8.40 (1H, d, $J = 7.4$ Hz, $H_{arom.}$), 7.75 (1H, d, $J = 7.6$ Hz, $H_{arom.}$), 7.59 (1H, dt, $J = 7.5$ Hz $J = 1.0$ Hz, $H_{arom.}$), 7.43 (1H, dt, $J = 7.5$ Hz $J = 0.9$ Hz, $H_{arom.}$), 4.79 (2H, *t*, $J = 9.5$ Hz, =NCH_2CH_2O–), 3.95 (2H, *t*, $J = 9.6$ Hz, =NCH_2CH_2O–), 0.95 [6H, s, ^2J(^{1}H–$^{117/119}$Sn) = 69.3/71.9 Hz, –SnMe]. ^{13}C NMR ppm: 171.2 [J(^{13}C–$^{117/119}$Sn) = 15.8 Hz, C1′], 143.5 [J(^{13}C–$^{117/119}$Sn) = 596/671 Hz, C1], 138.6 [J(^{13}C–$^{117/119}$Sn) = 42.2 Hz], 132.5 [J(^{13}C–$^{117/119}$Sn) = 62.7 Hz], 129.4 [J(^{13}C–$^{117/119}$Sn) = 11.7 Hz], 128.7 [J(^{13}C–$^{117/119}$Sn) = 29.3 Hz], 126.4 [J(^{13}C–$^{117/119}$Sn) = 41.6 Hz], 71.6 (C3′), 50.1 [J(^{13}C–$^{117/119}$Sn) = 11.9 Hz, C4′], 4.9 [J(^{13}C–$^{117/119}$Sn) = 528/553 Hz, –SnMe]. ^{117}Sn NMR ($CDCl_3$) ppm: −139.4. MS (EI) *m*/*z*: 408 (M^+−Me, 5), 360 (2), 316 (7), 296 (M^+−I, 100), 266 (43), 252 (9). Anal. Calcd for $C_{11}H_{14}I_1O_1N_1Sn_1$: C, 31.32; H, 3.35; N, 3.32; I, 30.08 Found: C, 31.57; H, 3.12; N, 3.32; I, 29.04%.

*2.1.2.4. 2-[(2-Iodo-diphenylstannyl)-phenyl]-4,5-dihydro-oxazole (**20**).* White crystals mp 209–211 °C, 98%. IR cm^{-1}(KBr): 3064, 3021, 2974, 2950, 2906, 2882, 1637, 1560, 1479, 1430, 1390, 1274, 1138, 1109, 1097, 1042, 927, 729, 696, 680. ^{1}H NMR ppm ($CDCl_3$): 8.70 (1H, d, $J = 7.2$ Hz, $H_{arom.}$), 7.89 (1H, d, $J = 7.5$ Hz, $H_{arom.}$), 7.83–7.62 (5H, m, $H_{arom.}$), 7.57 (1H, dt, $J = 7.5$ Hz $J = 1.1$ Hz, $H_{arom.}$), 7.45–7.26 (6H, m, $H_{arom.}$), 4.67 (2H, *t*, $J = 9.6$ Hz, =NCH_2CH_2O–), 3.71 (2H, *t*, $J = 9.6$ Hz, =NCH_2CH_2O–). ^{13}C NMR ppm ($CDCl_3$): 171.2 [J(^{13}C–$^{117/119}$Sn) = 21.6 Hz, C1′], 143.1 [J(^{13}C–$^{117/119}$Sn) = 710/744 Hz, C1], 142.5 [J(^{13}C–$^{117/119}$Sn) = 768/804 Hz, C_{Ph}], 139.3 [J(^{13}C–$^{117/119}$Sn) = 45.7 Hz], 135.7, 135.5 [J(^{13}C–$^{117/119}$Sn) = 50.2 Hz], 133.2 [J(^{13}C–$^{117/119}$Sn) = 70.0 Hz], 130.1 [J(^{13}C–$^{117/119}$Sn) = 12.4 Hz], 129.2, 129.0 [J(^{13}C–$^{117/119}$Sn) = 15.3 Hz], 128.4 [J(^{13}C–$^{117/119}$Sn) = 71.7/74.4 Hz], 126.7 [J(^{13}C–$^{117/119}$Sn) = 46.5 Hz], 71.5 (C3′), 50.3 [J(^{13}C–$^{117/119}$Sn) = 11.2 Hz, C4′]. ^{117}Sn NMR ($CDCl_3$) ppm: −229.7. MS (EI) *m*/*z*: 470 (M^+−Ph, 3), 420 (M^+−I, 100), 376 (8), 341 (2), 299 (9), 266 (12). Anal. Calcd for $C_{21}H_{18}I_1N_1O_1Sn_1$: C, 46.20; H, 3.32; N, 2.57; I, 23.24. Found: C, 46.77; H, 3.49; N, 2.67; I, 22.10%.

*2.1.3. General procedure for the preparation of diorganotin dibromides **21** and **22***

A solution of tetraorganotin compounds **12** and **14** (2.0 mmoles) and Br_2 (960 mg, 310 μL, 4.0 mmoles) in PhH (20 mL) was stirred at ambient temperature. The mixture was then evaporated and the crude product was filtered through a short column (SiO_2, ethyl acetate) to give the corresponding diorganotin dibromides **21** and **22**.

