One-Step Preparation, Structural Assignment, and X-ray Study of 2,2-Di-*n*-butyl- and 2,2-Diphenyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-ones Derived from Amino Acids

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Abstract: Twenty-four 2,2-di-*n*-butyl- and 2,2-diphenyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-ones, each having a transannular N → Sn bond, have been prepared by one-step reactions of α-amino acids (**1a**–**l**), salicylaldehyde (**2**), and either di-*n*-butyltin(IV) oxide (**3**) or diphenyltin(IV) oxide (**4**). The new methodology constitutes an easy, highly efficient one-step synthesis of diorganotin(IV) derivatives, such as **5a**–**l** and **6a**–**l**, from iminic tridentate ligands without isolation of the Schiff bases. The structures of all the compounds have been established by a combination of ^{1}H, ^{13}C, ^{15}N, and ^{119}Sn NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis. In all cases, the ^{119}Sn chemical shifts, as well as the $^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ coupling constants, are indicative of pentacoordinated tin atoms in solution. The structures of compounds **5a**, **d**, **f**, **6a**, **b**, **b-racemic**, **c**, **d**, **f**, **g**, and **l** have been established by single-crystal X-ray diffraction analyses. The tin atoms in **5d**, **f**, **6a**, **b**, **b-racemic**, **c**, **d**, **g**, and **l** each have a distorted trigonal-bipyramidal (TBP) geometry, with the oxygen atoms from the phenol and carboxylate moieties occupying the axial positions, and the imine nitrogen and phenyl or *n*-butyl substituents occupying the equatorial positions. Compounds **5a** and **6f** show distorted octahedral (DOC) geometries due to intermolecular coordination of the carbonyl oxygen to the tin atom, in a *trans* disposition to the N → Sn bond, leading to trimeric **5a** and a polymeric structure for compound **6f**. Additionally, measurement of the one-bond coupling constants $^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ in diphenyltin(IV) complexes (**6a**–**l**) and their correlation with the C-Sn-C bond angles has allowed the derivation of an equation that can be applied to assess the geometry around the tin atom for other diphenyltin(IV) compounds in solution.

Keywords: amino acids · NMR spectroscopy · organotin complexes · X-ray diffraction

Introduction

In recent years, we have been interested in the synthesis of boron compounds derived from *N*-alkyl-diethanolamines,[1] *N*-methyl-*N*-(1-methyl-2-phenyl-2-hydroxyethyl)glycines,[2] 2-substituted pyridines,[3] *N*-(2-hydroxybenzyl)-α-amino acids,[4] *N*-alkyliminodiacetic acids,[5] *N*-(2-hydroxyethyl)-*N*-alkyl-glycines,[6] *N*-alkyl-2,2′-diphenolamines,[7] 2,6-pyridinedimethanol and 2-salicylideneaminoethanol,[8–12] piperidine and piperazine alcohols,[13] α-amino acids,[14, 15] *N*-alkylaminodiacetic acids,[16] ephedrines and pseudoephedrines,[17] tridentate azomethine ligands,[18] ethanolamines,[19] aminodialcohols,[20] and *N*-salicylidene-4-aminobutanol,[21] as well as the self-assembly of boronic-salicylidene Schiff bases.[22] The driving force leading to the formation of these monomeric, dimeric, trimeric, and tetrameric compounds is the formation of N → B bonds. In general, the structure of the product is determined by the nature of the ligand, although in some cases it can be modulated by varying the reaction conditions. The distortion around the boron atom in these molecules can be quantified in terms of its tetrahedral character.[23]

In continuation of our studies concerning Schiff bases, we decided to prepare a series of ligands derived from amino acids. These ligands have the advantage that they can be prepared in situ, and allow the design and construction of new molecules based on tin chemistry. The synthesis of new organotin(IV) derivatives has been encouraged by the discovery of in vitro and in vivo antitumour activity,[24–31] whereby di-*n*-butyl-, tri-*n*-butyl-, and diphenyltin(IV) compounds were found to be the most active.[24–26, 28] Formerly, tri-*n*-butyltin compounds were reported as the most cytotoxic and the most active, although metabolization of such compounds leads to

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 DOI: 10.1002/chem.200204260

the di-*n*-butyl derivatives, which are much less toxic but comparable in inhibition efficiency.[27, 28] In particular, di-*n*-butyltin(IV) complexes of Schiff bases derived from α-amino acids have shown in vitro antimicrobial and antitumour activity.[30] These α-amino acid based molecules could be used as models for the investigation of reaction pathways resembling those of vitamin B_6 dependent enzymes, where pyridoxal subsystems are the most versatile of the available catalysts for homogeneous-phase transformations. The present compounds could be useful to realize studies similar to those described by Martell.[32] The pyridoxal reaction pathways, in relation to α-amino acid skeletons, are transamination, α-proton exchange, racemization at the α-carbon, α,β-C–C scission, α,β-elimination, and α- and γ-decarboxylations.[32]

Compounds **5a**, **b**, **e**, **h**, **i**, **6a**, **b**, **e**, **h**, and **i** have been prepared previously by a two-step procedure.[33] This previous route involved protection of the Schiff base as a metal salt, which displaces the equilibrium so as to avoid the formation of zwitterionic species and to preclude condensation. In the route described herein, this protection is not required and tin self-catalyses the process. The equimolecular reaction of an α-amino acid (**1a–l**) with salicylaldehyde (**2**) and either di-*n*-butyltin(IV) oxide (**3**) or diphenyltin(IV) oxide (**4**) leads to 2,2-di-*n*-butyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-ones (**5a–l**) or 2,2-diphenyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-ones (**6a–l**) (Schemes 1 and 2). A combination of ^{1}H, ^{13}C, ^{15}N, and ^{119}Sn NMR spectroscopy, IR spectroscopy, mass spectrometry, X-ray diffraction studies, and elemental analyses has allowed us to establish the structures of the diorganotin(IV) compounds, which, in all cases, show stabilizing N → Sn bonds. Moreover, measurement of the one-bond coupling constants $^1J(^{119}Sn,^{13}C)$ in diphenyltin(IV) complexes (**6a–l**) and their correlation with the C-Sn-C bond angles obtained from the X-ray data has led to a useful equation that allows an assessment of the geometry around the tin atom in other diphenyltin derivatives. The resulting equation complements the work related to dimethyl- and di-*n*-butyltin(IV) derivatives reported by Howard[34a] and by Holeček.[34b]

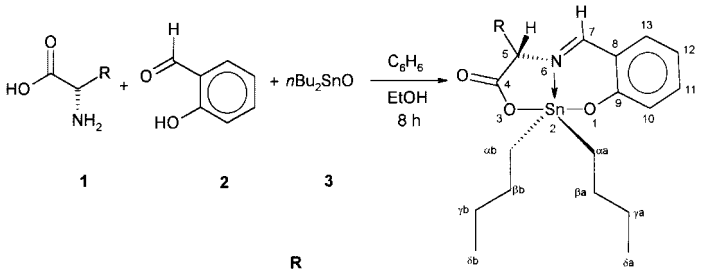
Abstract in Spanish: *En el presente estudio se describe la preparación de veinticuatro derivados del tipo 2,2-di-n-butil y 2,2-difenil-6-aza-1,3-dioxa-2-estanabenzociclo-nonen-4-onas unidos por enlaces transanulares N → Sn, mediante la reacción en un solo paso de α-aminoácidos (**1a–l**), salicilaldehido (**2**) y óxido de dibutilestaño(IV) (**3**) u óxido de difenilestaño(IV) (**4**). Esta metodología constituye una ruta fácil y altamente eficiente para la preparación de compuestos diorganoestánicos(IV) (**5a–l** y **6a–l**), a través de una síntesis de un solo paso sin aislar las bases de Schiff. La RMN de ^{1}H, ^{13}C, ^{15}N y ^{119}Sn, espectroscopia de IR, espectrometría de masas y el análisis elemental permitieron establecer la estructura de todos los compuestos. En todos los casos los desplazamientos químicos de ^{119}Sn, así como las constantes de acoplamiento $^1J(^{119}Sn,^{13}C)$ son características de átomos de estaño pentacoordinados en disolución. Las estructuras de los compuestos **5a**, **d**, **f**, **6a**, **b**, **b**-racemico, **c**, **d**, **f**, **g** y **l** se establecieron mediante estudios de difracción de rayos-X de monocristal. Los átomos de estaño en **5d**, **f**, **6a**, **b**, **b**-racemico, **c**, **d**, **g** y **l** presentan geometría de bipirámide trigonal (BPT) distorsionada, en la cual el oxígeno fenólico y el del carboxilato ocupan posiciones axiales, mientras que el nitrógeno imínico y los dos átomos de carbono de los fenilos o n-butilos son ecuatoriales. Los compuestos **5a** y **6f** presentan geometría octaédrica distorsionada (DOC) debido a la coordinación intermolecular del oxígeno carbonílico con el átomo de estaño en posición trans al enlace N → Sn, lo que conduce a una estructura trimérica para el compuesto **5a** y una estructura polimérica, para el compuesto **6f**. Adicionalmente, la medición de las constantes de acoplamiento a un enlace $^1J(^{119}Sn,^{13}C)$ en compuestos difenilestaño(IV) (**6a–l**) y la correlación contra los ángulos de enlace C-Sn-C condujo a una ecuación que permite establecer la geometría alrededor del átomo de estaño en solución para éstos derivados.*

Results and Discussion

Preparation: Initially, preparation of the Schiff bases was attempted by heating α-amino acids **1a–l** with salicylaldehyde (**2**) under reflux in ethanol/benzene mixtures, methanol or acetonitrile for 4, 8, or 12 h. The Schiff bases were obtained in poor yields (10–15%) due to insolubility of the α-amino acids and the formation of imine-zwitterionic species.

The modified procedure involves the sequential addition of equimolar amounts of the α-amino acid (**1a–l**), salicylaldehyde (**2**), and di-*n*-butyltin(IV) oxide (**3**) to benzene/ethanol (4:1) and then refluxing for 8 h. In the case of diphenyltin(IV) oxide (**4**) derivatives, the reagents were added to benzene/ethanol (1:1) and the mixture was refluxed for 12 h. In both cases, the Schiff base was formed in situ and reacts to provide **5a–l** or **6a–l** in yields between 75 and 94%. The new preparation is simple and the order of addition ensures that there is no structural change in the final products. The course of the reaction was followed by ^{1}H NMR, which showed that the first species formed is the diorganotin(IV) carboxylate. This species undergoes condensation with the aldehyde under formation of the N → Sn bond to provide 5-substituted 2,2-di-*n*-butyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-ones (**5a–l**) (Scheme 1) or 5-substituted 2,2-diphenyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-ones (**6a–l**) (Scheme 2). The products were obtained as yellow powders after concentration of the reaction mixture, redissolution of the residue in dichloromethane, and precipitation using hexane or petroleum ether. The α-amino acids used in this study were enantiomerically pure, except for **1c** and **1g**, which were racemic.

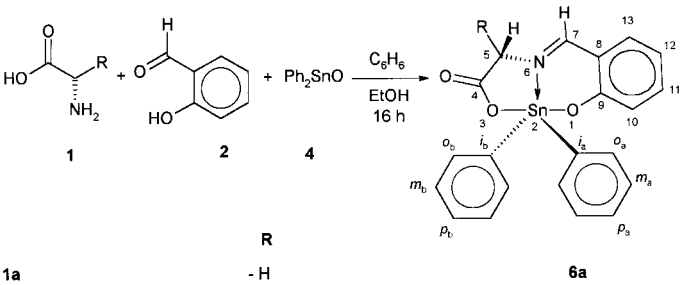
Optical rotations were determined using a non-coordinating solvent ($CHCl_3$) since it was observed that the use of polar protic solvents (MeOH) resulted in racemization of some of the α-amino acids, due to the formation of hexacoordinated species. Thus, measurements of the optical rotations of compounds **5j** and **6j** at different times were indicative of racemization, which can be attributed to the presence of an acidic proton and a strongly coordinating atom at the *p*-HO-C_6H_4 group. A plausible mechanism involving the enolic form of the amino acid fragment is outlined in Figure 1, and formation of this enolate can be promoted by an aromatic π-delocalized structure.



