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Synthesis and reactivity of β-stannylated phenylalanines

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Abstract: The free radical hydrostannation of a series of *N*-benzoyl and *N*-acetyl dehydrophenylalanine esters **2a–h** yields β-stannylated phenylalanine derivatives **3** and **4**. This addition of tin hydride to such unsaturated compounds simultaneously creates two new chiral centers leading to mixtures of two diastereomeric pairs of enantiomers. The reaction of 3-stannylated phenylalanine **3** with methanolic HCl yields chlorostannyl-substituted compounds **5** and **6** and, with one equivalent of bromine, the bromostannylated compounds **7** and **8** are formed. The bromostannylated phenylalanine derivative **7** reacts with one further equivalent of bromine to produce the dibromostannylated compound **9**. Even the chlorostannylated phenylalanine derivative **5** reacts with one further equivalent of HCl to give the dichlorostannylated compound **10**. The products were characterized by elemental analysis, infrared (IR), and multinuclear (^{1}H, ^{13}C, ^{119}Sn) nuclear magnetic resonance (NMR) spectroscopy. Attempts were made to assign the preferred conformation of the stannylated phenylalanine derivatives using Karplus-type relationship of coupling constants ^3J(H,H), ^3J(Sn,H), and ^3J(Sn,C=O). The results of these analyses have been confirmed by three crystal structure determinations.

Keywords: β-stannylated phenylalanines; hydrostannation; NMR spectroscopy; phenylalanine.

1 Introduction

Organotin compounds of phenylalanine have rarely been studied. No derivative is known where tin is occupying the α- or β-position of this amino acid. In *N*-benzoyl- [1], *N*-acetyl- [2], *N*-phthaloyl- [3], and *N*-formyl-phenylalanine [4] tin compounds, the tin component is always bound to the carboxylic group of the amino acid. On the other hand, phenylalanine derivatives in which the tin component is bound to the phenyl ring have been studied in more detail. 4-(Trimethylstannyl) phenylalanine derivatives are important substrates in ^{18}F-labelled fluorodestannylation reactions [5], in radioiodination reactions [6], as well as in cross-coupling reactions with aryl or vinyl iodides and triflates [7]. 6-Trimethylstannyl-dopa derivatives are starting compounds for 6-[^{18}F] fluoro-L-dopa, a substance with special importance in positron emission tomography for the examination of neurodegenerative diseases [8–10]. Due to the C/Si/Ge bioisosterism, new organic Ge drugs with antitumor activity and low toxicity were synthesized by the reaction of $Ph_3GeCH_2CH_2COOH$ or $Ph_3GeCH(Ph)CH_2COOH$ with amino acid ethyl ester hydrochlorides [11].

To the best of our knowledge, no tin-containing phenylalanines have been known until now in which the tin atom is bound to the β-carbon atom of this amino acid. With CAS number 1030617-77-6, the D-phenylalanine *N*-benzoyl-β-(triphenylstannyl)-ethyl ester exists but without any reference. Our research concerning *C*-stannylated amino acid derivatives [12–14], including 3-triorganostannylated alanine derivatives, was extended here to *C*-stannylated phenylalanines with the general formula $R_3SnCH(R^1)CH(NHCOR^2)COOR^3$. Some results of synthesis and reactivity of β-stannylated phenylalanines are described in this article.

2 Results and discussion

Hydrostannation is one of the most useful reactions for the preparation of organotin compounds containing functional groups [15–17]. The starting compounds to obtain C-stannylated phenylalanine derivatives by hydrostannation should be the corresponding dehydro amino acid **2**.

These dehydroamino acids **2** can be obtained from 4-arylidene-4,5-dihydro-5-oxazolones **1**, which were easily produced through Erlenmeyer synthesis.

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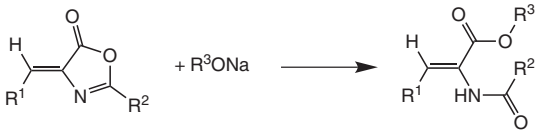
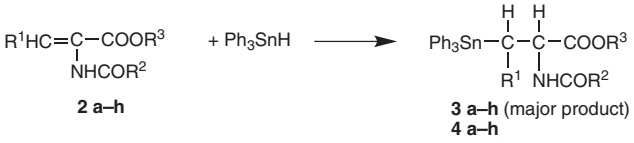


1 a–h 2 a–h

	R^1	R^2	R^3
a	Ph	Ph	Me
b	Ph	Me	Me
c	4-MeOPh	Ph	Me
d	4-MeOPh	Me	Me
e	Ph	Ph	*t*-Bu
f	4-MeOPh	Ph	*t*-Bu
g	4-MeOPh	Me	*t*-Bu
h	3,4-$(MeO)_2$Ph	Ph	*t*-Bu

(1)

According to Erlenmeyer [18, 19], these oxazolones are obtained as thermodynamically more stable *Z*-isomers [20]. The oxazolones themselves do not undergo addition reactions with Ph_3SnH, the starting material has been always recovered instead. The ring opening reaction of the oxazolones **1** by Na- or K-alcoholates yields the dehydro amino acids **2** (Eq. 1). The stereochemical orientation of the exocyclic double bond stays unchanged during the opening of the 1,5-bond [21, 22]. The hydrostannation reactions of **2a–h** were carried out under conditions favoring a free radical reaction, e.g. at 80°C, in the absence of solvent, in a nitrogen atmosphere, and in the presence of azobisisobutyronitrile (AIBN) as a free radical initiator. The β-stannylated phenylalanines **3a–h** and **4a–h** were obtained after heating these mixtures for several hours (Eq. 2).



2 a–h

3 a–h (major product)
4 a–h

(2)

The yields of β-stannylated phenylalanines are very good at more than 80%. **3** and **4** are colorless solids, which are easily soluble in diethylether, alcohols, and halogenated hydrocarbons, but less soluble in hydrocarbons. The stannylated phenylalanines **3** and **4** were characterized by elemental analysis, ^1H, ^{13}C and ^{119}Sn nuclear magnetic resonance (NMR), and infrared (IR) spectroscopy (see Experimental section).

The ^{119}Sn NMR spectra of the crude phenylstannylated products always show two well-separated signals. The addition of a tin hydride to unsaturated compounds such as **2** simultaneously creates two new chiral centers leading to mixtures of two diastereomeric pairs of enantiomers, each represented by one of the two signals. These signals are situated in the region for tetracoordination at the tin atom [23–25]. There are no interactions between tin and the functional groups of the molecule. The spectroscopic data of the stannylated phenylalanine derivatives **3** and **4** are given in the Experimental section. The ^{119}Sn signal of the major isomer of the methyl ester **3** is shifted to higher field (lower field in case of the *tert*-butyl ester) in comparison with the minor isomer **4**.

$\Delta\delta(^{119}Sn)$ of both diastereomeric forms of 3-triphenylstannyl substituted phenylalanines is about 4 ppm. The quantitative determination of the ratio of diastereomeric products formed in the hydrostannation reactions was unproblematic by integration of these two distinct signals. In the case of methylester derivatives this ratio is 1.9 to 1.6 for **3**, and 1.0 for **4**. In general, addition reactions with R_3SnH run without stereospecifity. The dominance of one of the two possible diastereomers in the product is reported for other olefinic systems and should be the result of the reversibility of the radical addition step [26]. The stereoisomers produced in higher yield (**3**) and the stereoisomers formed in lower yield (**4**) could be separated by fractionated crystallization or by column chromatography. In similar compounds – such as menthyl-2,3-diphenyl-3-(triphenylstannyl) propanoates – attempts to separate the diastereomers were not successful [27, 28].

The differences in the molecular structure of the diastereomeric compounds **3** and **4** are reflected in the NMR spectra especially by different vicinal spin–spin coupling constants. The dependence of these constants on the dihedral angle is expressed in the Karplus equation.

The Karplus-type curves [29] are well established as indicators of structural patterns. The publication of the Karplus-type equations for $^3J(^{119}Sn,^{13}C)$ by Doddrell et al. [30] and for $^3J(Sn,D)$ by Quintard et al. [31] have been widely used for structure elucidations; mostly of trimethylstannyl compounds [32–35]. Only a few articles have included triphenylstannyl derivatives [27, 36].

The use of the Karplus-type relationship enabled us to deduce the stereochemistry of **3c** and **4c** as examples. Thus, the ^1H NMR spectra of **3c** and **4c** show that the $^3J(H,H)$ coupling constants for the protons attached to C-2 and C-3 lie at 8.9 and 9.8, indicating dihedral angles of approximately 180°. The $^3J(Sn–C–C–H)$ coupling constant of 38.8 Hz for **3c** and of 32.6 Hz for **4c** suggest a dihedral angle close to 60°. The $^3J(Sn,C=O)$ coupling constants (see Experimental section) of 20.3 for **3c** and 40.4 Hz for **4c** correspond to a dihedral angle close to 60° in the case of compound **3c**, indicating an *R,S*- (likewise *S,R*-) configuration,

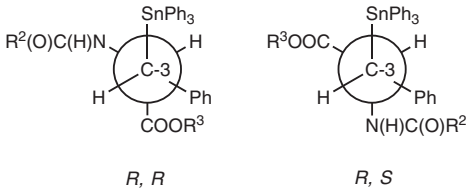
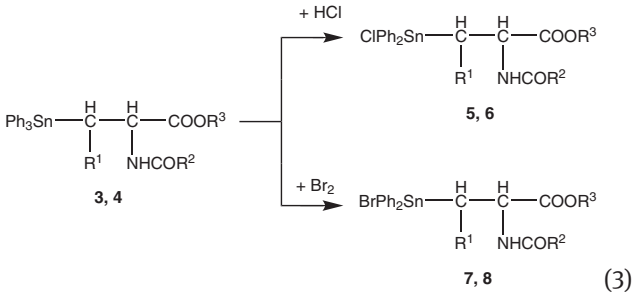


Fig. 1: Conformations of **3** and **4** (only one enantiomer of each compound is shown).

whereas the 140° angle [32] for **4c** suggests an *R,R*-configuration (*S,S*, respectively) (Fig. 1).