*2.1.3.1. 2-[2-Dibromo-methylstannyl)-phenyl]-4-S)-isopropyl-4,5-dihydro-oxazole (**21**).* Yellowish oil, 65%, $[\alpha]_D = +25.0$ ($CHCl_3$ $c = 1$). IR cm^{-1} (film): 3055, 2963, 2929, 2874, 1635, 1581, 1561, 1483, 1396, 1386, 1144, 1104, 732. ^{1}H NMR ($CDCl_3$) ppm: 8.41 (1H, d, $J = 7.4$ Hz, $H_{arom.}$), 7.85 (1H, dd, $J = 7.6$ Hz $J = 0.8$ Hz, $H_{arom.}$), 7.79 (1H, dt, $J = 7.5$ Hz $J = 1.2$ Hz, $H_{arom.}$), 7.60 (1H, dt, $J = 7.5$ Hz $J = 1.2$ Hz, $H_{arom.}$), 4.80 (1H, ddd, $J = 10.1$ Hz $J = 8.1$ Hz $J = 4.1$ Hz, =NCHCH_2O–, C3A′), 4.75 (1H, dd, $J = 10.1$ Hz $J = 9.0$ Hz, =NCHCH_2O–, C3B′), 4.58 (1H, *t*, $J = 8.3$ Hz, =NCHCH_2O–), 2.31–2.20 (1H, m, –CHMe$_2$), 1.47 [3H, s, ^2J(^{1}H–$^{117/119}$Sn) = 83.0/86.2 Hz, –SnMe], 1.04 (3H, d, $J = 6.8$ Hz, –CHMe_2), 0.91 (3H, d, $J = 6.8$ Hz, –CHMe_2). ^{13}C NMR ($CDCl_3$) ppm: 170.0 [J(^{13}C–$^{117/119}$Sn) = 38.8 Hz, C1′], 143.0 [J(^{13}C–$^{117/119}$Sn) = 865/905 Hz, C1], 136.6 [J(^{13}C–$^{117/119}$Sn) = 57.4 Hz], 133.6 [J(^{13}C–$^{117/119}$Sn) = 87.2 Hz], 130.9 [J(^{13}C–$^{117/119}$Sn) = 14.4 Hz], 128.0 [J(^{13}C–$^{117/119}$Sn) = 43.4 Hz], 126.6 [J(^{13}C–$^{117/119}$Sn) = 60.8 Hz], 72.6 (C3′), 67.8 [J(^{13}C–$^{117/119}$Sn) = 14.4 Hz, C4′], 29.9 (C5′), 19.1 (C6′), 15.4 (C6′), 12.2 [J(^{13}C–$^{117/119}$Sn) = 679/711 Hz, –SnMe]. ^{117}Sn NMR (C_6D_6) ppm: −227.4. MS (EI) *m*/*z*: 466 (M^+−Me, 17), 402 (100), 358 (12), 316 (31), 264 (11), 222 (24). HRMS (EI): calcd for $C_{12}H_{14}^{79}Br_2O_1N_1^{112}Sn_1$ 457.8490, found 457.8481.

*2.1.3.2. 2-[2-Dibromo-phenylstannyl-phenyl]-4-S-isopropyl-4,5-dihydro-oxazole (**22**).* Yellowish oil, 68%, $[\alpha]_D = +24.2$ ($CHCl_3$ $c = 1$). IR cm^{-1} (film): 3066, 2962, 2929, 2873, 1633, 1579, 1560, 1484, 1398, 1387, 1145, 1105, 731. ^{1}H NMR (C_6D_6) ppm: 8.78 (1H, d, $J = 7.2$ Hz, $H_{arom.}$), 7.75 (1H, dd, $J = 7.7$ Hz $J = 1.5$ Hz, $H_{arom.}$), 7.69 (1H, d, $J = 7.2$ Hz, $H_{arom.}$), 7.35-7.11 (6H, m, $H_{arom.}$), 3.85-3.73 (3H, m, =NCHCH_2O–), 1.86-1.77 (1H, m, -CHMe$_2$), 0.47 (6H, 2 × d, $J = 6.8$ Hz, –CHMe_2). ^{13}C NMR ($CDCl_3$) ppm: 169.9 [J(^{13}C–$^{117/119}$Sn) = 45.0 Hz, C1′], 142.4 [J(^{13}C–$^{117/119}$Sn) = 976/1023 Hz], 141.5 J(^{13}C–$^{117/119}$Sn) = 890/930 Hz], 136.9 [J(^{13}C–$^{117/119}$Sn) = 57.7 Hz], 133.6 [J(^{13}C–$^{117/119}$Sn) = 88.8 Hz], 133.5 [J(^{13}C–117/119Sn) = 66.6 Hz], 129.9 [J(^{13}C–$^{117/119}$Sn) = 18.9 Hz], 129.7, 128.6 [J(^{13}C–$^{117/119}$Sn) = 98.0 Hz], 128.2 [J(^{13}C–$^{117/119}$Sn) = 43.2 Hz], 126.7 [J(^{13}C–$^{117/119}$Sn) = 62.7 Hz], 72.7 (C3′), 67.8 (C4′), 29.4 [J(^{13}C–$^{117/119}$Sn) = 35.1 Hz, C5′]. ^{117}Sn NMR (C_6D_6) ppm: -288.5. MS (EI) *m*/*z*: 464

(M^+−Br, 100), 378 (19), 308 (9), 222 (8). HRMS (EI): calcd for $C_{18}H_{19}O_1N_1$ $^{79}Br_1$ $^{120}Sn_1$ 463.9672, found 463.9690.

*2.1.4. General procedure for the preparation of triorganotin hydrides **6**, **7**, **10**, **11** and diorganotin dihydrides **8** and **9***

A solution of $NaBH_4$ (567 mg, 15.0 mmoles) in ethanol (5 mL) was added to a solution of the corresponding triorganotin halide **17**–**22** (1.5 mmol) in ethanol (10 mL) and stirred at 0 °C for 5 min. The reaction mixture was treated with water (1 mL) and the crude product was extracted with pentane. The extracts were dried over anhydrous $MgSO_4$ and evaporated to afford the corresponding triorganotin hydride **6**–**11** or diorganotin dihydride **8**, **9** as colorless oil.

*2.1.4.1. 2-{2-[4-(S)-Isopropyl-2-oxazoline]-5-phenyl}-methyl-phenyltin hydride (**6**).* Mixture of two diastereoisomers 60/40, colorless oil, 94%. IR cm^{-1} (film): 3060, 1846, 1648, 1480, 10428, 1361, 1087, 728, 700. MS (EI) *m*/*z*: 400 (M^+−H, 78), 386 (100), 324 (87), 308 (69), 222 (43). HRMS (EI): calcd for $C_{19}H_{22}O_1N_1$ $^{120}Sn_1$ 400.0723, found 400.0734.