	R
1a	- H
1b	- $^{14}CH_3$
1c	- $^{14}CH_2{}^{15}CH_3$
1d	- $^{14}CH(^{15a}CH_3)(^{15b}CH_3)$
1e	- $^{14}CH_2{}^{15}CH(^{16a}CH_3)(^{16b}CH_3)$
1f	- $^{14}CH(^{17}CH_3)^{15}CH_2{}^{16}CH_3$
1g	- $^{14}CH_2{}^{15}CH_2{}^{16}CH_2{}^{17}CH_2{}^{18}CH_2{}^{19}CH_3$
1h	- $^{14}CH_2$-(C^{15}–C^{16}–C^{17}–C^{18})
1i	- $^{14}CH_2{}^{15}CH_2{}^{16}SCH_3$
1j	- $^{14}CH_2$-(C^{15}–C^{16}–C^{17}–C^{18}–OH)
1k	- $^{14}CH_2$-(C^{15}–C^{19}–C^{20}–C^{21}–C^{22}–C^{23}–N^{16}–C^{17}–C^{18}, H)
1l	- (C^{14}–C^{15}–C^{16}–C^{17})

5a	
5b	
5c	
5d	
5e	
5f	
5g	
5h	
5i	
5j	
5k	
5l	

Scheme 1. Preparation of 2,2-di-*n*-butyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-ones **5a**–**l**.



	R
1a	- H
1b	- $^{14}CH_3$
1c	- $^{14}CH_2{}^{15}CH_3$
1d	- $^{14}CH(^{15a}CH_3)(^{15b}CH_3)$
1e	- $^{14}CH_2{}^{15}CH(^{16a}CH_3)(^{16b}CH_3)$
1f	- $^{14}CH(^{17}CH_3)^{15}CH_2{}^{16}CH_3$
1g	- $^{14}CH_2{}^{15}CH_2{}^{16}CH_2{}^{17}CH_2{}^{18}CH_2{}^{19}CH_3$
1h	- $^{14}CH_2$-(C^{15}–C^{16}–C^{17}–C^{18})
1i	- $^{14}CH_2{}^{15}CH_2{}^{16}SCH_3$
1j	- $^{14}CH_2$-(C^{15}–C^{16}–C^{17}–C^{18}–OH)
1k	- $^{14}CH_2$-(C^{15}–C^{19}–C^{20}–C^{21}–C^{22}–C^{23}–N^{16}–C^{17}–C^{18}, H)
1l	- (C^{14}–C^{15}–C^{16}–C^{17})

6a	
6b	
6c	
6d	
6e	
6f	
6g	
6h	
6i	
6j	
6k	
6l	

Scheme 2. Preparation of 2,2-diphenyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-ones **6a**–**l**.

Spectroscopic data: Spectral characterization of the di-*n*-butyltin(IV) and diphenyltin(IV) compounds was based on ^{1}H, ^{13}C, 2D COLOC and NOESY, ^{15}N, and ^{119}Sn NMR experiments. The ^{1}H NMR spectra of compounds **5a**–**l** and **6a**–**l** show that the chemical shift for the HC=N proton (H-7) lies in the range $\delta = 8.22-8.43$ for compounds **5a**–**g**, **i**, **l**, **6a**–**g**, **i**, and **l**, while the presence of a CH_2-aryl group in **5h**, **j**, **k**, **6h**, **j**, and **k** shifts this signal to lower frequencies ($\delta = 7.57-7.08$, Figure 2). In all cases, the $^{3}J(^{119}Sn,^{1}H)$ coupling constants for H-7 (61.6 and 41.2 Hz) are larger than those for H-5 (50.3 and 16.2 Hz). The signals for each of the *n*-butyl and phenyl groups were assigned with the aid of 2D HETCOR and NOESY experiments. It was observed that in the case of *n*-butyl-substituted derivatives (**5a**–**l**), the most deshielded carbons correlate with the most deshielded hydrogen signals. In contrast, in the phenyl-substituted compounds (**6a**–**l**), the most deshielded carbons correlate with the most shielded proton signals, due to the anisotropic effect of the phenyl group.

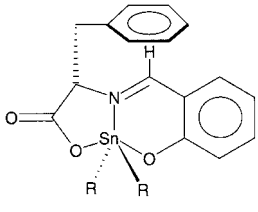


Figure 2. Shielding of H-7 due to -CH_2-aryl substituents.

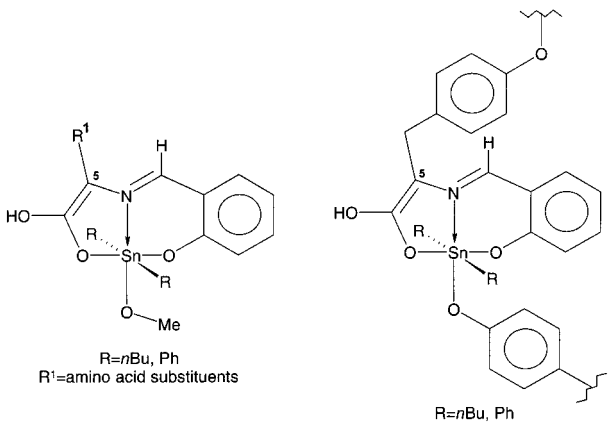


Figure 1. Proposed structure for the intermediate involved in racemization at position 5.

The ^{13}C NMR data for compounds **5a**–**l** and **6a**–**l** show that the signal of the carboxyl carbon (C-4) appears in the range $\delta = 174.7$ to 170.6, in agreement with data reported for analogous esters.[27] The signal of the imine carbon (C-7) is shifted from $\delta = 174.8$ to $\delta = 171.7$, showing a marked deshielding with respect to an imine group due to N→Sn coordination, which induces N=C bond polarization. C-4 and

C-7 were distinguished with the aid of 2D HETCOR NMR experiments, which allowed correlation of C-7 with H-7. Similarly, C-4 and C-9 were assigned on the basis of 2D COLOC NMR experiments ($^nJ(^{13}C,^1H) = 10$ Hz, where $n = 2$ or 3 bonds), which revealed the correlation between C-4 and H-5. The signals of the carbons that constitute the salicylidene fragment (C-8, C-9, C-10, C-11, C-12, and C-13) are little affected, that of C-9 experiencing the largest shift ($\delta = 169.9$ to $\delta = 169.0$) due to $O_{phenolic}-Sn$ ester formation. The signal of C-5 appears in the range $\delta = 74.6$ to $\delta = 57.2$, depending on the nature of the substituent. All 5-substituted derivatives (**5b–l** and **6b–l**) show evidence of an α-substituent effect, which shifts the signal by an average of 12 ppm to higher frequencies with respect to **5a** and **6a**. Compounds **5b–l** show diastereotopic *n*-butyl groups, which give rise to two signals; in general, the chemical shift order is C-β, C-γ, C-α, C-δ. Compounds **6b–l** also possess diastereotopic phenyl groups owing to the presence of a stereogenic carbon at position 5; this anisochronous behavior gives rise to different signals and the general trend for the chemical shifts is C-*ipso*, C-*ortho*, C-*para*, C-*meta*.

The ^{15}N NMR chemical shifts for compounds **5c–l** and **6a–l** appear in the range $\delta = -150.0$ to $\delta = -168.4$ (Tables 1 and 2) and confirm the existence of a coordinative $N \rightarrow Sn$ bond. These signals are shielded by 100 ppm compared with the values reported in the literature for non-coordinated imines.[35] All ^{15}N NMR chemical shifts were obtained using the INEPT[36] pulse sequence with the experimentally measured $^2J(^{15}N,^1H) = 6$ Hz, except in the case of compounds **5a** and **5b**, for which the ^{15}N NMR spectra could not be determined neither by INEPT nor by inverse gated decoupling (no NOE) experiments. The failure to observe the ^{15}N NMR signals of **5a** and **5b** can probably be attributed to a fast equilibrium between the coordinated and noncoordinated species and/or a conformational equilibrium involving the five-membered ring. The carbons located α to tin in **5a** and **5b** show broad ^{13}C NMR signals, even though the ^{119}Sn chemical shift and the $^1J(^{119}Sn,^{13}C)$ coupling constants are indicative of pentacoordination of the tin atom in solution.

In $CDCl_3$, the ^{119}Sn NMR chemical shifts for the type **5** compounds lie in the range $\delta = -192.4$ to -205.1 (Table 1), while those of the type **6** compounds are seen between $\delta = -335.5$ and -342.1 (Table 2), characteristic of pentacoordinated tin atoms in non-coordinating solvents. These signals shift to lower frequencies: $\delta = -216.1$ to -258.1 (type **5**) and $\delta = -369.4$ to -417.5 (type **6**), characteristic of hexacoordinated tin atoms, when the NMR spectra are recorded in $[D_6]$DMSO.[27] It was also found that the ^{119}Sn chemical shifts are not significantly concentration dependent; in general, the spectra of concentrated solutions (more than 100 mg of diorganotin(IV) compound per 0.4 mL of $CDCl_3$) showed an average shift to lower frequencies of just 1.5 ppm compared to

Table 1. ^{15}N and ^{119}Sn NMR chemical shifts [ppm] and coupling constants [Hz] of compounds **5a–l** in $CDCl_3$.

Compound	$\delta^{15}N$	$\delta^{119}Sn$		$^3J(^{119/117}Sn,^1H\text{-}7)$[a]	$^3J(^{119/117}Sn,^1H\text{-}5)$[a]	$J(^{119/117}Sn,^{13}C\alpha_a)$	$J(^{119/117}Sn,^{13}C\alpha_b)$	θ(C-Sn-C)
		$CDCl_3$	$[D_6]$DMSO					
5a	–	–192.4	–216.1	41.2	16.2	637/609	637/609	138.4–135.6
5b	–	–198.5	–221.9	47.0	29.3	631/590	612/571	137.8–131.8
5c	–156.9	–198.7	–241.1	47.2	31.9	624/595	605/578	137.1–132.5
5d	–164.7	–196.3	–232.3	47.2	35.2	633/604	592/566	138.0–131.3
5e	–160.3	–197.9	–234.9	46.0	35.9	614/587	608/581	136.1–132.8
5f	–163.3	–197.2	–234.2	47.2	34.0	632/603	590/566	137.9–131.3
5g	–162.3	–198.6	–229.7	47.0	30.9	622/597	606/579	136.9–132.6
5h	–168.4	–196.5	–226.5	47.3	32.2	621/593	603/578	136.8–132.5
5i	–164.1	–197.3	–234.8	46.5	31.9	615/590	603/578	136.2–132.5
5j	–164.1	–194.2	–258.1	47.7	36.6	615/590	597/572	136.2–131.9
5k[b]	–161.6	–197.8	–243.4	48.3	43.2	610/593	606/580	135.7–132.7
5l	–164.5	–205.1	–232.0	45.8	27.1	616/589	607/578	136.3–132.5

[a] Averaged values of unresolved $^3J(^{119/117}Sn,^1H)$ are shown. [b] $\delta(N_{indolyl}) = -252.74$.

Table 2. ^{15}N and ^{119}Sn NMR chemical shifts and coupling constants of compounds **6a–j** in $CDCl_3$.