The determination of the crystal structure of **4c** clearly demonstrated the *R,R*- (and *S,S*-) configuration and the tetracoordination of the tin atom with its tetrahedral structure (Fig. 2). There is no particular short distance. The dihedral angle between H(1)–C(1)–C(2)–H(2) (numbering according to Fig. 1) is 172.9°. Both enantiomers **4c** (*R,R*-configuration) and **4′c** (*S,S*-configuration) crystallize in one single crystal and are connected by hydrogen bonds (O3···N′ 3.087(2) Å, O3···H(N)′ 2.30 Å), O3···H(N)′–N′ 155.5(1)°) [37].



(3)

To study the reactivity of the stannylated phenylalanines, and to get some more information about the stereochemistry, the following reactions were undertaken (Eq. 3). The stannylated phenylalanines **3** and **4** show a chemical behavior typical for compounds with this substitution pattern. Halogen atoms can substitute the phenyl groups at the tin atom. The reaction of **3** with a methanolic solution of HCl yields the monochlorostannane **5**. In all tin compounds containing electronegative chloro or bromo substituents at the metal atom, the tin atom has a strong tendency to coordinate with donor groups. This acceptor behavior of the tin atom for functional groups may be readily observed by ^{119}Sn NMR spectroscopy because the coordination number of the tin atom increases upon association. Both the high field shift of the ^{119}Sn signal of **5** compared with $Ph_2EtSnCl$ (in $CDCl_3$: $\delta(^{119}Sn) = +17.2$ ppm) [38] and the increase of the $^2J(^{119}SnC^1H)$ coupling constant indicate pentacoordinated tin as a result of intramolecular interactions of this atom with one of the two donor groups of the phenylalanine. The ^{119}Sn signals of **5** are similar to

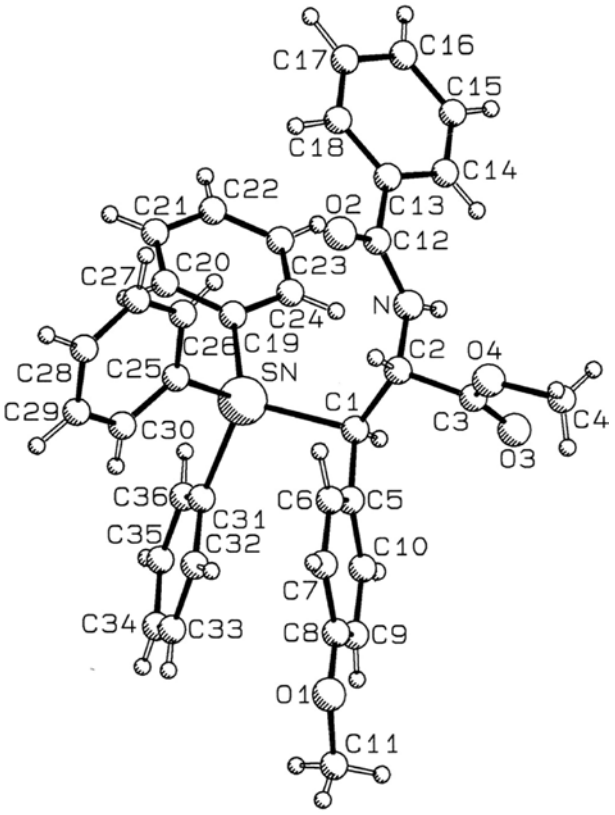


Fig. 2: Molecular structure of **4c** in the crystal (only the *R,R*-enantiomer is shown).

those found for 3-(diphenylchlorostannyl)-*N*-acetyl-alanine ethyl ester (in $CDCl_3$: $\delta(^{119}Sn) = -161.1$ ppm), where the tin is pentacoordinated by coordination with the amide C=O group [12].

The Sn coordination is also reflected in the IR spectra. One ν(C=O) band of **5** is bathochromically shifted by nearly 40 cm^{-1} compared with the corresponding band of **3**. On the basis of our research of Sn···C=O coordination in comparable systems [12], this shift can be allocated to a relation between the Lewis-acidic tin atom and the intramolecularly coordinated amide C=O group. The band for ester C=O is unchanged. We could clearly demonstrate the preferred interaction of the monohalogenated tin atom with the C=O function of amide group by crystal structure analysis of 3-(diphenylchlorostannyl)-*N*-acetyl-alanine ethyl ester [12]. The NMR data of the NH unit supports the existence of a coordination between the amide group and the tin atom. The NH signal is shifted downfield from the corresponding signal for the triphenylstannyl derivative. This kind of coordination is known to reduce the C=O stretching frequency and to have a deshielding effect on the NH protons of the coordinating group. The determination of the crystal structure of **5e** (Fig. 3) confirmed

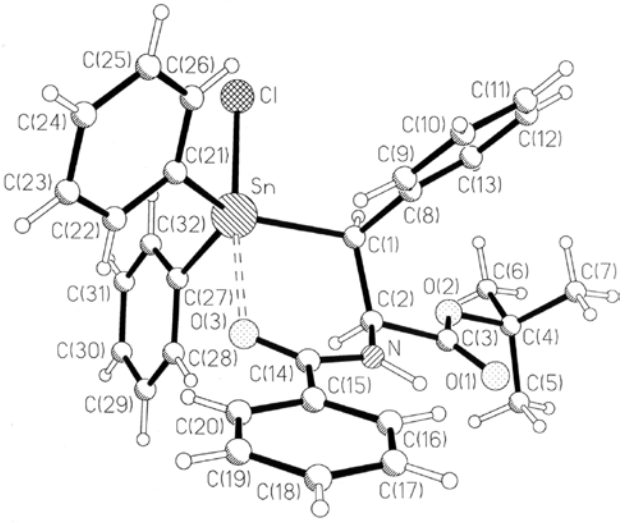


Fig. 3: Molecular structure of **5e** in the crystal (only the *R,S*-enantiomer is shown).

the Sn···O=C(-Ph)–NH interactions [37]. Compound **5e** has a trigonal-bipyramidal structure, where the equatorial positions are occupied by two phenyl groups and the carbon C(1) (numbering according to Fig. 3) of the amino acid chain, whereas the chlorine atom and the oxygen of the amide group are at axial positions forming an angle of 172.3(5)° (angle Cl–Sn–O = 172.9(1)° in $Ph_2Sn(Cl)CH_2$–CH(NHCOMe)COOEt [12]). The bond length of Sn–O(3) is 2.454(2) Å (bond length Sn–O = 2.368(5) Å in $Ph_2Sn(Cl)CH_2$–CH(NHCOMe)COOEt [12]) and the dihedral angle H(1)–C(1)–C(2)–H(2) (numbering according to Fig. 3) is –59.3°. Therefore, both enantiomers of **5e** clearly possess *R*/*S* and *S*/*R* configurations existing in a ratio of 1:1 in the crystal. Further details of the structural analysis are not discussed here.

The use of the Karplus-type relationship enabled us to deduce the stereochemistry of **5e** as an example. The ^{1}H NMR spectra of **5e** shows that the ^3J(H,H) coupling constant for the protons attached to C-2 and C-3 is 3.3 Hz, indicating a dihedral angle of approximately 60°. The ^3J(Sn–C–C–H) coupling constant of 34.8 Hz for **5e** suggests a dihedral angle close to 60°. The ^3J(Sn,C=O) coupling constant (see Experimental section) of 94.1 Hz corresponds to a dihedral angle close to 180° indicating an *R,S*- (likewise *R,S*-) configuration.

The reaction of **4** with HCl proceeds differently from findings for the reaction of **3** with HCl: the reaction of **4a–d** with an equimolar amount of methanolic HCl yields Ph_3SnCl as the main product (strong signal in the ^{119}Sn NMR spectra) with **6** only as a minor product. The poor stabilization of the products by intramolecular coordination should be the reason for this difference. Halodestannylation reactions were also found at different β-trialkylstannyl-3-phenyl-propanoates, where only the possibility of intramolecular stabilization yields β-halodialkylstannyl derivatives [39]. On the other hand, reactions of the *tert*-butyl esters **4e–h** with methanolic HCl gave **6e–h** in high yields. The ^{119}Sn signals of **6** in $CDCl_3$ solution are found in a region including those typical for tetracoordinated **4** and pentacoordinated **5**. Also, the IR spectra of **6** taken in chloroform are different from those of **5:** there is a sharp band in the range for the coordinated amide C=O and a further one for the uncoordinated amide C=O, suggesting equilibrium between coordinated and uncoordinated tin in solution. On the contrary, the IR spectra of **5** taken in $CHCl_3$ shows only one band for amide C=O, which is shifted bathochromically upon coordination.

The use of the Karplus-type relations enabled us to deduce the stereochemistry of **6f** as an example. The ^{1}H NMR spectra of **6f** shows that the ^3J(H,H) coupling constant for the protons attached to C-2 and C-3 is 8.0 Hz, indicating a dihedral angle of approximately 180°. The ^3J(Sn–C–C–H) coupling constant of 30 Hz for **6f** suggests a dihedral angle close to 60°. The ^3J(Sn,C=O) coupling constants (see Experimental section) of 37.8 Hz should correspond to a dihedral angle close to 140° [29] indicating an *R,R*- (likewise *S,S*-) configuration. The crystal structure of **6f** has been determined (Fig. 4). It shows strong Sn···O=C(-Ph)–NH interactions [40] with a trigonal–bipyramidal structure as in **5e**. The equatorial positions are occupied by two phenyl groups and the carbon C(13) (numbering according to Fig. 4) of the amino acid, whereas the chlorine atom and the oxygen atom of the amide group are at axial positions forming an angle of 174.2(1)°. The bond length of Sn–O(4) is 2.510(2) Å and the dihedral angle H(11)–C(13)–C(21)–H(19) (numbering according to Figure 4) is –179.78 (2.38)°. Therefore, the two enantiomers of **6f** clearly possess *R/R*- and *S/S*-configurations, respectively, existing in a ratio of 1:1 in the crystal.

The reactions of **3** and **4** with one equivalent of bromine yields the monobromostannanes **7** and **8**. The analysis of **7** and **8** shows strong differences as compared with the observations for the monochlorostannanes **5** and **6**. The ^{119}Sn signal of **7** (produced from major isomer **3**) is clearly high-field shifted indicating a pentacoordinated tin atom. After the addition of HMPT ($(Me_2N)_3P=O$), the ^{119}Sn signal of **7** shows no change.