Major diastereoisomer (*S*)-**6a**: ^{1}H NMR (toluene-D_8) ppm: 8.00–7.80 (1H, m, $H_{arom.}$), 7.75–7.50 (3H, m, $H_{arom.}$), 7.25–6.75 (5H, m, $H_{arom.}$), 6.66 [1H, m, $^1J(^1H–^{117/119}Sn)$ = 1933/2022 Hz, –SnH], 3.95–3.85 (1H, m, =NCHCH$_2$O–), 3.72–3.59 (2H, m, =NCHCH$_2$O–), 1.55–1.54 (1H, m, -C*H*Me$_2$), 0.91 (3H, d, J = 6.8 Hz, –CH*Me*$_2$), 0.72 (3H, d, J = 6.8 Hz, –CH*Me*$_2$), 0.63 [3H, d, J = 1.7 Hz, $^2J(^1H–^{117/119}Sn)$ = 63.3 Hz, –SnMe].^{13}C NMR (toluene-D_8) ppm: 165.9 [$J(^{13}C–^{117/119}Sn)$ = 11.5 Hz, C1′], 143.7 [$J(^{13}C–^{117/119}Sn)$ = 475/497 Hz, –C_{Ph}], 143.2 [$J(^{13}C–^{117/119}Sn)$ = 540/565 Hz, C1], 138.5, 138.3, 137.3, 137.1, 133.7, 133.3, 131.4, 131.1, 72.3 (C3′), 70.7 (C4′), 32.4 (C5′), 19.3 (C6′) 18.0 (C6′), −7.2 [$J(^{13}C–^{117/119}Sn)$ = 411/430 Hz, –SnMe]. ^{117}Sn NMR (toluene-D_8) ppm: −160.0.

Minor diastereoisomer (*R*)-**6b**: ^{1}H NMR (toluene-D_8) ppm: 8.00–7.80 (1H, m, $H_{arom.}$), 7.75–7.50 (3H, m, $H_{arom.}$), 7.25–6.75 (5H, m, $H_{arom.}$), 6.67 [1H, m,$^1J(^1H–^{117/119}Sn)$ = 1897/1985 Hz, –SnH], 3.95–3.85 (1H, m, =NCHCH$_2$O–), 3.72–3.59 (2H, m, =NCHC*H*$_2$O–, C3A′ and C3B′), 1.32–1.24 (1H, m, –C*H*Me$_2$), 0.76 (3H, d, J = 6.8 Hz, –CH*Me*$_2$), 0.54 (1H, d, J = 6.8 Hz, –CH*Me*$_2$), 0.65 [3H, d, J = 1.7 Hz, $J(^1H–^{117/119}Sn)$ = 59.9 Hz, –SnMe]. ^{13}C NMR (toluene-D_8) ppm: 166.1 [$J(^{13}C–^{117/119}Sn)$ = 11.5 Hz, C1′], 144.6 [$J(^{13}C–^{117/119}Sn)$ = 416/435 Hz, -C_{Ph}], 143.6 [$J(^{13}C–^{117/119}Sn)$ = 539/564 Hz, C1], 138.4, 138.3, 137.4, 137.1, 133.6, 133.3, 131.2, 131.1, 72.4 (C3′), 71.2 (C4′), 32.7 (C5′), 18.9 (C6′), 18.6 (C6′), −7.1 [$J(^{13}C–^{117/119}Sn)$ = 448/469 Hz, –SnMe]. ^{117}Sn NMR (toluene-D_8) ppm: −159.2.

*2.1.4.2. 2-{2-[4-(S)-Isopropyl-2-oxazoline]-5-phenyl}-n-butyl-methyltin hydride (**7**).* Mixture of two diastereoisomers 1.1/1.0, colorless oil, 97%. IR cm^{-1} (film): 3056, 1836, 1648, 1464, 1358, 1086, 1043, 728. MS (EI) *m*/*z*: 380 (M^+−H, 20), 366 (36), 324 (100), 308 (44), 222 (27). HRMS (EI): calcd for $C_{17}H_{26}O_1N_1$ $^{120}Sn_1$ 380.1036, found 380.1048.

Major diastereoisomer (*S*)-**7a**: ^{1}H NMR (toluene-D_8) ppm: 7.98 (1H, d, J = 1.4 Hz, $H_{arom.}$), 7.82 (1H, dd, J = 7.1 Hz J = 1.5 Hz, $H_{arom.}$), 7.22–7.12 (2H, m, $H_{arom.}$), 6.14 [1H, m, $^1J(^1H–^{117/119}Sn)$ = 1615/1688 Hz, –SnH], 3.97–3.91 (1H, m, =NCHCH$_2$O–), 3.74–3.67 (2H, m, =NCHCH$_2$O–), 1.75–1.55 (3H, m, –CH*Me*$_2$ and –CH_2CH$_2$CH$_2$CH$_3$), 1.44–1.35 (2H, m, –CH$_2$CH_2CH$_2$CH$_3$), 1.32–1.17 (2H, m, –CH$_2$CH$_2$CH_2CH$_3$), 0.94–0.87 (6H, m, –CH*Me*$_2$ and –CH$_2$CH$_2$CH$_2$CH_3), 0.74 (3H, d, J = 6.8 Hz, –CH*Me*$_2$), 0.49 [3H, d, J = 2.0 Hz, $^2J(^1H–^{117/119}Sn)$ = 56.9 Hz, –SnMe]. ^{13}C NMR (toluene-D_8) ppm: 165.8 [$J(^{13}C–^{117/119}Sn)$ = 9.6 Hz, C1′], 144.5 [$J(^{13}C–^{117/119}Sn)$ = 486/509 Hz, C1], 138.5 [$J(^{13}C–^{117/119}Sn)$ = 37.7 Hz], 137.4, 133.5 [$J(^{13}C–^{117/119}Sn)$ = 20.8 Hz], 131.0 [$J(^{13}C–^{117/119}Sn)$ = 49.9 Hz], 128.6, 72.7 [$J(^{13}C–^{117/119}Sn)$ = 4.4 Hz, C4′], 70.7 (C3′), 32.7 (C5′), 30.2 [$J(^{13}C–^{117/119}Sn)$ = 19.8 Hz, –CH$_2$CH$_2$CH_2CH$_3$], 27.3 [$J(^{13}C–^{117/119}Sn)$ = 66.1/69.0 Hz, –CH$_2$CH_2CH$_2$CH$_3$], 19.2 (C6′), 18.3 (C6′), 13.9 (–CH$_2$CH$_2$CH$_2$CH_3), 13.7 [$J(^{13}C–^{117/119}Sn)$ = 438/459 Hz, –CH$_2$CH$_2$CH$_2$CH$_3$], −8.5 [$J(^{13}C–^{117/119}Sn)$ = 346/361 Hz, –SnMe]. ^{117}Sn NMR (toluene-D_8) ppm: −112.1.