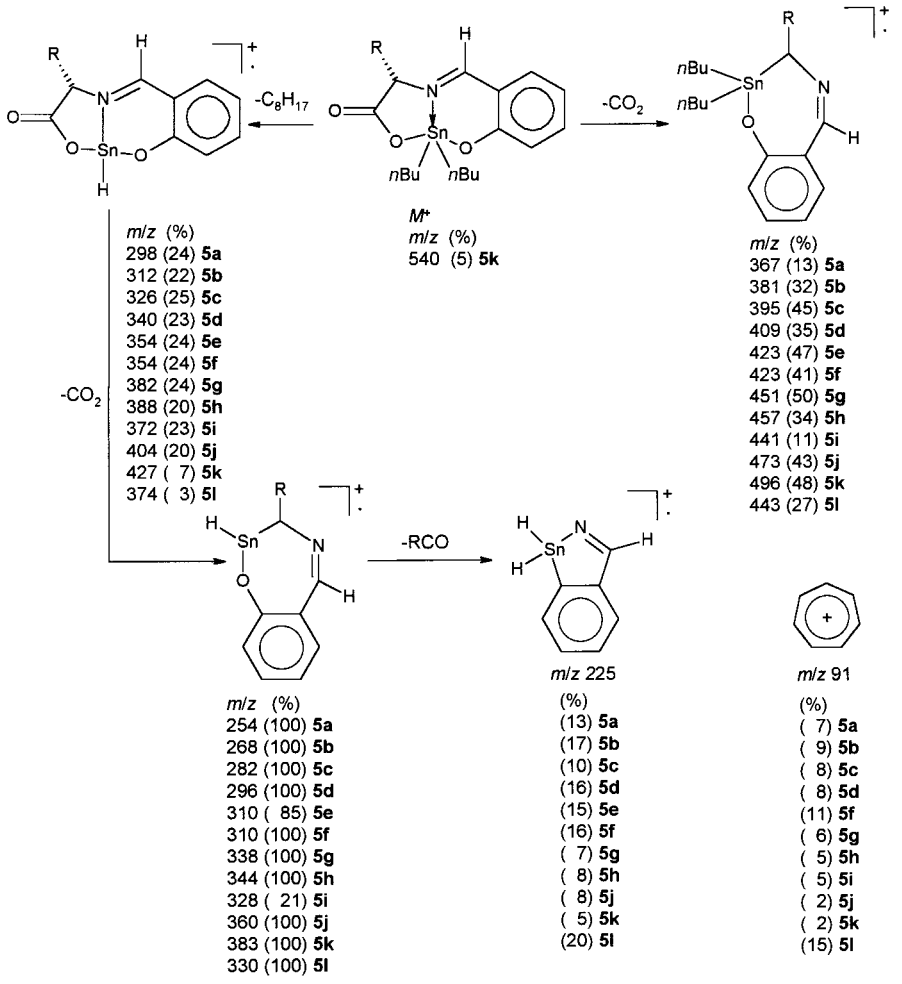
Compound	$\delta^{15}N$	$\delta^{119}Sn$		$^3J(^{119}Sn,^1H)$[a]		$J(^{119/117}Sn,^{13}C(o))$		$^2J(^{119/117}Sn,^{13}C(o))$[b]		$^3J(^{119/117}Sn,^{13}C(m))$[b]		$^4J(^{119}Sn,^{13}C(p))$	
		$CDCl_3$	$[D_6]$DMSO	H-7	H-5	a	b	a	b	a	b	a	b
6a	–164.8	–335.5	–416.6	58.3	22.8	1017.3/971.6	1017.3/971.6	56.1	56.1	88.2	88.2	17.7	17.7
6b	–160.1	–342.1	–417.5	59.4	35.9	1004.0/982.6	1004.2/982.8	57.9/55.8	57.7/55.7	90.0/86.2	90.3/86.5	18.5	18.5
6c	–163.9	–339.5	–399.4	59.7	36.6	1001.7/957.1	1005.7/967.0	56.1	55.3	87.6	86.9	16.9	16.9
6d	–165.5	–336.0	–369.4	59.7	39.9	994.3/958.4	1032.5/979.3	55.4	55.4	87.6	87.6	18.1	17.4
6e	–160.4	–340.4	–411.8	58.1	40.1	993.1/961.7	993.1/961.7	56.9	56.9	89.6/86.4	91.2/88.1	17.4	17.8
6f	–163.2	–337.6	–373.4	59.7	38.8	994.7/960.9	1016.3/980.9	56.9	56.9	86.1	86.1	18.5	16.9
6g	–162.6	–340.8	–397.1	59.1	37.6	1002.5/970.9	1011.1/979.2	55.3	55.3	90.6/86.6	89.5/85.5	18.0	18.1
6h	–168.4	–341.4	–403.9	59.6	50.3	1011.4/966.5	1053.9/1004.9	56.6	56.4	89.9/86.2	90.2/86.6	18.0	17.8
6i	–164.1	–341.8	–405.0	58.9	38.2	998.5/959.2	998.5/959.2	56.0	56.1	92.9/86.4	89.7/83.2	18.0	17.8
6j[c]	–150.0[d]	–340.3	–405.2	–	–	–	–	55.4	55.4	87.6	87.6	18.5	18.5
6k[e]	–160.1	–341.8	–400.0	61.6	41.0	1012.5/965.1	1018.1/970.5	55.4	55.4	87.6	89.2	18.1	16.9
6l	–164.7	–339.8	–414.0	58.9	28.2	1010.5/980.5	1023.8/993.4	57.0	56.5	88.3	88.3	17.7	17.5

[a] Averaged values of unresolved $^3J(^{119/117}Sn,^1H)$ are shown. [b] Averaged values of unresolved $^2J(^{119/117}Sn,^{13}C)$ are shown. [c] The sample was only sparingly soluble. [d] Chemical shift measured in $[D_6]$DMSO. [e] $\delta(N_{indolyl}) = -254.43$.

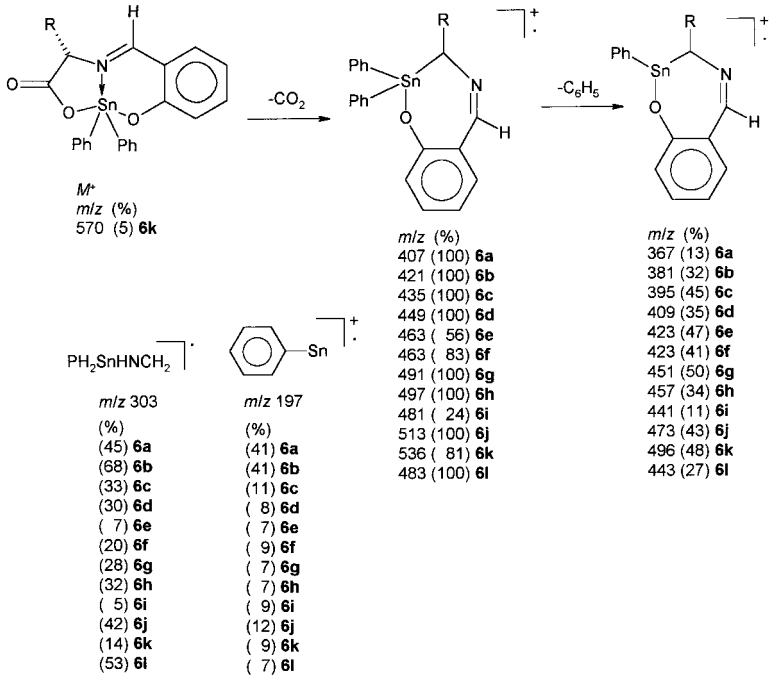
those measured from dilute solutions (less than 5 mg of diorganotin(IV) compound per 0.4 mL of $CDCl_3$).[27] Compounds **5a–l** show $^1J(^{119}Sn,^{13}C)$ values in the range 590 to 637 Hz (Table 1), as obtained from the ^{13}C NMR spectra, while compounds **6a–l** have $^1J(^{119}Sn,^{13}C)$ values in the range 993 to 1054 Hz (Table 2), in agreement with the values reported for analogous pentacoordinated tin derivatives.[27, 34b] Compounds possessing a stereogenic center exhibit two distinct coupling constants arising from the diastereotopic *n*-butyl or phenyl moieties, which show a geometry dependence. In the case of *n*-butyl groups, the largest coupling constant corresponds to the carbon on the same side as the methine proton (H-5). In addition, the $^1J(^{119}Sn,^{13}C)$ and $^1J(^{117}Sn,^{13}C)$ values allow the calculation of the bond angle for the C_α-Sn-C_α fragment, which is of the order of 135° [$|J(^{119}Sn,^{13}C)| = 9.99(\pm 0.73)\cdot\theta(\text{C-Sn-C}) - 746\ (\pm 100)$],[34b] suggesting that the tin atom has a slightly distorted TBP geometry in non-coordinating solvents ($CDCl_3$). The stereogenic center present in **6b–l** gives rise to two distinct coupling constants for the phenyl moieties; in contrast to the type **5** compounds, the larger value corresponds to the carbon opposite to the methine proton (H-5), as evidenced by 2D NMR NOESY experiments.

The IR spectra show at least four intense bands between 1684 and 1444 cm^{-1} due to the SnOC=O and C=N fragments.

In general, the mass spectra of the type **5** and type **6** compounds did not exhibit the molecular ion, the only exceptions being **5k** and **6k**. Losses of *n*-butyl or phenyl substituents, as well as decarboxylation of the amino acid fragment, are common fragmentations, and plausible fragmentation patterns are shown in Schemes 3 and 4. The ^{120}Sn isotope was used due



Scheme 3. Proposed fragmentation pattern for compounds **5a–l**.



Scheme 4. Proposed fragmentation pattern for compounds **6a–l**.

to its higher natural abundance, and the fragmentation pattern is in agreement with previous reports.[31] In all cases, type **5** compounds show loss of CO_2 and C_8H_{17} to give the base peak. In the diphenyl-substituted derivatives the base peak corresponds to $[M^+ - CO_2]$, and loss of C_6H_5 is observed.

X-ray structures: It has been reported that di-*n*-butyl- and diphenyl-substituted organotin compounds with rigid tridentate ligands tend to exist as monomeric species, both in solution and in the solid state. In contrast, methyl-substituted derivatives yield monomeric, dimeric, and/or oligomeric species, depending on the nature of the substituents and the coordination number of the tin atom.[34a, b, 37–49] Compounds **5a**, **d**, **f**, **6a**, **b**, **b-racemic**, **c**, **d**, **f**, **g**, and **l** were crystallized. The structures of **5a** (with a hexacoordinated tin atom) and **6a** (with a pentacoordinated tin atom) are shown in Figures 3 and 4, respectively. Crystal data, selected distances, and plane deviation are summarized for all structures in Tables 3 and 4.

Pentacoordinated tin atoms with trigonal bipyramidal (TBP) geometry: The X-ray structures of compounds **5d**, **f**, **6a**, **b**, **b-racemic**, **c**, **d**, **g**, and **l** confirmed the deductions made on the basis of the NMR data. In the solid state, the tin atom is pentacoordinated, presenting a distorted TBP geometry; the phenolic and carboxylic oxygens occupy axial positions while

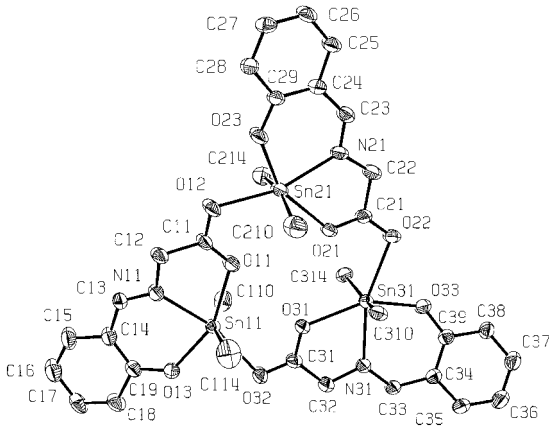


Figure 3. X-ray structure of trimeric compound **5a** (*n*-butyl groups have been omitted for clarity).

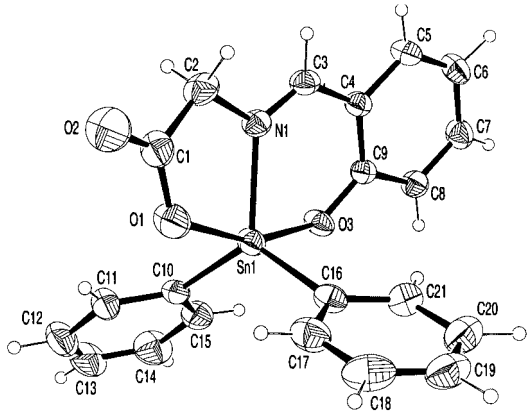


Figure 4. X-ray structure of compound **6a**.

the imine group and the two α-carbons of the organic substituents define the trigonal plane.

Crystals of enantiomerically pure **6b** were obtained from dichloromethane/hexane (2:3), while those of **6b-racemic** were obtained from hexane/dichloromethane/methanol (2:1:2). Racemization of the stereogenic center in enantiomerically pure **6b** was promoted in MeOH, leading to the formation of a racemic mixture that crystallized in a centrosymmetric space group ($P2_1/n$), while the compound obtained in chloroform crystallized in a chiral space group ($P2_12_12_1$). Compound **6d** crystallizes with two different molecules in the asymmetric unit; one is placed between the phenyl groups of the other and, consequently, the C-Sn-C angle of the second molecule increases due to close packing and steric hindrance. Compound **6g** crystallized in a two-layered arrangement from dichloromethane, with the hydrocarbon chain stacked on the same side. The position of the chain is fairly fixed, as evidenced by the observed deviations (maximum deviation 0.089 Å).