The Sn coordination of **7** is also reflected by the IR spectra taken in Nujol, KBr or chloroform. Compared with **3**, one of the two C=O bands of **7** is bathochromically shifted by nearly 40 cm^{-1}. This band belongs to the amide

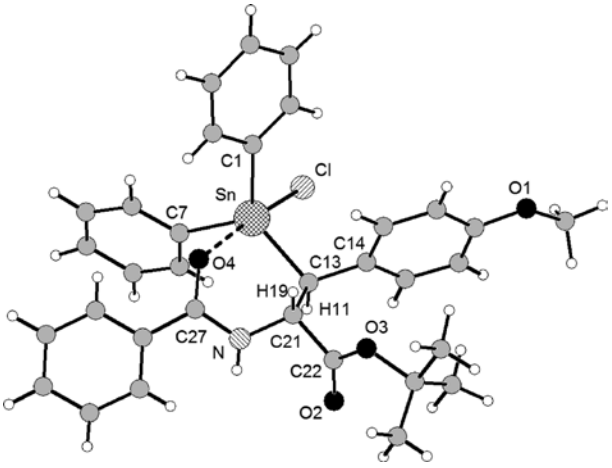


Fig. 4: Molecular structure of **6f** in the crystal.

C=O whereas the signal of the ester C=O stays unchanged. The intramolecular coordination of amide C=O to tin is clearly demonstrated by the fact that the carbonyl stretching frequency of compound **7** is the same both in the solid state and in solution.

Contrary to **7**, the ^{119}Sn signal of **8** is shifted in comparison with the signal of **4** by only 10–25 ppm to higher field. Moreover, the shift of the ^{119}Sn signal of **8** depends clearly on the concentration of the solution (see Experimental section). The higher concentration in chloroform causes a high field shift (**8d**). After the addition of a donor such as HMPT ($(Me_2N)_3P=O$), the ^{119}Sn signals of **7** and **8** are equal. The tin atom of the monobromostannane **8** is pentacoordinated after the addition of HMPT, with HMPT occupying one coordination position at the metal atom. The IR spectra of **8** in Nujol or KBr clearly shows a pentacoordination of the atom tin. Compared with **4**, the amide C=O band is bathochromically shifted by nearly 30 cm^{-1} whereas the ester C=O band remains unchanged. However, in the IR spectra of **8** in chloroform, a third strong ν(C=O) band appears between the bands for the ester C=O and that for the uncoordinated amide C=O indicating a coordinated amide C=O. This new signal of **8** observed in an unpolar solvent demonstrates an equilibrium between species with pentacoordinated and uncoordinated tin atoms.

The reaction of **7** with one further equivalent of bromine yields the dibromostannane **9**. The ^{119}Sn signal of **9** is shifted to a higher field as compared with dihalogenphenylethylstannane [$Ph(Et)SnCl_2$ in CD_2Cl_2: $\delta(^{119}Sn) = 44.4$ ppm; in $CDCl_3$: $\delta(^{119}Sn) = 39.6$ ppm] [41], but shifted to a lower field in comparison with the ^{119}Sn signal for 3-(dibromophenylstannane)-*N*-acetyl-alanine ethyl ester [in C_6D_6: $\delta(^{119}Sn) = -241.0$ ppm] [12].

Compared with **3**, the IR spectra of **9** in chloroform shows a bathochromic shift of amide C=O indicating a coordination of amide C=O at the tin atom. Likewise, the ester C=O band is shifted bathochromically.

The prolonged reaction of **5** overnight with one further equivalent of HCl yields the dichlorostannane **10**. The reaction of tetraorganostannanes with more than one equivalent of HCl is the usual method for the preparation of dichlorostannanes with mixed substituents [42, 43]. The ^{119}Sn signal of **10** is shifted to higher field compared with dichlorophenylethylstannane [41] and with **5**. This signal is comparable with the ^{119}Sn signal of **9** and is lying in the region standing for hexacoordinated tin [23]. This indicates that tin is hexacoordinated both in **9** and in **10**. Also, the IR spectra of **9** and of **10** in KBr are comparable. The bathochromic shift of amide C=O of **9** and **10** in comparison with **3** demonstrates its coordination to the tin atom. Likewise, the ester C=O band is shifted bathochromically in **9** and **10**. Also, in the light of earlier results [12], IR and NMR data reveal that tin in **9** and **10** is hexacoordinated by coordination of the amide C=O and ester C=O groups.

Reactions of **2c** with methyl- and butylstannyl hydride according to Eq. 2 were also successful, but the yields of stannylated phenylalanines depend strongly on the tin hydride used and vary from high (Ph_3SnH more than 80%) to low (Me_3SnH only 15%). The reaction of Me_3SnH with **2c**, for example, results in β-trimethylstannyl phenylalanine **11** and the hydrogenated product 4-$CH_3OC_6H_4$–CH_2–$CH(NHCOC_6H_5)COOCH_3$, whereas the reaction of Bu_3SnH with **2c** gives the β-tributylstannyl phenylalanine **12** in moderate yield. **11** and **12** are colorless solids that are very soluble in diethylether, alcohols, and halogenated hydrocarbons but less soluble in hydrocarbons. The alkylstannylated phenylalanines are better soluble than the phenylstannylated derivatives. The ^{119}Sn NMR spectra of the crude alkylstannylated products show only a single signal. No attempts were made to separate the respective diastereomeric mixtures.

3 Experimental section

All oxazolinones and dehydroamino acids were synthesized according to the literature [14]. The tin hydrides were prepared from R_3SnCl with $LiAlH_4$ according to van der Kerk et al. [44]. All operations with tin-containing compounds were carried out under dry nitrogen. The elemental microanalyses were determined using an Elemental Analyzer from Carlo Erba. Melting points were detected with a Kofler heating table microscope. The IR spectra

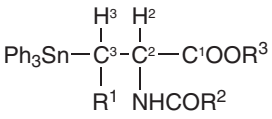


Fig. 5: Atom numbering adopted.

were recorded with a Zeiss specord or Mattson 5000 FT-IR spectrometer. All the NMR spectra were recorded in $CDCl_3$ solution using Bruker AC 80, WP 200, or Varian unity 500 spectrometers. Chemical shifts (δ) are reported in ppm and the coupling constants (J) are in Hz as absolute values without signs (Fig. 5). Tin coupling constants are related to the dominant isotop ^{119}Sn. The multiplicity "T" means that a dd appears with three signals.

3.1 General procedure for β-triphenylstannyl phenylalanines 3 and 4

2 (0.01 mol) and Ph_3SnH (0.011 mol) were mixed, AIBN (3 mol.%) was added and the mixture was heated to 80°C under stirring for 8 h. After the addition of 5 mL of methanol, the unsolved part was filtered off. The filtrate was treated with diethylether to crystallize **3/4**. The separation of **3** and **4** was successful by column chromatography (silica gel 60 MERCK, starting with diethylether-hexane vs. diethylether-methanol). Yields: 80%.

3.1.1 Phenylalanine *N*-benzoyl β-(triphenylstannyl) methyl ester

3a: M. p. 169°C. – IR (Nujol): ν = 1735 (COOMe), 1645 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 3.18 (s, 3H, OMe), 3.52 (d, 1 H, 3-H, ^2J(Sn,H) = 60.7 Hz, ^3J(3-H,2-H) = 10.3 Hz), 5.44 (dd, 1 H, 2-H, ^3J(Sn,H) = 34.8 Hz, ^3J(2-H,3-H) = 10.3 Hz), 6.28 (d, 1 H, NH), 7.03–7.40 (m, 25 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 172.5 (C-1, ^3J(Sn,C) = 16.9 Hz), 55.5 (C-2), 39.1 (C-3). – ^{119}Sn{^{1}H} NMR: δ = –121.3. – $C_{35}H_{31}NO_3Sn$ (632.33): calcd. C 66.48, H 4.94, N 2.21; found C 66.12, H 4.94, N 2.32.

4a: M. p. 170–173°C. – IR (KBr): ν = 1727 (COOMe), 1636 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 3.37 (s, 3H, OMe), 3.66 (d, 1 H, 3-H, ^2J(Sn,H) = 60.5 Hz, ^3J(3-H,2-H) = 9.3 Hz), 5.35 (dd, 1 H, 2-H, ^3J(Sn,H) = 31.5 Hz, ^3J(2-H,3-H) = 9.3 Hz), 6.52 (d, 1 H, NH), 7.04–7.40 (m, 25 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 173.0 (C-1, ^3J(Sn,C) = 42.2 Hz), 56.4 (C-2), 40.3 (C-3, ^1J(Sn,C) = 352.2 Hz). – ^{119}Sn{^{1}H} NMR: δ = –126.2. – $C_{35}H_{31}NO_3Sn$ (632.33): calcd. C 66.48, H 4.94, N 2.21; found C 66.75, H 4.94, N 2.17.

3.1.2 Phenylalanine *N*-acetyl β-(triphenylstannyl) methyl ester

3b: M. p. 168–170°C. IR (Nujol): ν = 1753 (COOMe), 1636 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.70 (s, 3 H, NCOMe), 3.39 (d, 1 H, 3-H, ^2J(Sn,H) = 62.5 Hz, ^3J(3-H,2-H) = 10.6 Hz), 3.70 (s, 3 H, OMe), 5.26 (dd, 1 H, 2-H, ^3J(Sn,H) = 32.8 Hz, ^3J(2-H,3-H) = 10.6 Hz), 5.68 (d, 1 H, NH), 7.00–7.44 (m, 20 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 172.5 (C-1, ^3J(Sn,C) = 17.9 Hz), 55.1 (C-2), 38.9 (C-3, ^1J(Sn,C) = 328.1 Hz). – ^{119}Sn{^{1}H} NMR: δ = –121.1. – $C_{30}H_{29}NO_3Sn$ (570.26): calcd. C 63.18, H 5.12, N 2.45; found C 62.91, H 5.10, N 2.47.