Minor diastereoisomer (*R*)-**7b**: ^{1}H NMR (toluene-D_8) ppm: 8.00 (1H, d, J = 1.4 Hz, $H_{arom.}$), 7.85 (1H, dd, J = 7.1 Hz J = 1.5 Hz, $H_{arom.}$), 7.22–7.12 (2H, m, $H_{arom.}$), 6.14 [1H, m, $^1J(^1H–^{117/119}Sn)$ = 1548/1615 Hz, –SnH], 3.97–3.91 (1H, m, =NCHCH$_2$O–), 3.74–3.67 (2H, m, =NCHCH$_2$O–), 1.75–1.55 (3H, m, –CH_2CH$_2$CH$_2$CH$_3$), 1.44–1.35 (2H, m, –CH$_2$CH_2CH$_2$CH$_3$), 1.32–1.17 (2H, m, –CH$_2$CH$_2$CH_2CH$_3$), 0.94–0.87 (6H, m, –CH*Me*$_2$ and –CH$_2$CH$_2$CH$_2$CH_3), 0.71 (3H, d, J = 6.8 Hz, –CH*Me*$_2$), 0.44 [3H, d, J = 2.0 Hz, $^2J(^1H–^{117/119}Sn)$ = 53.5 Hz, –SnMe].^{13}C NMR (toluene-D_8) ppm: 165.9 [$J(^{13}C–^{117/119}Sn)$ = 9.8 Hz, C1′], 144.7 [$J(^{13}C–^{117/119}Sn)$ = 485/508 Hz, C1], 138.7 [$J(^{13}C–^{117/119}Sn)$ = 38.1 Hz], 137.4, 133.5 [$J(^{13}C–^{117/119}Sn)$ = 20.8 Hz], 131.0 [$J(^{13}C–^{117/119}Sn)$ = 49.9 Hz], 128.6, 72.8 [$J(^{13}C–^{117/119}Sn)$ = 4.3 Hz, C4′], 70.6 (C3′), 32.6 (C5′), 30.1 [$J(^{13}C–^{117/119}Sn)$ = 20.9 Hz, –CH$_2$CH$_2$CH_2CH$_3$], 27.4 [$J(^{13}C–^{117/119}Sn)$ = 64.6/67.5 Hz, –CH$_2$CH_2CH$_2$CH$_3$], 19.3 (C6′), 18.1 (C6′), 13.9 (–CH$_2$CH$_2$CH$_2$CH_3), 13.4 [$J(^{13}C–^{117/119}Sn)$ = 423/442 Hz, −CH$_2$CH$_2$CH$_2$CH$_3$], -7.9 [$J(^{13}C–^{117/119}Sn)$ = 377/394 Hz, –SnMe]. ^{117}Sn NMR (toluene-D_8) ppm: −117.7.

*2.1.4.3. 2-{2-[4-(S)-isopropyl-2-oxazoline]-5-phenyl}-methyltin dihydride (**8**).* Yellowish oil, 95%. IR cm^{-1} (film): 3056, 2960, 2928, 2873, 1859, 1769, 1647, 1563, 1466, 1360, 1088, 1044, 965. ^{1}H NMR (toluene-D_8) ppm: 8.08–7.10 (4H, m, $H_{arom.}$), 6.17–6.04 [2H, 2 × *dq* J = 25.1 Hz J = 2.1 Hz, $^1J(^1H–^{117/119}Sn)$ = 1615/1703 Hz and 1888/1987, –SnH$_2$], 3.79 (1H, dd, J = 9.7 Hz, J = 8.2 Hz, =NCHCH_2O–, C3A′), 3.52 (1H, *t*, J = 8.9 Hz, =NCHCH_2O–, C3B′), 3.52 (1H, dt, J = 9.3 Hz, J = 6.8 Hz, =NC*H*CH$_2$O–), 1.35–1.28 (1H, m, –C*H*Me$_2$), 0.91 (3H, d, J = 6.7 Hz, –CH*Me*$_2$), 0.66 (3H, d, J = 6.7 Hz, –CH*Me*$_2$), 0.52 [3H, *t*, J = 2.0 Hz, $^1J(^1H–^{117/}$

^{119}Sn) = 65.5/62.3 Hz, –SnMe]. ^{13}C NMR (toluene-D$_8$) ppm: 165.7 [J(^{13}C–$^{117/119}$Sn) = 10.9 Hz, C1′], 142.4 [J(^{13}C–$^{117/119}$Sn) = 555/581 Hz, C1], 139.1 [J(^{13}C–$^{117/119}$Sn) = 43.9 Hz], 133.1 [J(^{13}C–$^{117/119}$Sn) = 22.1 Hz], 131.1 [J(^{13}C–$^{117/119}$Sn) = 56.4 Hz], 128.8, 127.9, 72.1 [J(^{13}C–$^{117/119}$Sn) = 5.2 Hz, C4′], 71.4 (C3′), 32.9 (–*C*HMe$_2$), 18.9 (–CH*Me*$_2$), 18.7 (–CH*Me*$_2$), −8.8 [J(^{13}C–$^{117/119}$Sn) = 432/453 Hz, –SnMe]. ^{117}Sn NMR (toluene-D$_8$) ppm: −225.9. MS (EI) m/z: 324 (M$^+$−H, 2).