Deviation of the tin atom from the plane of the salicylidene fragment can be attributed to the ring fusion and rigidity of the system. This deviation varies from 0.274(3) Å in **6l** to 0.991(4) Å in **6b**, and increases as the size of the substituent at the 5-position increases, except in the case of **6l**, in which the phenyl group reorganizes to relieve the steric strain. The N1 → Sn1 distances range from 2.145(4) Å in **6g** to 2.165(5) Å in **6d**. These values are shorter than those reported in the literature for *n*-butyl substituents (average of 2.206 Å for di-*n*-butyl-(3,4,5-trimethoxybenzoylsalicylahydrazonato)tin[43] and di-*n*-butyl-(salicylaldehyde semicarbazato-*O*,*O*′,*N*)tin[50]), but are similar to those previously reported for diphenyl derivatives (average of 2.180 Å for (*N*-(2-hydroxyacetophenone)-glycinato)-diphenyltin,[37] (*N*-(2-hydroxy-5-methylacetophenone)glycinato)-diphenyltin(IV),[51] (1,9-bis(*o*-phenolato)-2,3,7,8-tetraazanona-1,3,6,8-tetraene-4,6-diolato)bis(diphenyltin)benzene,[42] diphenyl-(2-hydroxy-*N*-(2-hydroxybenzylidene)anilinato)tin,[47] and diphenyl-(*O*-methyl-*β*-*N*-(salicylmethylidene)carbazate)tin(IV)[52]). The Sn1 – O1 distances range from 2.117(3) Å in **6a** to 2.159(3) Å in **6g**, and are thus similar to the values found in analogous carboxylic derivatives (2.139 Å).[37, 40] The Sn1 – O3 distances range from 2.060(2) Å in **6l** to 2.131(4) Å in **6f**, as would be expected for TBP compounds possessing di-*n*-butyl and diphenyl substituents (2.096 Å).[37, 40, 42, 43, 47, 50–52] The C_α-Sn-C_α bond angles are between 118.68° for **6b** and 129.4° for **6d**, compared to the reported literature value of 126.99°,[37, 42, 43, 47, 50–52] and the values calculated on the basis of NMR coupling constants for *n*-butyl substituents (135°, Table 5). The decrease in bond angle (by approximately 10°) can be attributed to the presence of the R groups and the resultant packing. The differences between the bond angles obtained from solid-state data and those determined in solution can be attributed to the relief of steric hindrance in non-coordinating solvents ($CDCl_3$). The O1-Sn1-O3 bond angles (Table 4) range from 154.5(3)° in **5f** to 161.82(8)° in **6l** and, as a result of ring fusion, the O1-Sn1-N1 angles are between 74.8(1)° in **6b** and 76.63(7)° in **6l**. The conformation of the six-membered ring depends mainly on the O3-Sn1-N1 angle, which has values between 80.6(3)° for **5f** and 85.39(8)° for **6l**. The environ-

Table 3. Crystal data and structure refinement for **5a**, **d**, **f**, **6a**, **b**, **b-racemic**, **c**, **d**, **f**, **g**, and **l**.

	5a	**5d**	**5f**	**6a**	**6b**	**6c**	**6d**	**6f**	**6g**	**6l**
empirical formula	$C_{102}H_{150}N_6O_{18}Sn_6 \cdot CHCl_3 \cdot \frac{1}{2}C_6H_{14}$	$C_{20}H_{31}NO_3Sn$	$C_{21}H_{33}NO_3Sn$	$C_{21}H_{17}NO_3Sn$	$C_{22}H_{19}NO_3Sn$	$C_{23}H_{21}NO_3Sn$	$C_{24}H_{23}NO_3Sn$	$C_{25}H_{25}NO_3Sn$	$C_{28}H_{29}NO_3Sn \cdot CH_2Cl_2$	$C_{27}H_{21}NO_3Sn$
formula weight	1270.07	452.15	466.17	450.05	464.07	478.10	492.13	506.15	619.13	526.14
crystal system	monoclinic	orthorhombic	orthorhombic	triclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Ia*	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	*Pcab*	$P2_12_12_1$
unit cell dimensions										
a [Å]	24.6956(3)	9.1870(11)	9.860(5)	9.3206(5)	8.6664(2)	12.3346(3)	9.8050(11)	9.1635(4)	10.086(5)	9.1908(2)
b [Å]	16.8131(2)	10.0001(9)	9.976(5)	9.4677(5)	9.3572(2)	9.9981(2)	17.171(2)	11.1248(4)	18.405(5)	15.6012(3)
c [Å]	30.6107(3)	23.465(3)	23.624(5)	11.1642(7)	24.9768(6)	16.9614(3)	26.171(3)	21.7376(10)	31.321(5)	15.8371(4)
α [°]	90	90	90	76.237(2)	90	90	90	90	90	90
β [°]	111.231(1)	90	90	88.410(2)	90	96.8430(10)	90	90	90	90
γ [°]	90	90	90	73.836(3)	90	90	90	90	90	90
V [Å^3]	11847.2	2155.8(4)	2323.7(17)	918.29(9)	2025.45(8)	2076.82(6)	4406.2(9)	2215.98(16)	5814(3)	2270.84(9)
Z	4	4	4	2	4	4	8	4	8	4
ρ [Mg m^{-3}]	1.467	1.393	1.333	1.628	1.522	1.529	1.484	1.517	1.415	1.539
μ [mm^{-1}]	1.374	1.202	1.117	1.411	1.282	1.253	1.183	1.179	1.090	1.154
θ [°]	1.41–27.45	2.38–25.93	2.22–27.25	2.31–27.45	3.60–27.47	3.44-27.49	2.22–25.97	3.44–27.47	3.02–27.47	3.64–27.47
coll. refls	35605	1564	2722	6971	13251	21295	4940	4523	4051	13489
indep. refls	22854	1564	2722	4140	4575	4715	4914	4140	4051	4994
[R_{int}]	[0.0477]	[0.0000]	[0.0000]	[0.0287]	[0.0447]	[0.0315]	[0.0121]	[0.0000]	[0.0000]	[0.0257]
compl. to θ [°]	27.45	25.96	27.25	27.45	27.47	27.49	25.97	27.47	27.47	27.47
[%]	[96.2]	[41.4]	[56.3]	[98.5]	[99.5]	[99.1]	[98.2]	[94.4]	[60.9]	[98.0]
data	22854	1564	2722	4140	4575	4715	4914	4523	4051	4994
restraints	827	0	0	0	0	4	0	0	0	0
parameters	1254	226	239	284	317	356	547	347	409	374
GoF on F^2	1.159	1.057	1.142	1.157	1.045	1.078	1.068	1.167	1.175	1.063
final R indices R_1	0.0514	0.0370	0.0602	0.0390	0.0352	0.0285	0.0309	0.0369	0.0435	0.0240
[$I > \sigma(I)$] wR_2	0.1371	0.0871	0.1754	0.1006	0.0529	0.0671	0.0814	0.0792	0.0950	0.0492
R indices R_1	0.0598	0.0370	0.0602	0.0516	0.0605	0.0365	0.0497	0.0445	0.0435	0.0311
(all data) wR_2	0.1506	0.0871	0.1754	0.1096	0.0590	0.0731	0.0904	0.0838	0.0950	0.0525
$\Delta\rho_{min}$ [e Å^3]	−1.161	−0.549	−0.631	−0.661	−0.506	−0.555	−0.456	−0.658	−0.466	−0.401
$\Delta\rho_{max}$ [eÅ^3]	1.070	0.370	0.463	1.331	0.686	0.725	0.366	0.992	0.369	0.537

ments around the tin atom in solution and in the crystalline state are practically the same, indicating that packing modifies the TBP shape only slightly.

Hexacoordinated tin atoms with distorted octahedral (DOC) shape: Crystals of compounds **5a** and **6f** were obtained from concentrated solutions in hexane/dichloromethane. In these crystals, self-coordination results in distorted octahedral (DOC) geometry around the tin atom. Three monomers of **5a** self-assemble through C=O···Sn coordination to produce a macrocyclic 12-membered ring structure with a trimeric [$Sn_3O_6C_3$] core (Figure 3). Compound **6f** crystallizes in a polymeric arrangement, in which intermolecular C=O···Sn coordination is again responsible for the coordination number of six at the tin atom. The compound does not undergo epimerization, crystallizing in a $P2_12_12_1$ orthorhombic chiral space group. The polymeric framework reorganizes so as to place the *sec*-butyl substituents in a syndiotactic orientation.

The distorted octahedral structures of **5a** and **6f** were compared with TBP derivatives of series **5** and **6** (Table 4). Compounds **5a** and **6f** have oxygen as the sixth atom of the coordination sphere of the tin atom, with a *trans* disposition to the N→Sn bond. The N→Sn distance in **5a** is 2.281(6) Å, and in **6f** it is 2.258(4) Å; these distances are longer than those reported for TBP derivatives. The two C–Sn distances are 2.121(9) and 2.117(9) Å in **5a** and 2.137(5) and 2.141(5) Å in **6f**, and are thus longer compared to the corresponding distances in TBP compounds (2.100 Å). The O1–Sn and O3–Sn bond lengths are 2.093(5) and 2.359(5) Å in **5a** and 2.205(3) and 2.131(4) Å in **6f**, and hence are equal to or longer than those found in related TBP derivatives (2.249 Å). The O1-Sn-O3 bond angles in **5a** and **6f** are 152.66(20)° and 155.05(13)°, respectively, similar to those in the TBP structures (152.40°). The C-Sn-C angles reflect the change from a pentacoordinated (158.3(4)° for **5a**) to a hexacoordinated tin atom (164.74(18)° for **6f**); the values are larger than those found in the TBP derivatives described herein (126.12°). The N→Sn···O2 bond angle in **5a** is 162.02°, while in macrocycle **6f** it is 150.09° due to self-assembly through intermolecular coordination of the carbonyl oxygen. The O1-Sn···O2 angle in **5a** is 126.78° (approaching from the salicylidene fragment), while in **6f** it is 77.08° (approaching from the carboxylate fragment). Distortion from TBP geometry in **5a** and in **6f** leads to distorted octahedral geometry, where the amino acid and salicylidene fragments lie on opposite sides with respect to the O-Sn-O plane.

A geometrically averaged substructure showing the mean lengths and angles over the nine compounds for which X-ray data are available is shown in Figure 5. These measurements were made by taking as reference the C4-C5-C6-C7-C8-C9-

Table 4. Selected distances, angles, and plane deviations of **5a**, **d**, **f**, **6a**, **b**, **b-rac**, **c**, **d**, **f**, **g**, and **l**.