4b: IR (Nujol): ν = 1726 (COOMe), 1646 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.54 (s, 3 H, NCOMe), 3.35 (s, 3 H, OMe), 3.49 (d, 1 H, 3-H, ^2J(Sn,H) = 62.5 Hz, ^3J(3-H,2-H) = 9.5 Hz), 5.24 ("T", 1 H, 2-H, ^3J(Sn,H) = 29.5 Hz, ^3J(2-H,3-H) = 9.5 Hz), 5.81 (d, 1 H, NH), 7.00–7.44 (m, 20 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 172.9 (C-1, ^3J(Sn,C) = 43.9 Hz) 55.6 (C-2), 40.6 (C-3, ^1J(Sn,C) = 355.0 Hz). – ^{119}Sn{^{1}H} NMR: δ = –125.2.

3.1.3 *p*-Methoxy-phenylalanine *N*-benzoyl β-(triphenylstannyl) methyl ester

3c: M. p. 165°C. – IR (Nujol): ν = 1735 (COOMe), 1660 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 3.20 (s, 3 H, OMe), 3.52 (d, 1 H, 3-H, ^2J(Sn,H) = 63.5 Hz, ^3J(3-H,2-H) = 9.8 Hz), 3.73 (s, 3 H, OMe), 5.39 (dd, 1 H, 2-H, ^3J(Sn,H) = 38.8 Hz, ^3J(2-H,3-H) = 9.8 Hz), 6.35 (d, 1 H, NH), 6.73–7.41 (m, 24 H, Ph). – ^{13}C NMR (74.91 MHz, $CDCl_3$): δ = 172.6 (C-1, ^3J(Sn,C) = 20.3 Hz), 55.2 (C-2), 38.0 (C-3, ^1J(Sn,C) = 356.3 Hz). – ^{119}Sn{^{1}H} NMR: δ = –122.8. – $C_{36}H_{33}NO_4Sn$ (662.35): calcd. C 65.28, H 5.02, N 2.11; found C 65.45, H 4.96, N 2.13.

4c: M. p. 184°C. IR (KBr): ν = 1723 (COOMe), 1657 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 3.40 (s, 3 H, OMe), 3.66 (d, 1 H, 3-H, ^2J(Sn,H) = 71.7 Hz, ^3J(3-H,2-H) = 8.9 Hz), 3.76 (s, 3 H, OMe), 5.32 ("T", 1 H, 2-H, ^3J(Sn,H) = 32.6 Hz, ^3J(2-H,3-H) = 8.9 Hz), 6.53 (d, 1 H, NH), 6.70–7.51 (m, 24 H, Ph). – ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 173.1 (C-1, ^3J(Sn,C) = 40.4 Hz), 55.8 (C-2), 39.4 (C-3, ^1J(Sn,C) = 363.0 Hz). – ^{119}Sn{^{1}H} NMR: δ = –126.5.

3.1.4 *p*-Methoxy-phenylalanine *N*-acetyl β-(triphenylstannyl) methyl ester

3d: M. p. 142°C. – IR (Nujol): ν = 1755 (COOMe), 1645 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 1.70 (s, 3 H, NCOMe), 3.17 (s, 3 H, OMe), 3.38 (d, 1 H,

3-H, ^{2}J(Sn,H) = 63.7 Hz, ^{3}J(3-H,2-H) = 9.7 Hz), 3.75 (s, 3 H, OMe), 5.21 (dd, 1 H, 2-H, ^{3}J(Sn,H) = 31.9 Hz, ^{3}J(2-H,3-H) = 9.7 Hz), 5.76 (d, 1 H, NH), 6.68–7.49 (m, 24 H, Ph). – ^{13}C NMR (74.91 MHz, $CDCl_3$): δ = 172.5 (C-1, ^{3}J(Sn,C) = 19.4 Hz), 55.0 (C-2), 37.7 (C-3, ^{1}J(Sn,C) = 357.3 Hz). – ^{119}Sn{^{1}H} NMR: δ = –122.6. – $C_{31}H_{31}NO_4Sn$ (600.28): calcd. C 62.02, H 5.20, N 2.33; found C 61.84, H 5.07, N 2.42.

4d: IR (Nujol): ν = 1740 (COOMe), 1645 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 1.54 (s, 3 H, NCOMe), 3.36 (s, 3 H, OMe), 3.43 (d, 1 H, 3-H, ^{3}J(3-H,2-H) = 9.3 Hz), 3.75 (s, 3 H, OMe), 5.21 (dd, 1 H, 2-H, ^{3}J(2-H,3-H) = 9.3 Hz), 5.90 (d, 1 H, NH), 6.68–7.48 (m, 24 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 172.8 (C-1, ^{3}J(Sn,C) = 45.4 Hz), 55.6 (C-2), 39.5 (C-3, ^{1}J(Sn,C) = 367.7 Hz). – ^{119}Sn{^{1}H} NMR: δ = –125.7.

3.1.5 Phenylalanine *N*-benzoyl β-(triphenylstannyl) *tert*-butyl ester

3e: M. p. 127°C. – IR (Nujol): ν = 1720 (COO), 1630 (NHCO) cm^{-1}. – ^{1}H NMR (499.84 MHz, $CDCl_3$, 25°C, TMS): δ = 1.27 (s, 9 H, *t*-Bu), 3.72 (d, 1 H, 3-H, ^{2}J(Sn,H) = 69.3 Hz, ^{3}J(3-H,2-H) = 6.0 Hz), 5.33 (dd, 1 H, 2-H, ^{3}J(Sn,H) = 46.8 Hz, ^{3}J(2-H,3-H) = 6.0 Hz), 6.45 (d, 1 H, NH), 7.02–7.44 (m, 25 H, Ph). – ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 171.3 (C-1, ^{3}J(Sn,C) = 40.7 Hz), 56.3 (C-2), 40.1 (C-3, ^{1}J(Sn,C) = 364.5 Hz). – ^{119}Sn{^{1}H} NMR: δ = –129.0. – $C_{38}H_{37}NO_3Sn$ (674.41): calcd. C 67.67, H 5.52, N 2.07; found C 67.63, H 5.46, N 2.06.

4e: M. p. 170°C. – IR (Nujol): ν = 1708 (COO), 1660 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 1.06 (s, 9 H, *t*-Bu), 3.51 (d, 1 H, 3-H, ^{2}J(Sn,H) = 54.5 Hz, ^{3}J(3-H,2-H) = 11.8 Hz), 5.21 (dd, 1 H, 2-H, ^{3}J(Sn,H) = 30.7 Hz, ^{3}J(2-H,3-H) = 11.8 Hz), 6.36 (d, 1 H, NH), 7.08–7.42 (m, 25 H, Ph). – ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 172.2 (C-1, ^{3}J(Sn,C) = 63.7 Hz), 56.7 (C-2), 41.3 (C-3, ^{1}J(Sn,C) = 352.6 Hz). – ^{119}Sn{^{1}H} NMR: δ = –123.9. – $C_{38}H_{37}NO_3Sn$ (674.41): calcd. C 67.67, H 5.52, N 2.07; found C 67.54, H 5.60, N 2.00.

3.1.6 *p*-Methoxy-phenylalanine *N*-benzoyl β-(triphenylstannyl) *tert*-butyl ester

3f: M. p. 146°C. – IR (Nujol): ν = 1728 (COO), 1645 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 1.30 (s, 9 H, *t*-Bu), 3.70 (d, 1 H, 3-H, ^{2}J(Sn,H) = 70.1 Hz, ^{3}J(3-H,2-H) = 5.4 Hz), 3.73 (s, 3 H, OMe), 5.28 (dd, 1 H, 2-H, ^{3}J(Sn,H) = 47.6 Hz, ^{3}J(2-H,3-H) = 5.4 Hz), 6.51 (d, 1 H, NH), 6.71–7.47 (m, 24 H, Ph). – ^{13}C NMR (20.149 MHz, $CDCl_3$): δ = 171.4 (C-1, ^{3}J(Sn,C) = 44.0 Hz), 56.6 (C-2), 39.1 (C-3). – ^{119}Sn{^{1}H} NMR: δ = –128.8. – $C_{39}H_{39}NO_4Sn$ (704.44): calcd. C 66.49, H 5.58, N 1.98; found C 66.56, H 5.62, N 2.05.

4f: M. p. 171°C. – IR (Nujol): ν = 1728 (COO), 1645 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 1.11 (s, 9 H, *t*-Bu), 3.49 (d, 1 H, 3-H, ^{2}J(Sn,H) = 56.3 Hz, ^{3}J(3-H,2-H) = 11.4 Hz), 3.76 (s, 3 H, OMe), 5.17 (dd, 1 H, 2-H, ^{3}J(Sn,H) = 31.3 Hz, ^{3}J(2-H,3-H) = 11.4 Hz), 6.37 (d, 1 H, NH), 6.70–7.46 (m, 24 H, Ph). – ^{13}C NMR (20.149 MHz, $CDCl_3$): δ = 172.2 (C-1, ^{3}J(Sn,C) = 60.8 Hz), 57.0 (C-2), 40.1 (C-3, ^{1}J(Sn,C) = 351.9 Hz). – ^{119}Sn{^{1}H} NMR: δ = –125.4. – $C_{39}H_{39}NO_4Sn$ (704.44): calcd. C 66.49, H 5.58, N 1.98; found C 66.42, H 5.60, N 1.97.

3.1.7 *p*-Methoxy-phenylalanine *N*-acetyl β-(triphenylstannyl) *tert*-butyl ester

3g: M. p. 178°C. – IR (Nujol): ν = 1713 (COO), 1665 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.26 (s, 9 H, *t*-Bu), 1.62 (s, 3 H, NCOMe), 3.60 (d, 1 H, 3-H, ^{2}J(Sn,H) = 70.5 Hz, ^{3}J(3-H,2-H) = 5.5 Hz), 3.73 (s, 3 H, OMe), 5.09 (dd, 1 H, 2-H, ^{3}J(Sn,H) = 39.9 Hz, ^{3}J(2-H,3-H) = 5.4 Hz), 5.85 (d, 1 H, NH), 6.67–7.57 (m, 19 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 171.1 (C-1, ^{3}J(Sn,C) = 46.8 Hz), 55.9 (C-2), 38.8 (C-3). – ^{119}Sn{^{1}H} NMR: δ = –129.2. – $C_{34}H_{37}NO_4Sn$ (642.36): calcd. C 63.57, H 5.80, N 2.18; found C 63.42, H 5.76, N 2.27.