*2.1.4.4. 2-{2-[4-(S)-isopropyl-2-oxazoline]-5-phenyl}-phenyltin dihydride (**9**).* Yellowish oil, 98%. IR cm^{-1} (film): 3063, 2973, 2929, 2878, 1871, 1647, 1580, 1455, 1379, 1090. ^{1}H NMR (toluene-D$_8$) ppm: 8.03 (1H, d, J = 7.7 Hz, H$_{arom.}$), 7.73–7.70 (1H, m, H$_{arom.}$), 7.30–7.00 (7H, m, H$_{arom.}$), 6.78–6.64 [2H, 2 × d, J = 23.9 Hz, ^1J(^{1}H–$^{117/119}$Sn) = 1853/1940 Hz and 2059/2155, –SnH$_2$], 3.75–3.67 (1H, m, =NC*H*CH$_2$O–), 3.57–3.45 (2H, m, =NCHC*H*$_2$O–, C3A′ and C3B′), 1.30–1.11 (1H, m, –C*H*Me$_2$), 0.88 (3H, d, J = 6.8 Hz, –CH*Me*$_2$), 0.69 (3H, d, J = 6.8 Hz, –CH*Me*$_2$). ^{13}C NMR (toluene-D$_8$) ppm: 166.1 [J(^{13}C–$^{117/119}$Sn) = 12.4 Hz, C1′], 141.6 [J(^{13}C–$^{117/119}$Sn) = 517/494 Hz, C$_{Ph}$], 141.4 [J(^{13}C–$^{117/119}$Sn) = 604/578 Hz, C1], 138.7 [J(^{13}C–$^{117/119}$Sn) = 45.8 Hz], 137.7 [J(^{13}C–$^{117/119}$Sn) = 41.5 Hz], 132.9 [J(^{13}C–$^{117/119}$Sn) = 23.2 Hz], 131.3 [J(^{13}C–$^{117/119}$Sn) = 58.3 Hz], 129.4, 129.1, 128.5, 127.5, 71.7 (4C'), 71.6 (C3′), 32.8 (-C*H*Me$_2$), 18.8 (–CH*Me*$_2$), 18.7 (–CH*Me*$_2$). ^{117}Sn NMR (toluene-D$_8$) ppm: -244.5. MS (EI) m/z: 386 (M$^+$−H, 8), 308 (23), 224 (25), 146 (100). HRMS (EI): calcd for C$_{18}$H$_{20}$O$_1$N$_1$ ^{120}Sn$_1$ 386.0567, found 386.0578.

*2.1.4.5. 2-(2-Oxazoline-5-phenyl)-dimethyltin hydride (**10**).* Yellowish oil 98%. IR cm^{-1}(film): 3055, 2975, 2906, 1840, 1750, 1562, 1481, 1360, 1329, 1257, 1125, 1085, 1042, 977, 944. ^{1}H NMR (toluene-D$_8$) ppm: 7.91 (1H, dd, J = 7.6 Hz J = 1.4 Hz, H$_{arom.}$), 7.81 (1H, dd, J = 7.1 Hz J = 1.6 Hz, H$_{arom.}$), 7.19 (1H, dt, J = 7.3 Hz J = 1.5 Hz, H$_{arom.}$), 7.14 (1H, dt, J = 7.5 Hz, J = 1.5 Hz, H$_{arom.}$), 6.09 [1H, ^1J(^{1}H–$^{117/119}$Sn) = 1597/1671 Hz, –SnH], 3.72 (2H, t, J = 9.5 Hz, =NCH$_2$CH$_2$O–), 3.41 (2H, t, J = 9.5 Hz, =NCH$_2$CH$_2$O–), 0.43 [6H, d, J = 1.9 Hz, ^2J(^{1}H–$^{117/119}$Sn) = 57.4/60.4 Hz, –SnMe$_2$]. ^{13}C NMR (toluene-D$_8$) ppm: 166.7 [J(^{13}C–$^{117/119}$Sn) = 10.6 Hz, C1′], 145.9 [J(^{13}C–$^{117/119}$Sn) = 520/544 Hz, C1], 138.4 [J(^{13}C–$^{117/119}$Sn) = 41.2 Hz], 133.3 [J(^{13}C–$^{117/119}$Sn) = 21.0 Hz], 131.0 [J(^{13}C–$^{117/119}$Sn) = 53.1 Hz], 128.6, 128.3, 127.8, 68.1 (C3′), 53.8 [J(^{13}C–$^{117/119}$Sn) = 5.2 Hz, C4′], −7.1 [J(^{13}C–$^{117/119}$Sn) = 401/420 Hz, –CH$_3$]. ^{117}Sn NMR (toluene-D$_8$) ppm: −128.8. MS (EI) m/z: 296 (M$^+$−H, 22), 282 (100), 266 (51), 252 (4), 238 (9), 222 (19). HRMS (EI); calc. for C$_{11}$H$_{14}$N$_1$O$_1$ ^{120}Sn$_1$ 296.0097 found 296.0085.

2-(2-Oxazoline-5-phenyl)-diphenyltin hydride 11: yellowish oil, 99%. IR cm^{-1}(KBr): 3062, 2958, 2930, 2878, 2275, 1843, 1727, 1650, 1579, 1562, 1480, 1428, 1365, 1265, 1193, 1127, 1087, 1073, 1043, 1022, 997. ^{1}H NMR (toluene-D$_8$) ppm: 7.93–7.85 (1H, m, H$_{arom.}$), 7.82–7.78 (1H, m, H$_{arom.}$), 7.67 (4H, m, H$_{arom.}$), 7.41 [1H, s, ^1J(^{1}H–$^{117/119}$Sn) = 1850/1937 Hz, –SnH], 7.25–7.05 (8H, m, H$_{arom.}$), 3.61 (1H, t, J = 9.5 Hz, =NCH$_2$CH$_2$O–), 3.27 (2H, t, J = 9.5 Hz, =NCH$_2$CH$_2$O–). ^{13}C NMR (toluene-D$_8$) ppm: 167.2 [J(^{13}C–$^{117/119}$Sn) = 14.9 Hz, C1′], 143.6 [J(^{13}C–$^{117/119}$Sn) = 575/601 Hz, C1], 142.8 [J(^{13}C–$^{117/119}$Sn) = 559/585 Hz, 2 × C$_{Ph}$Sn-], 138.8 [J(^{13}C–$^{117/119}$Sn) = 46.3 Hz], 137.5 [J(^{13}C–$^{117/119}$Sn) = 41.1 Hz], 133.1 [J(^{13}C–$^{117/119}$Sn) = 21.5 Hz], 131.5 [J(^{13}C–$^{117/119}$Sn) = 58.9 Hz], 68.7 (C3′), 53.0 [J(^{13}C–$^{117/119}$Sn) = 6.5 Hz, C4′]. ^{117}Sn NMR (toluene-D$_8$) ppm: -180.6. MS (EI) m/z: 420 (M$^+$−H, 56), 376 (10), 344 (100), 299 (21), 266 (49). HRMS (EI); calc. for C$_{21}$H$_{18}$N$_1$O$_1$ ^{120}Sn$_1$ 420.041 found 420.042.