	5a	5d	5f	6a	6b	6b-racemic	6c	6d	6f	6g	6l
bond lengths [Å]											
N1 – Sn1	2.281(6)	2.154(8)	2.160(8)	2.155(3)	2.148(3)	2.145(2)	2.148(2)	2.165(5)	2.258(4)	2.145(4)	2.157(2)
C – Sn1	2.121(9)	2.116(13)	2.108(14)	2.115(4)	2.109(3)	2.116(3)	2.113(3)	2.115(6)	2.137(5)	2.118(4)	2.123(3)
C – Sn1	2.117(9)	2.125(12)	2.122(14)	2.124(4)	2.119(4)	2.116(3)	2.113(3)	2.122(7)	2.141(5)	2.102(5)	2.124(3)
O1 – Sn1	2.359(5)	2.158(8)	2.145(7)	2.117(3)	2.140(2)	2.139(2)	2.151(2)	2.134(4)	2.205(3)	2.159(3)	2.121(2)
O3 – Sn1	2.093(5)	2.099(9)	2.112(8)	2.071(2)	2.073(2)	2.083(2)	2.083(2)	2.075(4)	2.131(4)	2.078(3)	2.060(2)
N1 – C3	1.281(10)	1.256(12)	1.285(13)	1.293(5)	1.299(5)	1.291(4)	1.294(4)	1.287(8)	1.286(6)	1.280(6)	1.300(3)
C1 – O1	1.255(9)	1.289(15)	1.311(14)	1.300(6)	1.297(5)	1.295(4)	1.290(3)	1.316(8)	1.273(6)	1.294(6)	1.290(3)
C1 – O2	1.262(9)	1.202(13)	1.255(15)	1.196(5)	1.221(4)	1.214(4)	1.220(3)	1.215(7)	1.249(5)	1.219(6)	1.206(3)
C1 – C2	1.517(11)	1.536(16)	1.490(15)	1.506(7)	1.511(6)	1.530(4)	1.531(4)	1.516(9)	1.499(7)	1.525(7)	1.541(4)
N1 – C2	1.453(10)	1.474(13)	1.448(14)	1.473(5)	1.467(5)	1.477(4)	1.464(3)	1.478(7)	1.483(6)	1.474(6)	1.492(3)
C3 – C4	1.438(11)	1.440(14)	1.414(14)	1.426(5)	1.436(5)	1.435(5)	1.432(4)	1.425(9)	1.437(7)	1.437(7)	1.431(4)
C4 – C9	1.404(11)	1.409(14)	1.424(17)	1.412(5)	1.408(5)	1.405(5)	1.415(4)	1.412(10)	1.421(8)	1.394(6)	1.407(4)
O3 – C9	1.312(9)	1.317(12)	1.285(13)	1.328(4)	1.342(4)	1.318(4)	1.320(3)	1.326(8)	1.306(6)	1.331(5)	1.326(3)
bond angles [°]											
C-Sn1-C	158.3(4)	126.1(6)	125.1(7)	125.90(14)	118.68(15)	122.63(12)	122.61(11)	129.4(3)	164.74(18)	123.83(18)	127.95(10)
O1-Sn1-O3	152.66(20)	156.0(4)	154.5(3)	160.03(13)	156.90(9)	159.07(9)	158.02(8)	159.39(17)	155.05(13)	156.62(12)	161.82(8)
N1-Sn1-O1	71.13(19)	75.7(4)	74.9(3)	76.30(12)	74.80(10)	76.01(9)	75.01(8)	75.72(18)	73.12(14)	75.10(13)	76.63(7)
N1-Sn1-O3	81.73(20)	81.3(3)	80.6(3)	84.06(10)	82.10(10)	83.28(9)	83.09(8)	83.78(18)	81.93(13)	82.54(12)	85.39(8)
N1-Sn1-C	99.18(30)	124.9(4)	109.3(5)	123.23(13)	121.50(13)	122.82(10)	120.48(9)	117.1(2)	100.19(17)	125.61(15)	111.98(9)
N1-Sn1-C	96.78(35)	108.6(5)	125.2(6)	110.62(12)	119.57(14)	114.30(11)	116.35(9)	113.4(2)	94.53(17)	110.18(16)	119.84(9)
O1-Sn1-C	86.45(37)	92.7(4)	95.8(5)	93.87(15)	95.85(12)	93.16(10)	91.73(9)	95.1(2)	96.26(16)	91.74(16)	93.88(10)
O1-Sn1-C	85.23(32)	94.9(4)	92.6(6)	93.82(15)	94.62(13)	95.42(11)	95.34(10)	93.6(2)	91.82(16)	96.84(15)	93.26(9)
O3-Sn1-C	100.42(38)	94.9(5)	98.8(5)	93.85(13)	95.23(12)	95.58(11)	97.78(10)	93.6(2)	87.72(18)	95.85(16)	95.31(10)
O3-Sn1-C	95.97(36)	98.9(5)	95.9(6)	96.51(13)	97.73(14)	95.81(12)	96.11(10)	95.2(2)	90.41(18)	97.19(15)	93.40(10)
Sn1-O1-C1	118.8(44)	120.3(9)	119.3(7)	120.7(3)	119.1(2)	119.1(2)	119.71(17)	119.0(4)	120.0(3)	118.7(3)	120.61(16)
Sn1-N1-C3	125.5(5)	125.3(8)	123.6(7)	126.3(2)	124.6(3)	126.3(2)	125.46(19)	124.3(4)	124.5(4)	126.4(3)	126.20(18)
Sn1-N1-C2	117.43(48)	114.7(7)	115.0(6)	114.4(3)	114.6(2)	114.22(19)	114.71(16)	115.8(4)	116.0(3)	113.5(3)	115.40(15)
Sn1-O3-C9	132.18(50)	126.5(8)	126.2(6)	130.3(2)	124.8(2)	129.5(2)	128.60(17)	127.9(4)	130.9(3)	127.8(3)	131.78(18)
O1-C1-C2	119.6(6)	115.4(11)	116.3(11)	115.8(3)	116.8(3)	124.6(3)	115.7(2)	117.8(6)	120.0(4)	115.8(4)	117.0(2)
C1-C2-N1	111.65(65)	110.9(9)	111.1(9)	112.2(4)	108.5(3)	108.9(2)	108.9(2)	109.4(5)	109.1(4)	107.9(4)	110.2(2)
O3-C9-C4	124.1(7)	122.5(11)	122.0(10)	122.4(3)	122.1(3)	122.8(3)	122.7(3)	122.8(6)	124.1(5)	122.7(4)	123.1(2)
C3-C4-C9	124.2(7)	123.4(11)	122.5(10)	124.1(3)	123.3(3)	123.5(3)	123.0(3)	124.2(6)	123.8(4)	123.5(4)	124.2(2)
N1-C3-C4	127.3(7)	125.4(10)	127.0(9)	127.4(3)	125.6(3)	127.0(3)	127.3(3)	127.2(6)	128.0(5)	126.3(5)	127.8(3)
torsion angles [°]											
C8-C9-O3-Sn1	– 165.0(7)	152.5(7)	150.4(9)	157.4(3)	145.2(3)	157.6(3)	155.3(2)	155.9(5)	160.9(4)	152.4(4)	165.30(19)
C5-C4-C3-N1	175.2(9)	– 175.4(9)	– 172.7(11)	– 173.8(4)	– 170.9(4)	– 174.4(4)	– 174.6(3)	177.4(6)	178.3(5)	– 173.8(5)	– 176.3(3)
deviation of mean plane [Å]											
plane: C4-C5-C6-C7-C8-C9-O3-C3											
Sn1	0.4262(92)	0.8626(87)	0.936(12)	– 0.569(4)	– 0.991(4)	0.619(5)	0.700(3)	– 0.652(7)	– 0.510(6)	– 0.765(5)	– 0.274(3)
N1	– 0.069(11)	1.134(14)	0.014(14)	– 0.150(4)	– 0.165(5)	0.073(4)	0.073(3)	– 0.039(8)	0.051(7)	– 0.122(6)	– 0.161(3)
plane: O1-C1-C2-O2											
Sn1	– 0.140(13)	0.126(15)	0.062(20)	– 0.025(9)	0.018(6)	0.258(5)	0.127(4)	0.180(10)	– 0.371(7)	– 0.223(7)	– 0.167(4)
N1	0.152(19)	0.356(15)	0.346(22)	– 0.131(8)	– 0.407(7)	0.517(5)	0.462(4)	– 0.209(10)	– 0.372(8)	– 0.595(8)	– 0.048(4)

O3-C3 (salicylidene moiety) and the O1-C1-C2-O2 (carboxylate moiety) planes to establish the rigidity of the molecular framework.

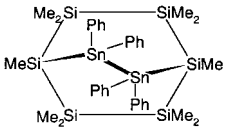
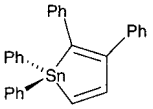
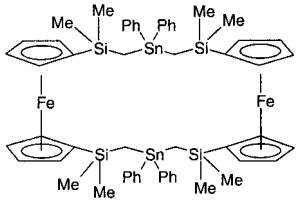
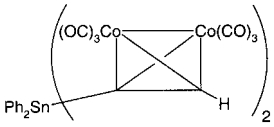
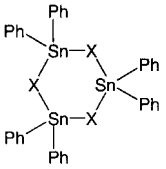
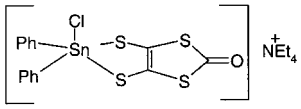
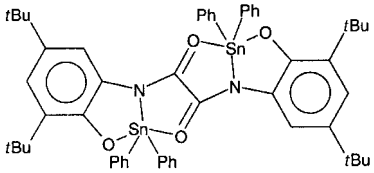
The results show that pentacoordinated tin compounds adopt an *anti* conformation, in contrast to the analogous boron derivatives,[4–6, 11, 19] which show a *syn* conformation, as depicted in Figure 6. The differences in conformational behavior can be attributed to the different sizes of the metals.

Correlations between NMR and X-ray data: Analysis of the data reveals various correlations between the NMR and X-ray diffraction data for both the dibutyl (**5d** and **5f**) and diphenyl (**6a**, **b**, **b-racemic**, **c**, **d**, **g**, and **l**) derivatives with pentacoordinated tin geometries. The figures for compounds **6b** and **b-racemic** have been averaged and are reported as **6b-avg** for general correlation purposes. Deviation of the tin atom from the salicylidene fragment defined by C4-C5-C6-C7-C8-C9-O3-C3 shows a linear correlation with the O1-Sn-O3 bond angle, for which the fitted equation is $Sn(dev) = 0.0825[\theta(O1\text{-}Sn\text{-}O3] + 13.733$, $R^2 = 0.8851$, indicating that the larger the O1-Sn-O3 angle, the less displaced the tin atom is with respect to the salicylidene fragment (Figure 7).

The correlation between the ^{15}N NMR chemical shifts and the C-Sn-C bond angles is defined by the equation: $\delta(^{15}N) = -0.5277[\theta(C\text{-}Sn\text{-}C)] - 97.628$, $R^2 = 0.7404$. This trend shows that the electronic density at the nitrogen atom is strongly influenced by the C-Sn-C bond angle, which implies that small changes in the tin geometry modify the chemical shift (Figure 8).

The next correlation ($\delta(C\text{-}7) = -3.7861[Sn(dev)] + 175.6$, $R^2 = 0.9135$) shows that the larger the size of the substituent, the greater the displacement of the tin atom. This is supported by the change in chemical shift at C-7, the signal of which is shifted to higher frequencies when the tin atom is coplanar

Table 5. Reported experimental data used to establish the $^1J(^{119}Sn,^{13}C)$ versus $\theta(C_{Ph}\text{-}Sn\text{-}C_{Ph})$ correlation.

Compound	$^1J(^{119}Sn,^{13}C)$ [Hz]	$\theta(C_{Ph}\text{-}Sn\text{-}C_{Ph})$ [°]	Ref. (graphic numbering)
	298	103.3	**53**
	463	105.7	**54**
	478	103.59	**55**
	630	111.83	**56**
	632	110.32	**57a**
X = Se	X = Se	580	109.85	**57b**
	X = Te	486	110.45	**57c**
	611	117.9	**58**
	955	125.9	**59**

A correlation between $^1J(^{119}Sn,^{13}C)$ and C_{Ph}-Sn-C_{Ph} was established for the diphenyltin(IV) compounds (series **6**) described in this work and those previously reported (Table 5).[53–59] The resulting equation has the form: $|^1J(^{119}Sn,^{13}C)| = 26.573[\theta(C_{Ph}\text{-}Sn\text{-}C_{Ph})] - 2354.5$, $R^2 = 0.8894$ (Figure 10). An exhaustive literature search for DOC *trans*-$Ph_2Sn^{IV}L$ derivatives had been expected to yield a variety of C_{Ph}-Sn-C_{Ph} values (L = ligand); however, no $|^1J(^{119}Sn,^{13}C)|$ data have been reported for any of the crystallized hexacoordinate diphenyltin(IV) compounds (CCDC files) and therefore this equation is only applicable to tetra- and pentacoordinated tin atoms bearing diphenyl substituents. When amino acid-salicylidene TBP compounds (**6a**, **b-avg**, **c**, **d**, **g**, and **l**) possessing a Ph_2Sn moiety were used for the correlation (Figure 11), the equation $|^1J(^{119}Sn,^{13}C)| = 3.2863[\theta(C_{Ph}\text{-}Sn\text{-}C_{Ph})] + 604.73$, $R^2 = 0.9659$, provided a better correlation.

Conclusion

It can be concluded that organotin(IV) compounds derived from amino acids can be easily prepared in one step under the described reaction conditions, taking advantage of a template effect of the tin atom, which increases the solubility and promotes the formation of the Schiff base.

The use of dilute solutions (≤ 0.5 mol%) during both the reaction and the crystallization process is important to avoid the formation of oligomeric species. In contrast, concentrated

with the salicylidene moiety so as to facilitate delocalization between the imine moiety and the aromatic ring (Figure 9).

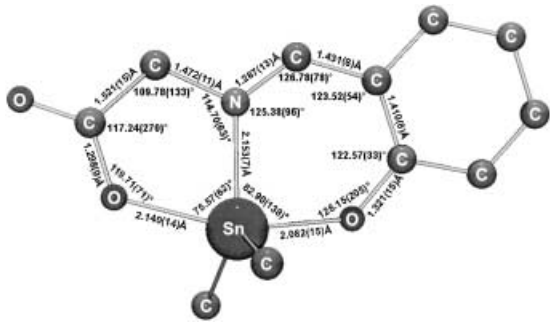


Figure 5. Geometrically averaged structure, as obtained from the X-ray data of the nine TBP diorganotin derivatives described in this study (standard deviations are shown in parentheses).