4g: IR (KBr): ν = 1713 (COO), 1665 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.07 (s, 9 H, *t*-Bu), 1.36 (s, 3 H, NCOMe), 3.29 (d, 1 H, 3-H, ^{2}J(Sn,H) = 57.0 Hz, ^{3}J(3-H,2-H) = 11.6 Hz), 3.73 (s, 3 H, OMe), 5.08 (dd, 1 H, 2-H, ^{3}J(2-H,3-H) = 11.6 Hz), 5.68 (d, 1 H, NH), 6.68–7.46 (m, 19 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 172.1 (C-1, ^{3}J(Sn,C) = 64.8 Hz), 56.0 (C-2), 40.8 (C-3, ^{1}J(Sn,C) = 357.5 Hz). – ^{119}Sn{^{1}H} NMR: δ = –125.5.

3.1.8 3,4-Dimethoxy-phenylalanine *N*-benzoyl β-(triphenylstannyl) *tert*-butyl ester

3h: M. p. 134°C. – IR (Nujol): ν = 1707 (COO), 1660 (NHCO) cm^{-1}. – ^{1}H NMR (200.06 MHz, $CDCl_3$, 25°C, TMS): δ = 1.31 (s, 9 H, *t*-Bu), 3.31 (s, 3 H, OMe), 3.66 (d, 1 H, 3-H, ^{3}J(3-H,2-H) = 5.2 Hz), 3.80 (s, 3 H, OMe), 5.26 (dd, 1 H, 2-H, ^{3}J(2-H,3-H) = 5.2 Hz), 6.49 (d, 1 H, NH), 6.57–6.70 (m, 3 H, Ph), 7.22–7.49 (m, 20 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 171.5 (C-1, ^{3}J(Sn,C) = 43.9 Hz), 56.5 (C-2), 39.3 (C-3). – ^{119}Sn{^{1}H} NMR: δ = –127.3.

4h: M. p. 156°C. – IR (Nujol): ν = 1709 (COO), 1653 (NHCO) cm^{-1}. – ^{1}H NMR (200.06 MHz, $CDCl_3$, 25°C, TMS): δ = 1.12 (s, 9 H, *t*-Bu), 3.39 (s, 3 H, OMe), 3.47 (d, 1 H, 3-H, ^{2}J(Sn,H) = 55.5 Hz, ^{3}J(3-H,2-H) = 11.2 Hz), 3.84 (s, 3 H, OMe), 5.22 (dd, 1 H, 2-H, ^{3}J(Sn,H) = 29.0 Hz, ^{3}J(2-H,3-H) = 11.2 Hz), 6.40 (d, 1 H, NH), 6.57–6.70 (m, 3 H, Ph), 7.11–7.41 (m,

20 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): $\delta = 172.1$ (C-1, ^3J(Sn,C) = 55.4 Hz), 56.7 (C-2), 40.6 (C-3). – ^{119}Sn{^{1}H} NMR: $\delta = -124.5$. – $C_{40}H_{41}NO_5Sn$ (734.46): calcd. C 65.41, H 5.62, N 1.90; found C 65.52, H 5.70, N 1.97.

3.2 General procedure for β-chlorodiphenylstannyl phenylalanines 5 and 6

One millimole of **3** or **4** dissolved in methanol was treated at –10°C with equimolar amounts of methanolic HCl. After warming to room temperature, the mixture was filtered, if necessary. The filtrate was concentrated and the solvent was evaporated *in vacuo*. The residue was crystallized after the addition of a small amount of CH_2Cl_2 and petroleum ether (b.p. 60–80°C). Recrystallization was repeated until the melting point showed no change.

3.2.1 Phenylalanine *N*-benzoyl β-(chlorodiphenylstannyl) methyl ester

5a: M. p. 187°C. – IR ($CHCl_3$): $\nu = 1733$ (COOMe), 1615 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.75$ (d, 1 H, 3-H, ^2J(Sn,H) = 104.0 Hz, ^3J(3-H,2-H) = 3.4 Hz), 3.76 (s, 3 H, OMe), 4.96 ("T", 1 H, 2-H, ^3J(Sn,H) = 38.0 Hz, ^3J(2-H,3-H) = 3.4 Hz), 7.01–8.18 (m, 20 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): $\delta = 171.0$ (C-1, ^3J(Sn,C) = 96.3 Hz), 58.7 (C-2), 44.7 (C-3). – ^{119}Sn{^{1}H} NMR: $\delta = -177.6$. – $C_{29}H_{26}ClNO_3Sn$ (590.68): calcd. C 58.97, H 4.43, N 2.37; found C 58.49, H 4.40, N 2.48.

6a: ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.64$ (s, 3 H, OMe), 3.72 (d, 1 H, 3-H, ^2J(Sn,H) = 90.3 Hz, ^3J(3-H,2-H) = 7.1 Hz), 5.21 ("T", 1 H, 2-H, ^3J(Sn,H) = 56.1 Hz, ^3J(2-H,3-H) = 7.1 Hz), 6.73 (d, 1 H, NH), 7.01–7.78 (m, 20 H, Ph). – ^{119}Sn{^{1}H} NMR: $\delta = -148.4$.

3.2.2 Phenylalanine *N*-acetyl β-(chlorodiphenylstannyl) methyl ester

5b: M. p. 200°C. – IR ($CHCl_3$): $\nu = 1735$ (COOMe), 1622 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 2.13$ (s, 3 H, NCOMe), 3.65 (d, 1 H, 3-H, ^2J(Sn,H) = 99.8 Hz, ^3J(3-H,2-H) = 3.1 Hz), 3.70 (s, 3 H, OMe), 4.78 ("T", 1 H, 2-H, ^3J(Sn,H) = 35.0 Hz, ^3J(2-H,3-H) = 3.1 Hz), 6.96–8.09 (m, 15 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): $\delta = 170.9$ (C-1, ^3J(Sn,C) = 97.3 Hz), 58.3 (C-2), 44.5 (C-3, ^1J(Sn,C) = 537.4 Hz). – ^{119}Sn{^{1}H} NMR: $\delta = -178.0$. – $C_{24}H_{24}ClNO_3Sn$ (528.61): calcd. C 54.53, H 4.57, N 2.65; found C 54.39, H 4.62, N 2.99.

3.2.3 *p*-Methoxy-phenylalanine *N*-benzoyl β-(chlorodiphenylstannyl) methyl ester

5c: M. p. 205°C. – IR (Nujol): $\nu = 1735$ (COOMe), 1615 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.71$ (s, 3 H, OMe), 3.73 (d, 1 H, 3-H, ^2J(Sn,H) = 103.3 Hz, ^3J(3-H,2-H) = 3.0 Hz), 3.77 (s, 3 H, OMe), 4.93 ("T", 1 H, 2-H, ^3J(Sn,H) = 36.3 Hz, ^3J(2-H,3-H) = 3.0 Hz), 7.68 (d, 1 H, NH), 6.65–8.35 (m, 19 H, Ph). – ^{13}C NMR (74.91 MHz, $CDCl_3$): $\delta = 171.3$ (C-1, ^3J(Sn,C) = 94.2 Hz), 58.5 (C-2), 43.8 (C-3). – ^{119}Sn{^{1}H} NMR: $\delta = -175.4$. – $C_{30}H_{28}ClNO_4Sn$ (620.71): calcd. C 58.05, H 4.55, N 2.25; found C 57.89, H 4.56, N 2.34.

3.2.4 *p*-Methoxy-phenylalanine *N*-acetyl β-(chlorodiphenylstannyl) methyl ester

5d: M. p. 202°C. – IR (Nujol): $\nu = 1720$ (COOMe), 1615 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 2.11$ (s, 3 H, NCOMe), 3.61 (d, 1 H, 3-H, ^2J(Sn,H) = 105.5 Hz, ^3J(3-H,2-H) = 3.0 Hz), 3.71 (s, 3 H, OMe), 3.73 (s, 3 H, OMe), 4.74 ("T", 1 H, 2-H, ^3J(Sn,H) = 34.0 Hz, ^3J(2-H,3-H) = 3.0 Hz), 6.67–8.09 (m, 15 H, Ph + NH). – ^{13}C NMR (50.32 MHz, $CDCl_3$): $\delta = 170.8$ (C-1, ^3J(Sn,C) = 98.8 Hz), 58.2 (C-2), 43.2 (C-3, ^1J(Sn,C) = 566.6 Hz). – ^{119}Sn{^{1}H} NMR: $\delta = -178.5$. – $C_{25}H_{26}ClNO_4Sn$ (558.63): calcd. C 53.75, H 4.69, N 2.50; found C 53.52, H 4.70, N 2.57.

3.2.5 Phenylalanine *N*-benzoyl β-(chlorodiphenylstannyl) *tert*-butyl ester

5e: M. p. 205°C. – IR (KBr): $\nu = 1720$ (COO), 1613 (NHCO) cm^{-1}. – IR ($CHCl_3$): $\nu = 1725$ (COO), 1613 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.37$ (s, 9 H, *t*-Bu), 3.72 (d, 1 H, 3-H, ^2J(Sn,H) = 106.7 Hz, ^3J(3-H,2-H) = 3.3 Hz), 4.84 ("T", 1 H, 2-H, ^3J(Sn,H) = 34.8 Hz, ^3J(2-H,3-H) = 3.3 Hz), 7.12–8.21 (m, 21 H, Ph + NH). – ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 169.6$ (C-1, ^3J(Sn,C) = 94.1 Hz), 58.2 (C-2), 44.6 (C-3). – ^{119}Sn{^{1}H} NMR: $\delta = -182.5$. – $C_{32}H_{32}ClNO_3Sn$ (632.76): calcd. C 60.74, H 5.09, N 2.21; found C 60.92, H 4.95, N 2.27.