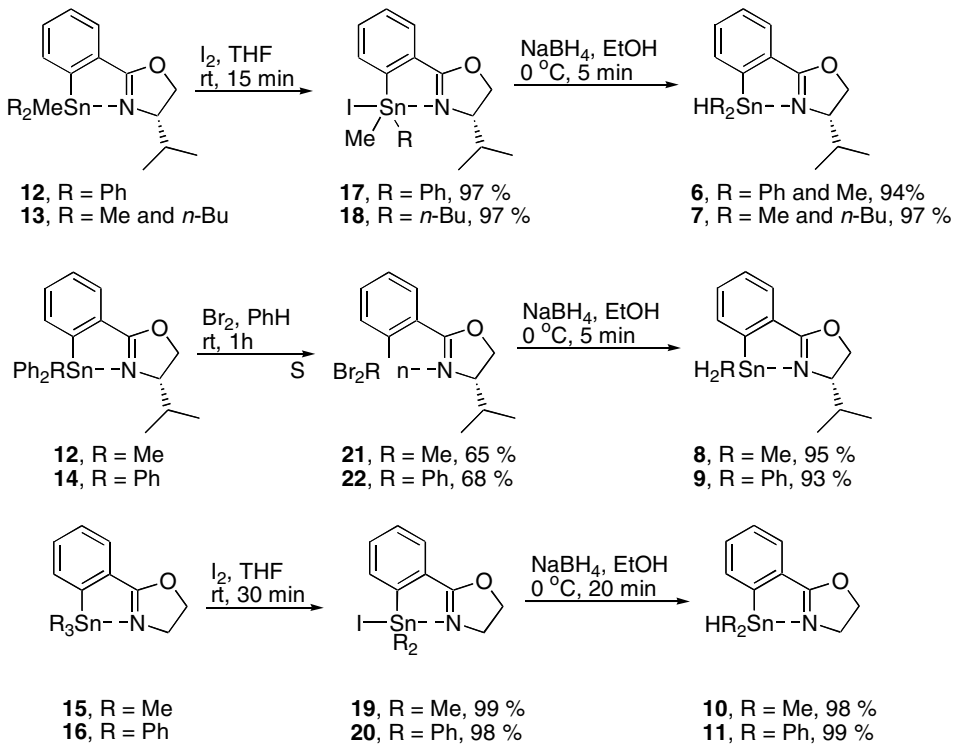
3. Results and discussion

3.1. Synthesis of the tin hydrides

Triorganotin hydrides **1**–**5** have already been reported [9–11]. The synthesis of the remaining triorganotin hydrides and diorganotin dihydrides involved treatment of R$_3$SnX (Ph$_2$SnMeI for **6** and **8**, Me$_2$Sn-*n*-BuI for **7**, Me$_3$SnCl for **10**, Ph$_3$SnCl for **9** and **11**) with the *o*-lithiophenyl-oxazole prepared by metallation of 2-(4-bromophenyl)-4-isopropyl-4,5-dihydro-oxazole with *n*-butyl lithium in THF at −70 °C (Scheme 1). Treatment of tetraorganotin compounds **12**–**13** and **15**–**16** with stoichiometric amounts of iodine in THF at ambient temperatures gave the corresponding triorganotin iodides: **17** (*a*/*b* = 56/44, 97%), **18** (*a*/*b* = 57/43, 97%), **19** (99%), **20** (98%). The ease of the bond cleavage could be ascribed to nucleophilic assistance by the imine group, i.e. labilization of the Sn–C bond in a *trans* position with respect to the coordinating nitrogen atom [12–14]. Treatment of tetraorganotin compounds **12** and **14** with excess of bromine in benzene resulted in the formation of the corresponding diorganotin dibromides **21** (65%) and **22** (68%). Reduction of triorganotin iodides **17**–**20** and diorganotin dibromides **21**–**22** with NaBH$_4$ in ethanol at 0 °C afforded triorganotin hydrides: **6** (*a*/*b* = 60/40, 94%), **7** (*a*/*b* = 53/47, 97%), **8** (95%), **9** (93%), **10** (98%), **11** (99%). The diastereomeric triorganotin hydrides (**6** and **7**) do not racemize and can be stored at low temperatures under argon for several weeks without decomposition [15]. The diorganotin dihydrides (**8** and **9**) appear to be relatively stable at −20 °C. At higher temperatures they undergo decomposition with gas evolution. The ^{117}Sn NMR spectra of these mixtures indicated the presence of several tin containing species, which could not be identified.

3.2. Structure in solution of the triorganotin hydrides

Determination of the absolute configuration of the tin atom in diastereomeric intramolecularly coordinated organotin hydrides constitutes a serious problem. Only in one case was it possible to perform an X-ray crystal



Scheme 1. The preparation of triorganotin hydrides **6**, **7**, **10**, **11** and diorganotin dihydrides **8** and **9**.

structure determination of *t*-butyl-8-(dimethylamino)-naphthyl-(-)-menthyltin hydride **23** (Fig. 2). X-ray investigation of **23** revealed 1:1 pairs of both epimers. In solution, the epimers are in a ratio of 40/60. They show an identical configuration of the chiral ligand but a different configuration at the asymmetric tin center. The absolute configuration is assigned to R_{Sn} for **23a** and S_{Sn} for **23b** [16]. The menthyl and naphthyl groups as well as hydrogen atom attached to the tin are in equatorial positions. The *tert*-butyl group and nitrogen atom are in axial positions. Fortunately, the molecular structure of triorganotin hydride **23** corresponds well with those derived from the NMR data supporting equatorial position of the hydrogen atom at the tin.