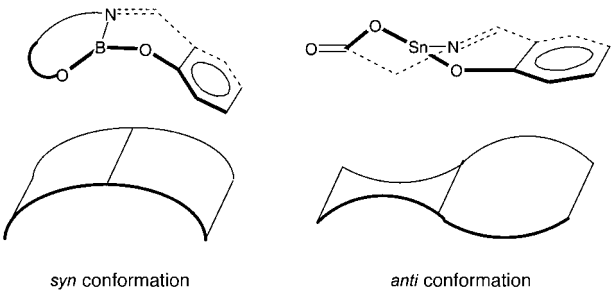


Figure 6. Conformations of the tridentate ligand according to metal size.

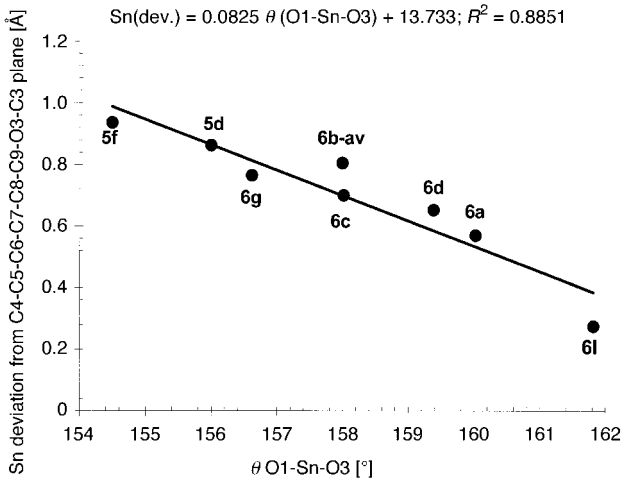


Figure 7. Correlation between the θ(O1-Sn-O3) bond angle and Sn deviation from the salicylidene plane.

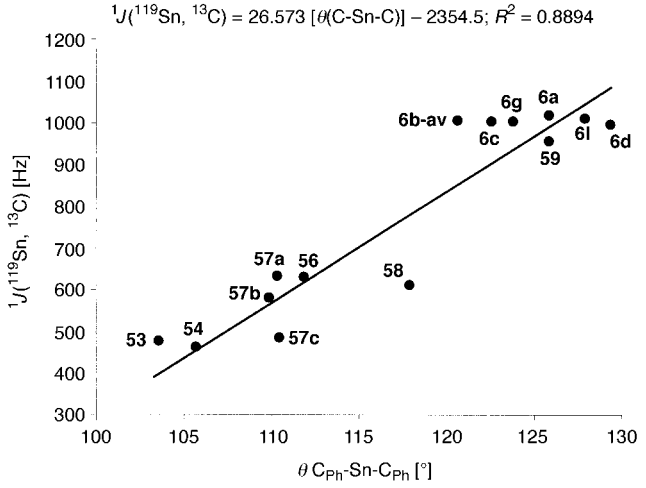


Figure 10. Correlation between $^1J(^{119}Sn,^{13}C)$ values and C_{Ph}-Sn-C_{Ph} bond angles for compounds of type **6** and other reported diphenyltin(IV) derivatives.

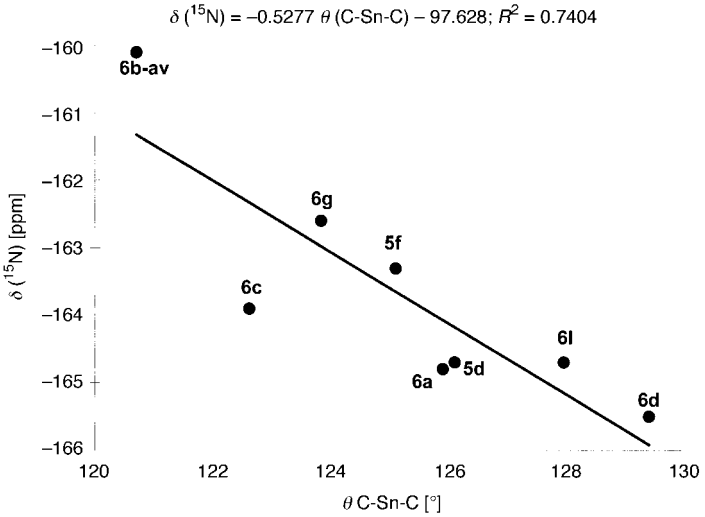


Figure 8. Correlation between the θ(C-Sn-C) bond angle and $\delta(^{15}N)$.

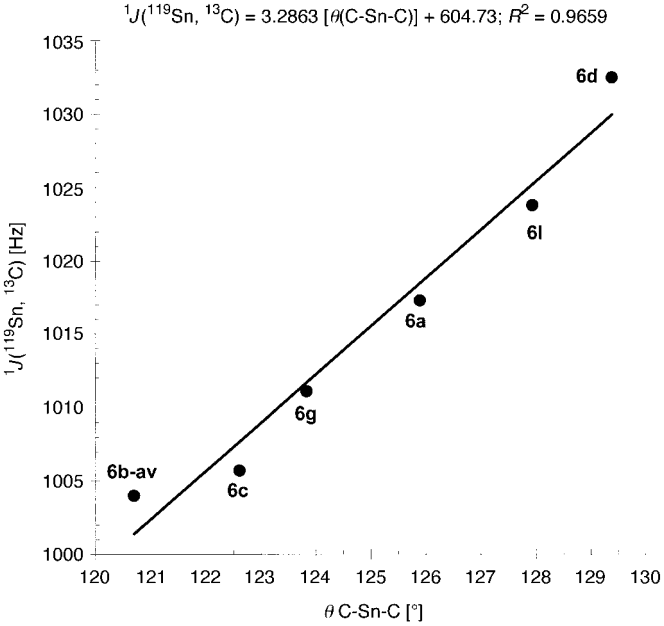


Figure 11. Correlation between $^1J(^{119}Sn,^{13}C)$ and C_{Ph}-Sn-C_{Ph} bond angle for type **6** TBP compounds.

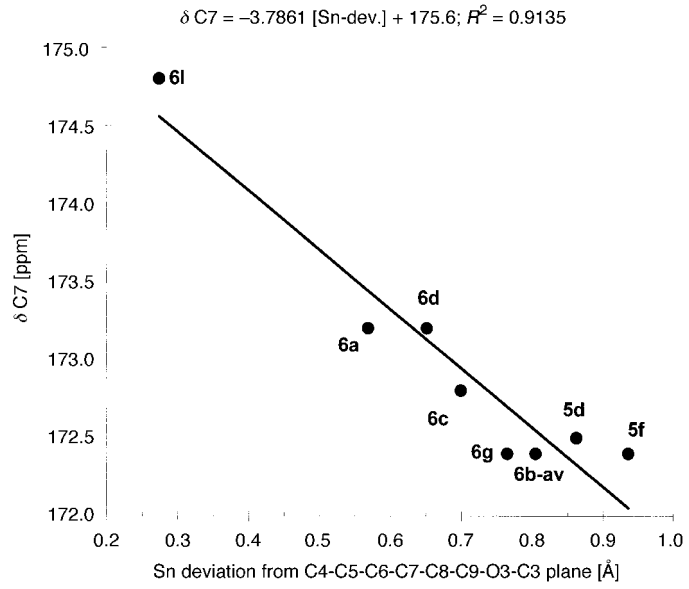


Figure 9. Deviation of the tin atom from the salicylidene plane vs. δ(C-7).

solutions favor self-assembly of the monomers and the formation of trimeric C=O···Sn hexacoordinated structures, as in case of compound **5a**, or polymeric structures as found for **6f**.

The reported dibutyltin(IV) (**5a–l**) and diphenyltin(IV) derivatives (**6a–l**) were synthesized in benzene/ethanol mixtures. From the ^{119}Sn NMR spectra recorded from samples in $CDCl_3$ solution, it can be concluded that all compounds are pentacoordinated, although in [D_6]DMSO the stannoxide derivatives exist as hexacoordinated species, as evidenced by an average shift of $\Delta\delta = 40$ ppm to lower frequency due to Me_2S=O···Sn solvation.

Almost all of the compounds crystallized with the tin atom in TBP geometry. Evaluation of geometrical factors determined from X-ray diffraction studies revealed a twisted ligand arrangement for the diorganotin compounds, even in the

absence of steric factors (compound **6a**), whereby ring fusion is responsible for the deviation from planarity.

Interaction of pentacoordinated tin compounds possessing a stereogenic center with protic solvents can lead to racemization, as evidenced by the X-ray structure of compound **6b-racemic**, as well as by measurements of optical rotation at different times.

Four correlations between the X-ray data and NMR measurements that reflect the behavior of these tin compounds in solution and in the solid state have been identified. These trends provide a background for the study of new derivatives, and show that slight changes in the geometry of the tin atom lead to changes in electron density (correlation of δ(C-7) and δ^{15}N with bond angle). The correlation found between $^1J(^{119}Sn,^{13}C)$ and $\theta(C_{Ph}\text{-}Sn\text{-}C_{Ph})$ for diphenyltin(IV) compounds complements previously established relationships for dimethyl- and di-*n*-butyltin(IV) derivatives.

Experimental Section

All chemicals were commercial grade and were used without purification. Glycine (**1a**), L-alanine (**1b**), 2-aminobutyric acid (**1c**), L-valine (**1d**), L-leucine (**1e**), L-isoleucine (**1f**), 2-aminooctanoic acid (**1g**), L-phenylalanine (**1h**), L-methionine (**1i**), L-tyrosine (**1j**), L-tryptophan (**1k**), L-phenylglycine (**1l**), salicylaldehyde (**2**), di-*n*-butyltin(IV) oxide (**3**), and diphenyltin(IV) oxide (**4**) were purchased from Aldrich; benzene and ethanol were purchased from Fermont Co.

Instrumentation: NMR experiments were performed on Jeol ECLIPSE-400, Jeol GSX-270, and Bruker AVANCE-300 spectrometers. ^{1}H NMR spectra were recorded at 399.785, 300.13, and 270.167 MHz using spectral widths of 8000, 6200, and 4000 Hz and acquisition times of 2.05, 2.64, and 4.04 s, respectively. In all cases, the spectra were obtained using 16384 data points, a 45° pulse width, and 16 scans. The ^{13}C{^{1}H} NMR spectra were recorded at 100.535, 75.468, and 57.94 MHz using spectral widths of 25189, 17360, and 17000 Hz and acquisition times of 1.55, 1.52, and 1.86 s, respectively, with 16384 data points and at least 1024 scans. The ^{15}N NMR spectra were recorded using the INEPT[36] pulse sequence with $|^2J(^{15}N,^1H)| = 6$ Hz at 40.518 and 30.423 MHz using spectral widths of 4600 and 3500 Hz and acquisition times of 2.238 and 1.346 s, respectively, with 8192 data points and at least 2048 scans. The ^{119}Sn spectra were recorded at 149.051 and 100.726 MHz using spectral widths of 12048 and 10080 Hz, acquisition times of 0.5 and 0.4 s, respectively, 16384 data points, and at least 1024 scans. HETCOR, NOESY, and COLOC NMR experiments were performed using standard pulse sequences. ^{1}H and ^{13}C chemical shifts [ppm] are quoted relative to internal $SiMe_4$ (TMS) ($\delta^1H = 0$, $\delta^{13}C = 0$), ^{119}Sn chemical shifts are referenced to $SnMe_4$ ($\delta^{119}Sn = 0$), and ^{15}N chemical shifts are referenced to $MeNO_2$ as a neat liquid ($\delta^{15}N = 0$). Coupling constants are quoted in Hz. Infrared spectra were recorded from samples in KBr pellets on a Perkin Elmer 16F PC FT-IR spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 59940-A spectrometer at 20 eV electron impact. Melting points were measured in open capillary tubes on a Gallenkamp MFB 595 apparatus and are uncorrected. Elemental analyses were determined in a Barioel apparatus. Optical rotations were measured for solutions in $CHCl_3$ and CH_3OH in a 1 dm^3 cell with a Perkin Elmer 241 polarimeter at 25 °C, immediately and then 3 d after dissolution.