6e: M. p. 202°C. – IR (KBr): $\nu = 1700$ (COO), 1600 (NHCO) cm^{-1}. – IR ($CHCl_3$): $\nu = 1715$ (COO), 1665 (very strong), 1610 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.36$ (s, 9 H, *t*-Bu), 3.61 (d, 1 H, 3-H, ^2J(Sn,H) = 84.9 Hz, ^3J(3-H,2-H) = 8.4 Hz,), 5.25 (dd, 1 H, 2-H, ^3J(Sn,H) = 39.5 Hz, ^3J(2-H,3-H) = 8.4 Hz), 6.72 (d, 1 H, NH), 7.04–7.97 (m, 20 H, Ph). – ^{119}Sn{^{1}H} NMR: $\delta = -139.2$.

3.2.6 *p*-Methoxy-phenylalanine *N*-benzoyl β-(chlorodiphenylstannyl) *tert*-butyl ester

5f: M. p. 185°C. – IR (Nujol): $\nu = 1730$ (COO), 1610 (NHCO) cm^{-1}. – IR (KBr): $\nu = 1725$ (COO), 1613 (NHCO) cm^{-1}, IR ($CHCl_3$): $\nu = 1724$ (COO), 1615 (NHCO) cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.39$ (s, 9 H, *t*-Bu), 3.68 (d, 1 H, 3-H, $^2J(Sn,H) = 99.1$ Hz, $^3J(3\text{-H},2\text{-H}) = 3.2$ Hz), 3.71 (s, 3 H, OMe), 4.81 ("T", 1 H, 2-H, $^3J(Sn,H) = 33.8$ Hz, $^3J(2\text{-H},3\text{-H}) = 3.2$ Hz), 6.65–8.17 (m, 20 H, Ph + NH).– ^{13}C NMR (125.70 MHz, $CDCl_3$): $\delta = 169.7$ (C-1, $^3J(Sn,C) = 97.4$ Hz), 58.5 (C-2), 43.6 (C-3, $^1J(Sn,C) = 564.8$ Hz). – $^{119}Sn\{^1H\}$ NMR: $\delta = -181.0$. – $C_{33}H_{34}ClNO_4Sn$ (662.79): calcd. C 59.80, H 5.17, N 2.11; found C 59.57, H 5.15, N 2.15.

6f: M. p. 179°C. – IR (KBr): $\nu = 1707$ (COO), 1595 (NHCO) cm^{-1}. – IR ($CHCl_3$): $\nu = 1715$ (COO), 1665 (very strong), 1600 (NHCO) cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.37$ (s, 9 H, *t*-Bu), 3.56 (d, 1 H, 3-H, $^2J(Sn,H) = 85.5$ Hz, $^3J(3\text{-H},2\text{-H}) = 8.0$ Hz), 3.75 (s, 3 H, OMe), 5.20 ("T", 1 H, 2-H, $^3J(Sn,H) = 30.0$ Hz, $^3J(2\text{-H},3\text{-H}) = 8.0$ Hz), 6.66 (d, 1 H, NH), 6.71–7.87 (m, 19 H, Ph). – ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 175.0$ (C-1, $^3J(Sn,C) = 37.8$ Hz), 56.9 (C-2), 44.9 (C-3, $^1J(Sn,C) = 513.6$ Hz). – $^{119}Sn\{^1H\}$ NMR: $\delta = -137.4$.

3.2.7 *p*-Methoxy-phenylalanine *N*-acetyl β-(chlorodiphenylstannyl) *tert*-butyl ester

5g: M. p. 179°C. – IR (Nujol): $\nu = 1720$ (COO), 1613 (NHCO) cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.35$ (s, 9 H, *t*-Bu), 2.12 (s, 3 H, NCOMe), 3.57 (d, 1 H, 3-H, $^3J(3\text{-H},2\text{-H}) = 3.5$ Hz), 3.74 (s, 3 H, OMe), 4.62 ("T", 1 H, 2-H, $^3J(2\text{-H},3\text{-H}) = 3.5$ Hz), 6.72–8.11 (m, 15 H, Ph + NH). – ^{13}C NMR (20.149 MHz, $CDCl_3$): $\delta = 169.3$ (C-1, $^3J(Sn,C) = 98.2$ Hz), 57.8 (C-2), 43.3 (C-3). – $^{119}Sn\{^1H\}$ NMR: $\delta = -181.1$. – $C_{28}H_{32}ClNO_4Sn$ (600.71): calcd. C 55.98, H 5.37, N 2.33; found C 55.56, H 5.19, N 2.29.

6g: M. p. 161–163°C. – IR (Nujol): $\nu = 1720$ (COO), 1613 (NHCO) cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.33$ (s, 9 H, *t*-Bu), 1.74 (s, 3 H, NCOMe), 3.40 (d, 1 H, 3-H, $^3J(3\text{-H},2\text{-H}) = 8.5$ Hz), 3.74 (s, 3 H, OMe), 4.98 (dd, 1 H, 2-H, $^3J(2\text{-H},3\text{-H}) = 8.5$ Hz), 6.10 (d, 1 H, NH), 6.72–7.82 (m, 14 H, Ph). – $^{119}Sn\{^1H\}$ NMR: $\delta = -138.8$.

3.2.8 3,4-Dimethoxy-phenylalanine *N*-benzoyl β-(chlorodiphenylstannyl) *tert*-butyl ester

5h: M. p. 149–153°C – IR (Nujol): $\nu = 1715$ (COO), 1610 (NHCO) cm^{-1}. – ^1H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): $\delta = 1.43$ (s, 9 H, *t*-Bu), 3.13 (s, 3 H, OMe), 3.67 (d, 1 H, 3-H, $^2J(Sn,H) = 105.1$ Hz, $^3J(3\text{-H},2\text{-H}) = 2.9$ Hz), 3.78 (s, 3 H, OMe), 4.81 (dd, 1 H, 2-H, $^3J(Sn,H) = 38.6$ Hz, $^3J(2\text{-H},3\text{-H}) = 2.9$ Hz), 6.41–6.71 (m, 3 H, Ph), 7.19–8.19 (m, 16 H, Ph + NH). – ^{13}C NMR (125.70 MHz, $CDCl_3$): $\delta = 169.7$ (C-1, $^3J(Sn,C) = 93.9$ Hz), 58.4 (C-2), 43.8 (C-3). – $^{119}Sn\{^1H\}$ NMR: $\delta = -176.9$. – $C_{34}H_{36}ClNO_5Sn$ (692.81): calcd. C 58.94, H 5.23, N 2.02; found C 58.52, H 5.40, N 2.11.

3.3 General procedure for β-bromo-diphenylstannyl phenylalanines 7 and 8

One millimole of **3** or **4** dissolved in $CHCl_3$ was treated at –30°C with equimolar amounts of bromine dissolved in $CHCl_3$. After warming to room temperature, the mixture was filtered, if necessary. The filtrate was concentrated by evaporation of the solvent *in vacuo*. The residue was crystallized after the addition of a small amount of CH_2Cl_2 and petroleum ether (b.p. 60–80°C). Recrystallization was repeated until the melting point showed no change.

3.3.1 Phenylalanine *N*-benzoyl β-(bromodiphenylstannyl) methyl ester

7a: M. p. 167°C. – IR (KBr): $\nu = 1741$ (COOMe), 1607 (NHCO) cm^{-1}. – ^1H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.77$ (s, 3 H, OMe), 3.81 (d, 1 H, 3-H, $^2J(Sn,H) = 98.4$ Hz, $^3J(3\text{-H},2\text{-H}) = 2.9$ Hz), 4.98 ("T", 1 H, 2-H, $^3J(Sn,H) = 37.8$ Hz, $^3J(2\text{-H},3\text{-H}) = 2.9$ Hz), 7.02–8.25 (m, 21 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): $\delta = 171.0$ (C-1, $^3J(Sn,C) = 97.7$ Hz), 58.3 (C-2, $^2J(Sn,C) = 11.0$ Hz), 45.7 (C-3, $^1J(Sn,C) = 540.5$ Hz). – $^{119}Sn\{^1H\}$ NMR: $\delta = -172.0$.

8a: M. p. 177°C. – IR (Nujol): $\nu = 1740$ (COOMe), 1610 (NHCO) cm^{-1}. ^1H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.66$ (s, 3 H, OMe), 3.77 (d, 1 H, 3-H, $^2J(Sn,H) = 86.6$ Hz, $^3J(3\text{-H},2\text{-H}) = 7.1$ Hz), 5.27 ("T", 1 H, 2-H, $^3J(Sn,H) = 48.8$ Hz, $^3J(2\text{-H},3\text{-H}) = 7.1$ Hz), 6.66 (d, 1 H, NH), 7.07–7.94 (m, 20 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): $\delta = 175.2$ (C-1, $^3J(Sn,C) = 24.9$ Hz), 56.7 (C-2), 46.5 (C-3, $^1J(Sn,C) = 485.7$ Hz). – $^{119}Sn\{^1H\}$ NMR: $\delta = -139.3$.

3.3.2 Phenylalanine *N*-acetyl β-(bromodiphenylstannyl) methyl ester

7b: M. p. 207°C. – IR ($CHCl_3$): $\nu = 1733$ (COOMe), 1623 (NHCO) cm^{-1}, IR (KBr): $\nu = 1720$ (COOMe), 1600 (NHCO) cm^{-1}. – ^1H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): $\delta = 2.10$ (s, 3 H, NCOMe), 3.71 (d, 1 H, 3-H, $^2J(Sn,H) = 97.5$ Hz,

^3J(3-H,2-H) = 3.0 Hz), 3.71 (s, 3 H, OMe), 4.79 ("T", 1 H, 2-H, ^3J(Sn,H) = 35.5 Hz, ^3J(2-H,3-H) = 3.0 Hz), 6.99–8.15 (m, 16 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 170.9 (C-1, ^3J(Sn,C) = 95.7 Hz), 58.0 (C-2, ^2J(Sn,C) = 10.0 Hz), 45.2 (C-3, ^1J(Sn,C) = 536.6 Hz). – ^{119}Sn{^{1}H} NMR: δ = –172.7.