The structures of other reported Sn–N coordinated triorganotin hydrides either do not unambigously show a position of the hydrogen atom or are assumed to have the equatorial hydrogen atoms. This assumption could be true taking into account that the $^1J(^1H–^{117/119}Sn)$ couplings in most of the reported hydrides are larger than the $^1J(^1H–^{117/119}Sn)$ couplings in noncoordinated ones with

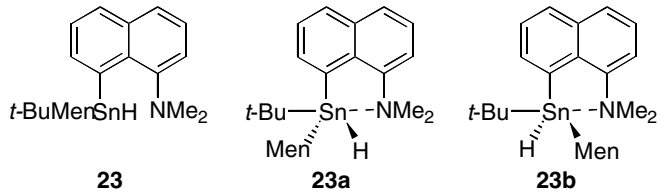


Fig. 2. Two epimers (**23a** and **23b**) of *t*-butyl-8-(dimethylamino)-naphthyl-(-)-menthyltin hydride **23**.

similar substituent patterns [17]. This is because the Sn–N coordination influences the hybridization of the tin center increasing s-character in the equatorial positions [18,19]. In principle, the same could hold (in reverse) for organotin hydrides possesing the axial hydrogen atom attached to tin. Moreover, both values of the $^1J(^1H–^{117/119}Sn)$ couplings could be also affected by temperature. This assumption seems intuitively reasonable. Namely, at lower temperatures structures of the coordinated organotin hydrides are expected to be more rigid enhancing the strength of the intramolecular Sn–N coordination. To the best of our knowledge the variation of the $^1J(^1H–^{117/119}Sn)$ couplings as a function of temperature has not been reported yet. To experimentally test it, the ^1H NMR spectra of organotin hydrides **1**–**11** were measured at 303, 273 and 253 K in toluene-D_8. The results are shown in Table 1.

The ^1H NMR measurements of triorganotin hydrides **1**–**7,10,11** in toluene-D_8 at different temperatures show noticeable differences in the $^1J(^1H–^{117/119}Sn)$ couplings, although the diastereomeric ratios of triorganotin hydrides **4**–**7** do not change with temperature. For triorganotin hydrides **1**, **2**, **4a**, **5a**, **7a/b** and **10** a decrease of the $^1J(^1H–^{117/119}Sn)$ couplings with decreasing temperature was observed (ca. 32–100 Hz). On the other hand, for triorganotin hydrides **3**, **4b**, **5b**, **6a/b** an opposite trend was observed (ca. 28–66 Hz). In two cases (hydrides **9** and **11**) the influence of temperature on the $^1J(^1H–^{117/119}Sn)$ couplings seems to be negligible (~1 Hz). As previously described, analysis of the NOEs observed for triorganotin hydrides **4a/b** and **5a/b** clearly proved that in solution two diastereomeric triorganotin hydrides with

Table 1
The $^{1}J(^{1}H–^{117/119}Sn)$ values of triorganotin hydrides **1**–bf 7, **10**, **11** and diorganotin dihydrides **8**, **9**

Organotin hydride	$^{1}J(^{1}H–^{117/119}Sn)$ 253 K	$^{1}J(^{1}H–^{117/119}Sn)$ 273 K	$^{1}J(^{1}H–^{117/119}Sn)$ 303 K
1	1622/1695	1642/1718	1677/1753
2	1333/1395	1357/1420	1434/1503
3	2104/2203	2091/2188	2070/2167
4a	1384/1448	1426/1493	1480/1549
4b	1887/1974	1850/1936	1823/1908
5a	1284/1344	1360/1423	1380/1444
5b	1727/1806	1707/1785	1692/1770
6a	1971/2064	1957/2048	1933/2022
6b	1925/2013	1911/2000	1897/1985
7a	1583/1656	1592/1670	1615/1688
7b	1493/1561	1516/1592	1548/1615
8	1565/1639	1592/1667	1615/1703
	1919/2006	1913/2001	1888/1987
9	1853/1940	1852/1938	2059/2155
	2083/2180	2073/2169	1853/1940
10	1540/1611	1560/1633	1597/1671
11	1851/1938	1850/1937	1850/1937

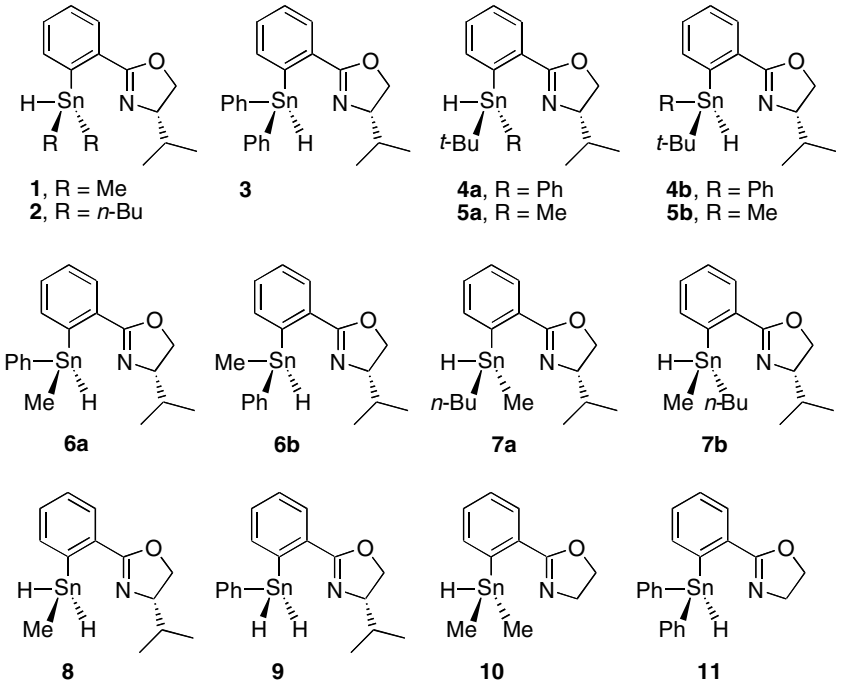


Fig. 3. Structures of organotin hydrides **1**–**11**.

hydrogen atoms in axial(**a**)/equatorial(**b**) positions are present [11]. Therefore, in triorganotin hydrides **1**, **2**, **4a**, **5a**, **7a/b** and **10** the position of hydrogen atoms could be ascribed as axial. Consequently, in triorganotin hydrides **3**, **4b**, **5b**, **6a/b** the position of hydrogen atoms seems to be equatorial (Fig. 3).