General procedure: The reaction flask was first charged with a 4:1 mixture of benzene/ethanol (100 mL). Then, a mixture of the α-amino acid (**1**) (60 mmol), salicylaldehyde (**2**) (60 mmol), and either di-*n*-butyltin(IV) oxide (**3**) (60 mmol) or diphenyltin(IV) oxide (**4**) (60 mmol) in 1:1 benzene/ethanol (100 mL) was added with stirring. The reaction mixture was heated to reflux for 8 h in the case of di-*n*-butyl oxide and for 12 h with diphenyl oxide, although complete dissolution of the reactants was accomplished after 2.5 h. After completion of the reaction, the solution was concentrated to dryness using a vacuum pump, the solid was redissolved in CH_2Cl_2 (10 mL), and precipitated with hexane or petroleum ether (70 mL) to obtain **5a–l** or **6a–l** as yellow powders.

2,2-Di-*n*-butyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-one (5a): Yellow solid, 88.5% yield; m.p. 128–129 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.38 (br s, 1H; H-7), 7.40 (ddd, $J_o = 8.4$, 7.7 Hz, $J_m = 1.8$ Hz, 1H; H-11), 7.14 (dd, $J_o = 7.7$ Hz, $J_m = 1.8$ Hz, 1H; H-13), 6.78 (br d, $J_o = 8.4$ Hz, 1H; H-10), 6.71 (ddd, $J_o = 8.4$, 7.7 Hz, $J_m = 0.9$ Hz, 1H; H-12), 4.32 (s, 2H; H-5), 1.58 (m, 4H; H-βa, H-βb), 1.49 (m, 4H; H-αa, H-αb), 1.30 (sext, $J = 7.3$ Hz, 4H; H-γa, H-γb), 0.83 (t, $J = 7.3$ Hz, 6H; H-δa, H-δb); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 172.7$ (C-7), 171.2 (br s; C-4), 169.4 (C-9), 137.8 (C-11), 135.4 (C-13), 122.6 (C-10), 117.1 (C-8, C-12), 57.7 (C-5), 26.9 ($^2J(^{119}Sn,^{13}C) =$ 34.6 Hz; C-βa, C-βb), 26.6 ($^3J(^{119}Sn,^{13}C) = 96.9$ Hz; C-γa, C-γb), 22.7 (br s; C-αa, C-αb), 13.6 (C-δa, C-δb); IR (KBr): $\tilde{\nu} = 3033$, 2956, 2924, 2854, 1626, 1588, 1468, 1450, 536 cm^{-1}; MS (20 eV): *m*/*z* (%): 367 (13) [$M^+(^{120}Sn) - CO_2$], 365 (10) [$M^+(^{118}Sn) - CO_2$], 363 (5) [$M^+(^{116}Sn) - CO_2$], 354 (11), 352 (8), 350 (5), 298 (24), 296 (18), 294 (10), 254 (100), 252 (76), 250 (42), 225 (13), 223 (9), 221 (4), 91 (7); elemental analysis calcd (%) for $C_{17}H_{25}NO_3Sn$: C 49.79, H 6.14, N 3.42;[33] found: C 49.83, H 6.24, N 3.36. Suitable crystals were obtained from a hexane/dichloromethane/methanol mixture (2:2:3).

(5*S*)-2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-methyl-2-stannabenzocyclononen-4-one (5b): Yellow solid, 88.2% yield; m.p. 106–107 °C; $[\alpha]_D^{25} = -10.0$ ($c =$ 0.10, EtOH); $[\alpha]_D^{25} = -8.4$ ($c = 0.25$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.36$ (br s, 1H; H-7), 7.42 (ddd, $J_o = 8.5$, 7.9 Hz, $J_m = 1.7$ Hz, 1H; H-11), 7.18 (dd, $J_o = 7.9$ Hz, $J_m = 1.7$ Hz, 1H; H-13), 6.78 (br d, $J_o = 8.5$ Hz, 1H; H-10), 6.73 (ddd, $J_o = 8.5$, 7.9 Hz, $J_m = 0.9$ Hz, 1H; H-12), 4.17 (q, $J = 7.5$ Hz, 1H; H-5), 1.71 (m, 2H; H-βa), 1.63 (d, $J = 7.5$ Hz, 3H; H-14), 1.58 (m, 2H; H-αa), 1.55 (m, 2H; H-βb), 1.39 (m, 2H; H-αb), 1.38 (sext, $J = 7.3$ Hz, 2H; H-γa), 1.28 (sext, $J = 7.3$ Hz, 2H; H-γb), 0.91 (t, $J = 7.3$ Hz, 3H; H-δa), 0.82 (t, $J = 7.3$ Hz, 3H; H-δb); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 174.7$ (br s; C-4), 172.6 (C-7), 169.7 (C-9), 138.3 (C-11), 135.9 (C-13), 122.9 (C-10), 117.6 (C-8), 117.5 (C-12), 64.1 (C-5), 27.4 (C-βa), 27.3 (C-βb), 27.1 (C-γa), 26.9 (C-γb), 22.9 (C-14), 22.7 (br s; C-αa), 22.3 (br s; C-αb), 14.0 (C-δa), 13.9 (C-δb); IR (KBr): $\tilde{\nu} = 2956$, 2924, 2870, 2854, 1622, 1586, 1466, 1444, 542 cm^{-1}; MS: *m*/*z* (%): 381 (32) [$M^+(^{120}Sn) - CO_2$], 379 (24) [$M^+(^{118}Sn) - CO_2$], 377 (13) [$M^+(^{116}Sn) - CO_2$], 368 (12), 366 (9), 364 (5), 312 (22), 310 (16), 308 (9), 268 (100), 266 (83), 264 (47), 225 (17), 223 (11), 221 (3), 91 (9); elemental analysis calcd (%) for $C_{18}H_{27}NO_3Sn$: C 50.98, H 6.42, N 3.30;[33] found: C 50.92, H 6.48, N 3.42.

2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-ethyl-2-stannabenzocyclononen-4-one (5c): Yellow solid, 92.9% yield; m.p. 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.28$ (br s, 1H; H-7), 7.39 (ddd, $J_o = 8.4$, 7.7 Hz, $J_m = 1.6$ Hz, 1H; H-11), 7.17 (dd, $J_o = 8.0$ Hz, $J_m = 1.6$ Hz, 1H; H-13), 6.76 (br d, $J_o = 8.4$ Hz, 1H; H-10), 6.71 (dd, $J_o = 8.0$, 7.7 Hz, 1H; H-12), 3.98 (dd, $J = 6.2$, 5.9 Hz, 1H; H-5), 2.11–1.89 (m, 2H; H-14), 1.71 (m, 2H; H-βa), 1.58 (m, 2H; H-αa), 1.45 (m, 2H; H-βb), 1.37 (m, 2H; H-γa), 1.35 (m, 2H; H-αb), 1.24 (m, 2H; H-γb), 0.99 (t, $J = 7.3$ Hz; H-15), 0.89 (t, $J = 7.3$ Hz, 3H; H-δa), 0.77 (t, $J = 7.3$ Hz, 3H; H-δb); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 173.8$ (C-4), 172.2 (C-7), 169.4 (C-9), 137.8 (C-11), 135.5 (C-13), 122.6 (C-10), 117.3 (C-8), 117.2 (C-12), 69.8 (C-5), 29.2 (C-14), 27.0 (C-βa), 26.9 (C-βb), 26.7 (C-γa), 26.5 (C-γb), 22.2 (C-αa), 21.6 (C-αb), 13.6 (C-δa), 13.5 (C-δb), 9.6 (C-15); IR (KBr): $\tilde{\nu} = 2956$, 2920, 2872, 2852, 1618, 1560, 1466, 1448, 546, 458 cm^{-1}; MS: *m*/*z* (%): 395 (44) [$M^+(^{120}Sn) - CO_2$], 393 (32) [$M^+(^{118}Sn) - CO_2$], 391 (18) [$M^+(^{116}Sn) - CO_2$)], 382 (15), 380 (14), 378 (9), 326 (25), 324 (18), 322 (10), 282 (100), 280 (79), 278 (49), 225 (10), 223 (5), 221 (1), 91 (8); elemental analysis calcd (%) for $C_{19}H_{29}NO_3Sn$: C 52.09, H 6.67, N 3.20; found: C 52.29, H 6.64, N 3.16.

(5*S*)-2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-isopropyl-2-stannabenzocyclononen-4-one (5d): Yellow solid, 87.2% yield; m.p. 171–173 °C; $[\alpha]_D^{25} = -92.1$ ($c = 0.24$, EtOH); $[\alpha]_D^{25} = -225.1$ ($c = 0.09$, MeOH); $[\alpha]_D^{25} = -226.9$ ($c =$ 0.09, MeOH, after 3 d); $[\alpha]_D^{25} = -201.8$ ($c = 0.25$, $CHCl_3$); $[\alpha]_D^{25} = -203.4$ ($c = 0.25$, $CHCl_3$, after 3 d); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.24$ (br, 1H; H-7), 7.41 (ddd, $J_o = 8.8$, 7.9 Hz, $J_m = 1.8$ Hz, 1H; H-11), 7.18 (dd, $J_o =$ 7.9 Hz, $J_m = 1.8$ Hz, 1H; H-13), 6.80 (br d, $J_o = 8.8$ Hz, 1H; H-10), 6.74 (ddd, $J_o = 8.8$, 7.9 Hz, $J_m = 0.9$ Hz, 1H; H-12), 3.83 (dd, $J = 4.8$, 0.7 Hz, 1H; H-5), 2.30 (dhept, $J = 6.6$, 4.8 Hz, 1H; H-14), 1.76 (m, 2H; H-βa), 1.65 (m, 2H; H-αa), 1.42 (m, 2H; H-βb), 1.38 (sext, $J = 7.3$ Hz, 2H; H-γa), 1.30 (m, 2H; H-αb), 1.24 (sext, $J = 7.3$ Hz, 2H; H-γb), 1.07 (d, $J = 6.6$ Hz, 3H; H-15a), 1.04 (d, $J = 6.6$ Hz, 3H; H-15b), 0.93 (t, $J = 7.3$ Hz, 3H; H-δa), 0.77 (t, $J = 7.3$ Hz, 3H; H-δb); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 173.2$ (C-4), 172.5 (C-7), 169.6 (C-9), 137.7 (C-11), 135.5 (C-13), 122.7 (C-10), 117.4 (C-

12), 117.3 (C-8), 74.6 (C-5), 34.5 (C-14), 26.9 (C-βa, C-βb), 26.7 (C-γa), 26.5 (C-γb), 22.5 (C-αa), 20.9 (C-αb), 19.1 (C-15b), 18.3 (C-15a), 13.6 (C-δa), 13.5 (C-δb); IR (KBr): $\tilde{\nu}$ = 2956, 2922, 2872, 2856, 1614, 1540, 1468, 1444, 586, 458 cm^{-1}; MS: *m*/*z* (%): 409 (35) [M^+(^{120}Sn) – CO_2], 407 (27) [M^+(^{118}Sn) – CO_2], 405 (15) [M^+(^{116}Sn) – CO_2], 396 (17), 394 (20), 392 (13), 340 (22), 338 (17), 336 (9), 296 (100), 294 (80), 292 (45), 225 (15), 223 (10), 221 (2), 91 (8); elemental analysis calcd (%) for $C_{20}H_{31}NO_3Sn$: C 53.13, H 6.91, N 3.10; found: C 53.05, H 6.87, N 3.12. Suitable crystals were obtained using a 2:1 mixture of hexane/dichloromethane.