8b: M. p. 206°C. – IR (Nujol): ν = 1739 (COOMe), 1640 (NHCO) cm^{-1}, IR ($CHCl_3$): ν = 1736 (COO), 1680, 1630 (NHCO) cm^{-1}. ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.83 (s, 3 H, NCOMe), 3.62 (d, 1 H, 3-H, ^2J(Sn,H) = 86.5 Hz, ^3J(3-H,2-H) = 7.5 Hz), 3.65 (s, 3 H, OMe), 5.08 ("T", 1 H, 2-H, ^3J(Sn,H) = 43.9 Hz, ^3J(2-H,3-H) = 7.5 Hz), 6.05 (d, 1 H, NH), 7.01–7.92 (m, 15 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 175.3 (C-1, ^3J(Sn,C) = 28.9 Hz), 56.2 (C-2), 46.5 (C-3, ^1J(Sn,C) = 450.0 Hz). – ^{119}Sn{^{1}H} NMR: δ = –134.9 (5% solution), –156.6 (concentrated solution).

3.3.3 *p*-Methoxy-phenylalanine *N*-benzoyl β-(bromodiphenylstannyl) methyl ester

7c: M. p. 212°C. – IR (KBr): ν = 1734 (COOMe), 1610 (NHCO) cm^{-1}. – ^{1}H NMR (200.06 MHz, $CDCl_3$, 25°C, TMS): δ = 3.68 (s, 3 H, OMe), 3.74 (d, 1 H, 3-H, ^2J(Sn,H) = 101.0 Hz, ^3J(3-H,2-H) = 3.7 Hz), 3.74 (s, 3 H, OMe), 4.90 (dd, 1 H, H_B, ^3J(Sn,H) = 32.6 Hz, ^3J(2-H,3-H) = 3.7 Hz), 6.63–8.18 (m, 20 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 171.1 (C-1, ^3J(Sn,C) = 99.7 Hz), 58.5 (C-2), 44.0 (C-3, ^1J(Sn,C) = 552.4 Hz). – ^{119}Sn{^{1}H} NMR: δ = –171.0.

8c: M. p. 179°C. – IR (Nujol): ν = 1743 (COOMe), 1607 (NHCO) cm^{-1}, IR ($CHCl_3$): ν = 1733 (COO), 1670, 1606 (NHCO) cm^{-1}. ^{1}H NMR (200.06 MHz, $CDCl_3$, 25°C, TMS): δ = 3.64 (s, 3 H, OMe), 3.71 (d, 1 H, 3-H, ^2J(Sn,H) = 88.3 Hz, ^3J(3-H,2-H) = 7.0 Hz), 3.75 (s, 3 H, OMe), 5.19 ("T", 1 H, 2-H, ^3J(Sn,H) = 52.0 Hz, ^3J(2-H,3-H) = 7.0 Hz), 6.65 (d, 1 H, NH), 6.73–7.90 (m, 19 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 175.2 (C-1, ^3J(Sn,C) = 24.9 Hz), 56.4 (C-2), 45.8 (C-3, ^1J(Sn,C) = 497.7 Hz). – ^{119}Sn{^{1}H} NMR: δ = –134.9.

3.3.4 *p*-Methoxy-phenylalanine *N*-acetyl β-(bromodiphenylstannyl) methyl ester

7d: M. p. 210°C. – IR (Nujol): ν = 1710 (COOMe), 1600 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 2.10 (s, 3 H, NCOMe), 3.67 (d, 1 H, 3-H, ^2J(Sn,H) = 99.6 Hz, ^3J(3-H,2-H) = 3.1 Hz), 3.71 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 4.76 ("T", 1 H, 2-H, ^3J(Sn,H) = 34.4 Hz, ^3J(2-H,3-H) = 3.1 Hz), 6.69–8.15 (m, 15 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 170.8 (C-1, ^3J(Sn,C) = 95.7 Hz), 58.3 (C-2), 44.4 (C-3, ^1J(Sn,C) = 549.6 Hz). – ^{119}Sn{^{1}H} NMR: δ = –171.2.

8d: M. p. 152°C. – IR (Nujol): ν = 1747 (COOMe), 1613 (NHCO) cm^{-1}, IR ($CHCl_3$): ν = 1740 (COO), 1680, 1615 (NHCO) cm^{-1}. ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.83 (s, 3 H, NCOMe), 3.57 (d, 1 H, 3-H, ^2J(Sn,H) = 84.5 Hz, ^3J(3-H,2-H) = 7.6 Hz), 3.64 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 5.02 ("T", 1 H, 2-H, ^3J(Sn,H) = 45.9 Hz, ^3J(2-H,3-H) = 7.6 Hz), 6.01 (d, 1 H, NH), 6.73–7.85 (m, 14 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 174.7 (C-1, ^3J(Sn,C) = 28.9 Hz), 56.8 (C-2), 45.6 (C-3, ^1J(Sn,C) = 490.3 Hz). – ^{119}Sn{^{1}H} NMR: δ = –137.3.

3.3.5 Phenylalanine *N*-benzoyl β-(bromodiphenylstannyl) *tert*-butyl ester

7e: M. p. 188°C. – IR (Nujol): ν = 1705 (COO), 1605 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 1.38 (s, 9 H, *t*-Bu), 3.78 (d, 1 H, 3-H, ^2J(Sn,H) = 101.2 Hz, ^3J(3-H,2-H) = 3.2 Hz), 4.85 ("T", 1 H, 2-H, ^3J(Sn,H) = 34.8 Hz, ^3J(2-H,3-H) = 3.2 Hz), 7.13–8.23 (m, 21 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 169.6 (C-1, ^3J(Sn,C) = 92.7 Hz), 58.3 (C-2), 45.5 (C-3, ^1J(Sn,C) = 536.5 Hz). – ^{119}Sn{^{1}H} NMR: δ = –177.3, –179.5 (with HMPT). – $C_{32}H_{32}BrNO_3Sn$ (677.21): calcd. C 56.75, H 4.76, N 2.07; found C 56.68, H 4.77, N 1.95.

8e: M. p. 186°C. – IR (Nujol): ν = 1705 (COO), 1600 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 1.36 (s, 9 H, *t*-Bu), 3.66 (d, 1 H, 3-H, ^2J(Sn,H) = 82.6 Hz, ^3J(3-H,2-H) = 8.2 Hz), 5.27 (dd, 1 H, 2-H, ^3J(Sn,H) = 27.0 Hz, ^3J(2-H,3-H) = 8.2 Hz), 6.66 (d, 1 H, NH), 7.07–7.83 (m, 20 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 174.9 (C-1, ^3J(Sn,C) = 37.9 Hz), 56.6 (C-2), 46.6 (C-3, ^1J(Sn,C) = 480.7 Hz). – ^{119}Sn{^{1}H} NMR: δ = –131.6, –170.4 (with HMPT). – $C_{32}H_{32}BrNO_3Sn$ (677.21): calcd. C 56.75, H 4.76, N 2.07; found C 56.71, H 4.64, N 2.08.

3.3.6 *p*-Methoxy-phenylalanine *N*-acetyl β-(bromodiphenylstannyl) *tert*-butyl ester

7g: M. p. 176°C. – IR (Nujol): ν = 1720 (COO), 1610 (NHCO) cm^{-1}, IR ($CHCl_3$): ν = 1715 (COO), 1610 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.36 (s, 9 H, *t*-Bu), 2.08 (s, 3 H, NCOMe), 3.64 (d, 1 H, 3-H, ^2J(Sn,H) = 104.9 Hz, ^3J(3-H,2-H) = 3.5 Hz), 3.75 (s, 3 H, OMe), 4.64 ("T", 1 H, 2-H, ^3J(Sn,H) = 31.5 Hz, ^3J(2-H,3-H) = 3.5 Hz), 6.70–8.14 (m, 15 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 169.1 (C-1,

^3J(Sn,C) = 96.8 Hz), 57.8 (C-2), 43.5 (C-3). – ^{119}Sn{^{1}H} NMR: δ = –174.9.

8g: IR (Nujol): ν = 1720 (COO), 1613 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.34 (s, 9 H, *t*-Bu), 1.72 (s, 3 H, NCOMe), 3.46 (d, 1 H, 3-H, ^2J(Sn,H) = 81.5 Hz, ^3J(3-H,2-H) = 8.5 Hz), 3.75 (s, 3 H, OMe), 5.02 (dd, 1 H, 2-H, ^3J(Sn,H) = 26.9 Hz, ^3J(2-H,3-H) = 8.5 Hz), 6.01 (d, 1 H, NH), 6.71–8.09 (m, 14 H, Ph). – ^{119}Sn{^{1}H} NMR: δ = –130.4.

3.3.7 3,4-Dimethoxy-phenylalanine *N*-benzoyl β-(bromodiphenylstannyl) *tert*-butyl ester

7h: IR (Nujol): ν = 1720 (COO), 1610 (NHCO) cm^{-1}, IR ($CHCl_3$): ν = 1724 (COO), 1613 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.44 (s, 9 H, *t*-Bu), 3.15 (s, 3 H, OMe), 3.73 (d, 1 H, 3-H, ^2J(Sn,H) = 99.1 Hz, ^3J(3-H,2-H) = 2.7 Hz), 3.79 (s, 3 H, OMe), 4.83 (dd, 1 H, 2-H, ^3J(Sn,H) = 38.1 Hz, ^3J(2-H,3-H) = 2.7 Hz), 6.66–6.71 (m, 3 H, Ph), 7.19–8.27 (m, 16 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 169.5 (C-1, ^3J(Sn,C) = 98.6 Hz), 58.5 (C-2), 44.0 (C-3). – ^{119}Sn{^{1}H} NMR: δ = –172.1.

8h: IR (Nujol): ν = 1725 (COOMe), 1600 (NHCO) cm^{-1}, IR ($CHCl_3$): ν = 1725 (COO), 1667, 1600 (NHCO) cm^{-1}. ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 1.40 (s, 9 H, *t*-Bu), 3.43 (s, 3 H, OMe), 3.61 (d, 1 H, 3-H, ^2J(Sn,H) = 82.9 Hz, ^3J(3-H,2-H) = 7.8 Hz), 3.70 (s, 3 H, OMe), 5.27 ("T", 1 H, 2-H, ^3J(Sn,H) = 25.1 Hz, ^3J(2-H,3-H) = 7.8 Hz), 6.54–6.83 (m, 3 H, Ph), 7.07–7.90 (m, 16 H, Ph + NH). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 171.5 (C-1, ^3J(Sn,C) = 43.9 Hz), 56.5 (C-2), 39.3 (C-3). – ^{119}Sn{^{1}H} NMR: δ = –133.3.