Additionally, for triorganotin hydrides **1**, **2** and **3** the ^{1}H NMR NOE differential experiments were taken at ambient temperatures. Analysis of the NOEs observed for the triorganotin hydrides are in agreement with the conclusions drawn from the ^{1}H NMR low temperature experiments. The most significant NOEs observed for triorganotin hydrides **1**–**3** are presented in Fig. 4. Irradiation of the hydrogen attached to tin in **1** or **2** leads to observation of an NOE (2.6% for **1**, 5.4% for **2**) at H6 and methyl (2.6% for **1**) or protons of the methylene groups (3.5% for **2**) directly attached to the tin. In the case of hydride **3** irradiation of the hydrogen attached to tin causes ^{1}H NOE effect at protons of methyls from the isopropyl group (1.2% and 1.7%). Additionally, the hydrogen atom at the tin interacts with a proton (H5′) of the isopropyl group supporting its equatorial position.

It was of interest to find whether values of the $^{1}J(^{13}C–^{117/119}Sn)$ couplings are also influenced by temperature. In fact similar effects as in case of the $^{1}J(^{1}H–^{117/119}Sn)$ couplings were observed but the changes of the $^{1}J(^{13}C–^{117/119}Sn)$ are rather small (<20 Hz). For triorganotin hydride **1** where the methyl groups are equatorial and two diastereomeric

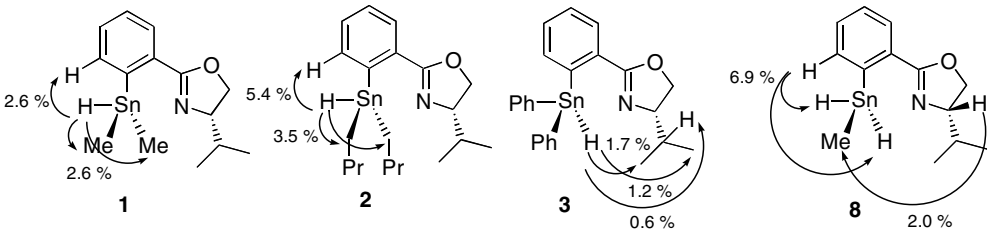


Fig. 4. ^{1}H NMR NOE results of triorganotin hydrides **1**–**3** and diorganotin dihydride **8**.

Table 2
The selected $^{1}J(^{13}C–^{117/119}Sn)$ couplings of triorganotin hydrides **1** and **5**

Organotin hydride	$^{1}J(^{13}C–^{117/119}Sn)$ C_1*tert*-Butyl	$^{1}J(^{13}C–^{117/119}Sn)$ C_1Ligand	$^{1}J(^{13}C–^{117/119}Sn)$ C_1 Me
1			
303 K	–	144.3 (514/537)	−7.0 (402/421) −7.4 (373/390)
229 K		143.7 (516/540)	−7.2 (409/429) −7.7(374/392)
5a			
303 K	26.3 (489/512)	144.8(447/468)	−7.4 (363/380)
205 K	26.1 (505/528)	144.9 (456/477)	−7.0 (374/392)
5b			
303 K	26.1 (489/511)	144.1 (443/464)	−9.1 (287/301)
205 K	26.0 (495/522)	Not detected	−9.1 (269/280)

organotin hydrides **5a** and **5b** where the methyl group is either axial (**5a**) or equatorial (**5b**) the $^{1}J(^{13}C–^{117/119}Sn)$ couplings are presented in Table 2. In case of triorganotin hydride **1** increasing value of the $^{1}J(^{13}C–^{117/119}Sn)$ coupling is observed only for one methyl whereas the $^{1}J(^{13}C–^{117/119}Sn)$ of the second methyl does not seems to be affected by lower temperature. It could mean that the $^{1}J(^{13}C–^{117/119}Sn)$ of the equatorial methyl on the same side as the isopropyl group is more sensitive towards changes of temperature. For diastereomeric triorganotin hydrides **5a** and **5b** at lower temperature the $^{1}J(^{13}C–^{117/119}Sn)$ couplings of the methyl group are smaller and bigger, respectively.

Diorganotin dihydrides **8** and **9** contain two hydrogen atoms directly attached to the tin. Relatively little spectroscopic data are available on such compounds. The $^{1}J(^{1}H–^{117/119}Sn)$ couplings of noncoordinated dihydrides with similar substituent patterns, i.e. $PhMeSnH_2$ and Ph_2SnH_2 are 1771/1835 and 1842/1928 Hz, respectively [20]. Comparison of the $^{1}J(^{1}H–^{117/119}Sn)$ couplings between pairs $PhMeSnH_2$/**8** and Ph_2SnH_2/**9** indicates that the Sn-N coordination causes a strong $^{1}J(^{1}H–^{117/119}Sn)$ coupling decrease and increase for **8** and a negligible /strong $^{1}J(^{1}H–^{117/119}Sn)$ coupling increase for **9**. The temperature variation in $^{1}J(^{1}H–^{117/119}Sn)$ couplings of the dihydrides is likely the result of axial/equatorial positions of hydrogens attached to the tin. In case of compound **8** one hydrogen atom is axial and the other one equatorial. In case of compound **9** both of hydrogen atoms are equatorial. Due to the intramolecular Sn–N coordination the $^{117/119}Sn$ satellites of Sn-H signals in the ^{1}H NMR spectra are doubbled. It can be explained in terms of an additional H–Sn–H magnetic interaction (25.1 Hz for **8** and 23.9 Hz for **9**).

In conclusion, we have shown that positions of hydrogen atoms in organotin hydrides **1**–**11** may be established by means of the low-temperature NMR investigations. Although the concluded structures of organotin hydrides **1**–**11** are within a family of organotin hydrides containing ''imine'' type of nitrogen the presented approach might be of interest for organotin hydrides containing ''amine'' kind of nitrogen.

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