3.4 β-Dibromophenylstannyl phenylalanine 9

To a stirred solution of 1 mmol of the monobromo tin compound **7** in 10 mL chloroform at –20°C was added dropwise a solution of 1 mmol of bromine in $CHCl_3$. After stirring for 1 h at room temperature, the solvent was removed under vacuum. The residue was crystallized from ether/petroleum ether (b.p. 60–80°C).

3.4.1 Phenylalanine *N*-benzoyl β-(dibromophenylstannyl) methyl ester

9a: M. p. 163°C. – IR (KBr): ν = 1710 (COOMe), 1600 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 3.84 (s, 3 H, OMe), 3,99 (d, 1 H, 3-H, ^2J(Sn,H) = 117.2 Hz, ^3J(3-H,2-H) = 3.2 Hz), 5.22 ("T", 1 H, 2-H, ^3J(Sn,H) = 57.1 Hz, ^3J(2-H,3-H) = 3.2 Hz), 7.08–7.99 (m, 16 H, Ph + NH). – ^{119}Sn{^{1}H} NMR: δ = –215.0.

3.4.2 Phenylalanine *N*-acetyl β-(dibromophenylstannyl) methyl ester

9b: M. p. 177°C. – IR (KBr): ν = 1697 (COOMe), 1606 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 2.16 (s, 3H, NCOMe), 3.80 (s, 3H, OMe), 3,89 (d, 1 H, 3-H, ^2J(Sn,H) = 116.9 Hz, ^3J(3-H,2-H) = 3.0 Hz), 5.03 ("T", 1 H, 2-H, ^3J(Sn,H) = 60.5 Hz, ^3J(2-H,3-H) = 3.0 Hz), 7.04–7.93 (m, 11H, Ph + NH). – ^{119}Sn{^{1}H} NMR: δ = –214.3.

3.4.3 *p*-Methoxy-phenylalanine *N*-acetyl β-(dibromophenylstannyl) methyl ester

9d: IR (KBr): ν = 1708 (COOMe), 1609 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 2.16 (s, 3 H, NCOMe), 3.75 (s, 3 H, OMe), 3.79 (s, 3 H, OMe), 3.86 (d, 1 H, 3-H, ^2J(Sn,H) = 117.2 Hz, ^3J(3-H,2-H) = 3.2 Hz), 4.99 ("T", 1 H, 2-H, ^3J(Sn,H) = 58.7 Hz, ^3J(2-H,3-H) = 3.2 Hz), 6.76–7.93 (m, 10 H, Ph + NH). – ^{119}Sn{^{1}H} NMR: δ = –215.2.

3.5 β-Dichlorophenylstannyl phenylalanine 10

A stirred solution of 1 mmol of the monochloro tin compound **5** in methanol was treated at –10°C with 1 mmol of methanolic HCl. After stirring for 1 h at –10°C and overnight at room temperature, the mixture was filtered, if necessary. The filtrate was concentrated by evaporation in vacuo. The residue was crystallized after the addition of a small amount of CH_2Cl_2 and petroleum ether (b.p. 60–80°C). Yield: 60%.

3.5.1 Phenylalanine *N*-benzoyl β-(dichlorophenylstannyl) methyl ester

10a: IR (KBr): ν = 1698 (COOMe), 1610 (NHCO) cm^{-1}. – ^{1}H NMR (200.06 MHz, $CDCl_3$, 25°C, TMS): δ = 3.85 (s, 3 H, OMe), 3.94 (d, 1 H, 3-H, ^2J(Sn,H) = 118.8 Hz, ^3J(3-H,2-H) = 3.0 Hz), 5.22 ("T", 1 H, 2-H, ^3J(Sn,H) = 56.7 Hz, ^3J(2-H,3-H) = 3.0 Hz), 7.10–7.99 (m, 15 H, phenyl). – ^{119}Sn{^{1}H} NMR: δ = –207.2.

3.5.2 *p*-Methoxy-phenylalanine *N*-acetyl β-(dichlorophenylstannyl) methyl ester

10d: IR (KBr): ν = 1695 (COOMe), 1608 (NHCO) cm^{-1}. – ^{1}H NMR (499.88 MHz, $CDCl_3$, 25°C, TMS): δ = 2.13 (s, 3 H, NCOMe), 3.75 (s, 3 H, OMe), 3.78 (d, 1 H, 3-H, ^{2}J(Sn,H) = 122.5 Hz, ^{3}J(3-H,2-H) = 3.3 Hz), 3.79 (s, 3 H, OMe), 4.99 ("T", 1 H, 2-H, ^{3}J(Sn,H) = 56.1 Hz, ^{3}J(2-H,3-H) = 3.3 Hz), 6.76–7.90 (m, 10 H, phenyl + NH). – ^{119}Sn{^{1}H} NMR: δ = –209.6.

3.5.3 *p*-Methoxy-phenylalanine *N*-benzoyl β-(trimethylstannyl) methyl ester 11

2c (0.02 mol) and Me_3SnH (0.04 mol) were mixed in 20 mL THF. AIBN (3 mol.%) was added and the mixture was heated to 70°C under stirring for 12 h. The solvent and volatile products were eliminated in vacuum. The residue was purified by column chromatography (silica gel 60 MERCK, starting with diethylether-hexane 1:1 vs. diethylether-hexane 3:2).

Yield: 15%. M. p. 150–155°C. – IR (Nujol): ν = 1741 (COOMe), 1633 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 2.92 (d, 1 H, 3-H, ^{2}J(Sn,H) = 62.0 Hz, ^{3}J(3-H,2-H) = 7.9 Hz), 3.66 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 5.22 ("T", 1 H, 2-H, ^{3}J(2-H,3-H) = 7.9 Hz), 6.53 (d, 1 H, NH), 6.78–7.73 (m, 9 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 173.3 (C-1, ^{3}J(Sn,C) = 25.8 Hz), 55.6 (C-2), 37.9 (C-3, ^{1}J(Sn,C) = 311.0 Hz). – ^{119}Sn{^{1}H} NMR: δ = 7.58. – $C_{21}H_{27}NO_4Sn$ (476.14): calcd. C 52.97, H 5.71, N 2.94; found C 53.09, H 5.75, N 2.99.

3.5.4 *p*-Methoxy-phenylalanine *N*-benzoyl β-(tributylstannyl) methyl ester 12

2c (0.04 mol) and Bu_3SnH (0.05 mol) were mixed in 5 mL THF. AIBN (3 mol.%) was added and the mixture was heated to 80°C under stirring for 12 h. After the addition of 5 mL of methanol, the unreacted **2c** was filtered off and the volume of the filtrate reduced under vacuum. The residue was purified by column chromatography (silica gel 60 MERCK, starting with diethylether-hexane 1:1 vs. diethylether-methanol). Yield: 35%.

M. p. 103°C. – IR (Nujol): ν = 1740 (COOMe), 1630 (NHCO) cm^{-1}. – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C, TMS): δ = 0.81 (t, 9 H, CH_3), 1.26 (m, 18 H, CH_2), 2.85 (d, 1 H, 3-H, ^{2}J(Sn,H) = 52.0 Hz, ^{3}J(3-H,2-H) = 10.1 Hz), 3.78 (s, 6 H,

Table 1: Crystal structure data for **4c**, **5e**, and **6f**.

	4c [37]	5e [37]	6f [40]
Formula	$C_{36}H_{33}NO_4Sn$	$C_{32}H_{32}ClNO_3Sn$	$C_{33}H_{34}ClNO_4Sn$
M_r	662.3	632.7	662.7
Temperature, K	293	293	293
Crystal size, mm^3	0.34 × 0.30 × 0.27	0.40 × 0.36 × 0.34	0.31 × 0.29 × 0.20
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	9.923(1)	10.476(9)	9.937(1)
b, Å	10.422(1)	15.620(1)	13.059(2)
c, Å	15.568(2)	18.392(2)	13.706(2)
α, deg	90.015(9)	90.0	65.25(1)
β, deg	99.263(11)	94.779(7)	73.16(1)
γ, deg	98.914(9)	90.0	84.03(1)
V, Å^3	1569.3(3)	2999.1(5)	1545.5(4)
Z	2	4	2
D_{calcd}, g cm^{-3}	1.40	1.40	1.42
μ(MoK_α), mm^{-1}	0.85	0.97	0.95
F(000), *e*	676	1288	676
hkl range	±10, ±11, ±16	±12, +18, +22	±13, ±17, ±18
Refl. measured	8253	5811	22 511
Refl. unique/R_{int}	4128/0.0152	5583/0.032	6891/0.0573
Param. refined	382	347	361
$R(F)/wR(F^2)$[a] (all refl.)	0.0182/0.0449	0.0540/0.0826	0.0384/0.0824
GoF (F^2)[b]	1.078	1.005	0.712
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.23/–0.21	1.11/–0.45	0.48/–0.97
CCDC	1557853	1557854	1543484

[a] $R1 = ||F_o| - |F_c|| / \Sigma |F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$.

OMe), 5.19 (dd, 1 H, 2-H, ^3J(2-H,3-H) = 10.1 Hz), 6.30 (d, 1 H, NH), 6.74–7.66 (m, 9 H, Ph). – ^{13}C NMR (125.71 MHz, $CDCl_3$): δ = 172.7 (C-1, ^3J(Sn,C) = 16.9 Hz), 55.6 (C-2), 35.4 (C-3, ^1J(Sn,C) = 246.4 Hz). – ^{119}Sn{^{1}H} NMR: δ = –10.4. – $C_{30}H_{45}NO_4Sn$ (602.38): calcd. C 59.81, H 7.53, N 2.32; found C 59.88, H 7.21, N 2.38.

3.6 Crystallographic studies

Crystal data and details on the data collection are summarized in Table 1. Intensities were collected on a STOE STADI 4 (**4c** and **5e**) and on a STOE IPDS (**6f**) diffractometer using MoK_α radiation (λ = 0.71073 Å). The molecular structures were solved by direct methods and refined by full-matrix least-squares routines using the programs SHELXS/L-97 (**4c** and **5e**) and SHELXS/L-2014/7 [45–50] (**6f**).

CCDC 1557853 (**4c**), 1557854 (**5e**), and 1543484 (**6f**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data_request/cif.

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