(5*S*)-2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-isobutyl-2-stannabenzocyclononen-4-one (5e): Yellow solid, 82.5% yield; m.p. 90 – 92 °C; $[\alpha]_D^{25} = -136.9$ (*c* = 0.10, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (br s, 1H; H-7), 7.42 (ddd, J_o = 8.5, 7.8 Hz, J_m = 1.7 Hz, 1H; H-11), 7.18 (dd, J_o = 7.8 Hz, J_m = 1.7 Hz, 1H; H-13), 6.80 (br d, J_o = 8.5 Hz, 1H; H-10), 6.74 (ddd, J_o = 8.5, 7.8 Hz, J_m = 0.5 Hz, 1H; H-12), 4.09 (dd, *J* = 8.8, 5.6 Hz, 1H; H-5), 1.92 (m, 2H; H-15), 1.75 (m, 2H; H-βa), 1.71 (m, 2H; H-14), 1.64 (m, 2H; H-αa), 1.41 (m, 2H; H-αb), 1.40 (m, 2H; H-βb), 1.36 (sext, *J* = 7.3 Hz, 2H; H-γa), 1.24 (sext, *J* = 7.3 Hz, 2H; H-γb), 0.99 (d, *J* = 6.5 Hz; H-16a), 0.98 (d, *J* = 6.5 Hz; H-16b), 0.93 (t, *J* = 7.3 Hz, 3H; H-δa), 0.79 (t, *J* = 7.3 Hz, 3H; H-δb); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 174.6 (C-4), 172.1 (C-7), 169.7 (C-9), 138.1 (C-11), 135.8 (C-13), 123.0 (C-10), 117.7 (C-12), 117.4 (C-8), 68.1 (C-5), 45.7 (C-14), 27.4 (C-βa), 27.3 (C-βb), 27.1 (C-γa), 26.9 (C-γb), 24.3 (C-15), 23.3 (C-16b), 22.3 (C-16a), 22.5 (C-αa), 22.0 (C-αb), 14.0 (C-δa), 13.9 (C-δb); IR (KBr): $\tilde{\nu}$ = 2954, 2924, 2866, 1620, 1586, 1468, 1446, 596 cm^{-1}; MS: *m*/*z* (%): 423 (47) [M^+(^{120}Sn) – CO_2], 421 (35) [M^+(^{118}Sn) – CO_2], 419 (19) [M^+(^{116}Sn) – CO_2], 410 (16), 408 (13), 406 (7), 380 (100), 378 (75), 376 (41), 354 (24), 352 (19), 350 (10), 310 (85), 308 (68), 306 (39), 266 (15), 264 (11), 262 (6), 225 (15), 223 (9), 221 (1), 91 (11); elemental analysis calcd. (%) for $C_{21}H_{33}NO_3Sn$: C 54.11, H 7.14, N 3.00;[33] found: C 54.26, H 7.21, N 3.12.

(5*S*)-2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-*sec*-butyl-2-stannabenzocyclononen-4-one (5f): Yellow solid, 80.5% yield; m.p. 97 – 98 °C; $[\alpha]_D^{25} = -250.0$ (*c* = 0.10, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (br s, 1H; H-7), 7.40 (dd, J_o = 8.4, 7.6 Hz, 1H; H-11), 7.18 (d, J_o = 7.6 Hz, 1H; H-13), 6.79 (br d, J_o = 8.4 Hz, 1H; H-10), 6.73 (dd, J_o = 8.4, 7.6 Hz, 1H; H-12), 3.92 (d, *J* = 4.4 Hz, 1H; H-5), 1.95 (m, 1H; H-14), 1.76 (m, 2H; H-βa), 1.68 (m, 1H; H-15a), 1.65 (m, 2H; H-αa), 1.41 (sext, *J* = 7.3 Hz, 2H; H-γa), 1.38 (m, 2H; H-βb), 1.29 (m, 1H; H-15b), 1.28 (m, 2H; H-αb), 1.23 (sext, *J* = 7.3 Hz, 2H; H-γb), 1.03 (d, *J* = 7.0 Hz; H-17), 0.95 (t, *J* = 7.4 Hz, 3H; H-16), 0.92 (t, *J* = 7.3 Hz, 3H; H-δa), 0.77 (t, *J* = 7.3 Hz, 3H; H-δb); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 172.9 (C-4), 172.4 (C-7), 169.5 (C-9), 137.7 (C-11), 135.5 (C-13), 122.7 (C-10), 117.3 (C-12, C-8), 73.5 (C-5), 42.0 (C-14), 34.5 (C-14), 27.0 (C-βa), 26.9 (C-βb), 26.6 (C-γa), 26.5 (C-γb), 25.3 (C-15), 22.5 (C-αa), 20.9 (C-αb), 15.2 (C-17), 13.6 (C-δa), 13.5 (C-δb), 11.8 (C-16); IR (KBr): $\tilde{\nu}$ = 2952, 2920, 2868, 2854, 1614, 1540, 1466, 1446, 522, 458 cm^{-1}; MS: *m*/*z* (%): 423 (41) [M^+(^{120}Sn) – CO_2], 421 (31) [M^+(^{118}Sn) – CO_2], 419 (17) [M^+(^{116}Sn) – CO_2], 410 (18), 408 (17), 406 (10), 394 (30), 392 (23), 390 (13), 354 (24), 352 (18), 350 (10), 310 (100), 308 (78), 306 (44), 280 (9), 278 (6), 276 (3), 225 (15), 223 (9), 221 (1), 91 (6); elemental analysis calcd (%) for $C_{21}H_{33}NO_3Sn$: C 54.11, H 7.14, N 3.00; found: C 53.94, H 7.01, N 2.93. Suitable crystals for X-ray analysis were obtained using a 3:1 mixture of hexane/dichloromethane.

2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-*n*-hexyl-2-stannabenzocyclononen-4-one (5g): Yellow solid, 85.7% yield; m.p. 68 – 69 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (br s, 1H; H-7), 7.40 (ddd, J_o = 8.4, 7.7 Hz, J_m = 1.5 Hz, 1H; H-11), 7.16 (dd, J_o = 7.7 Hz, J_m = 1.5 Hz, 1H; H-13), 6.77 (br d, J_o = 8.4 Hz, 1H; H-10), 6.71 (ddd, J_o = 8.4, 7.7 Hz, J_m = 1.0 Hz, 1H; H-12), 4.02 (dd, *J* = 6.7, 5.5 Hz, 1H; H-5), 1.98 (m, 1H; H-14a), 1.87 (m, 1H; H-14b), 1.74 (m, 2H; H-βa), 1.62 (m, 2H; H-αa), 1.61 (m, 2H; H-17), 1.49 (m, 2H; H-βb), 1.46 (m, 2H; H-16), 1.41 (m, 2H; H-γa), 1.37 (m, 2H; H-15), 1.36 (m, 2H; H-αb), 1.26 (m, 4H; H-γb, H-18), 0.91 (t, *J* = 7.3 Hz, 3H; H-δa), 0.83 (t, *J* = 6.3 Hz; H-19), 0.79 (t, *J* = 7.3 Hz, 3H; H-δb); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 174.2 (C-4), 172.5 (C-7), 169.8 (C-9), 138.1 (C-11), 135.8 (C-13), 123.0 (C-10), 117.6 (C-8, C-12), 69.3 (C-5), 36.2 (C-14), 31.5 (C-15), 27.0 (C-βa), 28.9 (C-16), 26.9 (C-βb), 26.7 (C-γa), 26.5 (C-γb), 25.0 (C-17), 22.5 (C-18), 22.2 (C-αa), 21.6 (C-αb), 14.0 (C-19), 13.5 (C-δa), 13.4 (C-δb); IR (KBr): $\tilde{\nu}$ = 2956, 2926, 2856, 2360, 2344, 2332, 1618, 1560, 1466, 1448, 558 cm^{-1}; MS: *m*/*z* (%): 451 (50) [M^+(^{120}Sn) – CO_2], 449 (36) [M^+(^{118}Sn) – CO_2], 447 (20) [M^+(^{116}Sn) – CO_2], 438 (15), 436 (12), 434 (7), 394 (23), 392 (17), 390 (10), 382 (24), 380 (36), 378 (25), 338 (100), 336 (80), 334 (49), 225 (7), 223 (4), 221 (1), 91 (5); elemental analysis calcd. (%) for $C_{23}H_{37}NO_3Sn$: C 55.89, H 7.55, N 2.83; found: C 55.98, H 7.50, N 2.85.

(5*S*)-2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-benzyl-2-stannabenzocyclononen-4-one (5h): Yellow solid, 94.2% yield; m.p. 145 – 147 °C; $[\alpha]_D^{25} = -318.4$ (*c* = 0.10, EtOH); $[\alpha]_D^{25} = 861.79$ (*c* = 0.094, MeOH, immediately after preparation); $[\alpha]_D^{25} = -147.9$ (*c* = 0.094, MeOH, after 3 d); $[\alpha]_D^{25} = -443.0$ (*c* = 0.105, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25} = -454.8$ (*c* = 0.105, $CHCl_3$, after 3 d); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (br s, 1H; H-7), 7.36 (dd, J_o = 8.4, 7.3 Hz, 1H; H-11), 7.22 (m, 5H; H-16, H-17, H-18), 6.76 (d, J_o = 7.3 Hz, 1H; H-13), 6.73 (br d, J_o = 8.4 Hz, 1H; H-10), 6.62 (t, J_o = 7.3 Hz, 1H; H-12), 4.17 (dd, *J* = 8.8, 3.3 Hz, 1H; H-5), 3.50 (dd, *J* = 13.9, 3.3 Hz; H-14a), 3.03 (dd, *J* = 13.9, 9.2 Hz; H-14b), 1.65 (m, 2H; H-βa), 1.47 (m, 2H; H-αa), 1.43 (m, 2H; H-βb), 1.37 (m, 2H; H-γa), 1.34 (m, 2H; H-αb), 1.22 (m, 2H; H-γb), 0.91 (t, *J* = 7.3 Hz, 3H; H-δa), 0.77 (t, *J* = 7.3 Hz, 3H; H-δb); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 173.2 (C-4), 172.5 (C-7), 169.4 (C-9), 137.7 (C-11), 135.4 (C-13), 135.2 (C-15), 130.3 (C-17), 129.0 (C-16), 127.5 (C-18), 122.5 (C-10), 117.1 (C-12), 116.8 (C-8), 69.9 (C-5), 41.9 (C-14), 27.1 (C-βa), 26.9 (C-βb), 26.7 (C-γa), 26.5 (C-γb), 21.8 (C-αa), 21.6 (C-αb), 13.6 (C-δa), 13.5 (C-δb); IR (KBr): $\tilde{\nu}$ = 2956, 2924, 2870, 2852, 2670, 1616, 1540, 1470, 1444, 540 cm^{-1}; MS: *m*/*z* (%): 457 (33) [M^+(^{120}Sn) – CO_2], 455 (25) [M^+(^{118}Sn) – CO_2], 453 (14) [M^+(^{116}Sn) – CO_2], 444 (13), 442 (9), 440 (5), 388 (20), 386 (15), 384 (8), 344 (100), 342 (77), 340 (44), 238 (19), 236 (13), 234 (5), 225 (8), 223 (5), 221 (2), 91 (5); elemental analysis calcd (%) for $C_{24}H_{31}NO_3Sn$: C 57.63, H 6.25, N 2.80;[33] found: C 57.80, H 6.28, N 2.90.

(5*S*)-2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-(2-methylsulfanylethyl)-2-stannabenzocyclononen-4-one (5i): Yellow solid, 81.4% yield; m.p. 170 – 172 °C; $[\alpha]_D^{25} = -75.3$ (*c* = 0.219, MeOH, immediately after preparation); $[\alpha]_D^{25} = -75.1$ (*c* = 0.219, MeOH, after 3 d) $[\alpha]_D^{25} = -77.94$ (*c* = 0.263, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25} = -77.80$ (*c* = 0.263, $CHCl_3$, after 3 d); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (br s, 1H; H-7), 7.39 (ddd, J_o = 7.0, 6.6 Hz, J_m = 1.8 Hz, 1H; H-11), 7.16 (dd, J_o = 8.1 Hz, J_m = 1.8 Hz, 1H; H-13), 6.76 (br d, J_o = 8.4 Hz, 1H; H-10), 6.71 (dd, J_o = 8.1, 7.0 Hz, 1H; H-12), 4.27 (dd, *J* = 7.7, 5.8 Hz, 1H; H-5), 2.69 (m, 1H; H-15a), 2.50 (m, 1H; H-15b), 2.32 (m, 1H; H-14a), 2.07 (s, 3H; H-16), 2.03 (m, 1H; H-14b), 1.71 (m, 2H; H-βa), 1.60 (m, 2H; H-αa), 1.48 (m, 2H; H-βb), 1.38 (m, 2H; H-γa), 1.35 (m, 2H; H-αb), 1.23 (m, 2H; H-γb), 0.89 (t, *J* = 7.3 Hz, 3H; H-δa), 0.77 (t, *J* = 7.3 Hz, 3H; H-δb); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 173.5 (C-4), 172.9 (C-7), 169.5 (C-9), 137.9 (C-11), 135.5 (C-13), 122.6 (C-10), 117.3 (C-12), 117.2 (C-8), 66.7 (^2J(^{119}Sn,^{13}C) = 15.4 Hz; C-5), 34.9 (C-14), 29.6 (C-15), 27.0 (C-βa), 26.9 (C-βb), 26.6 (^3J(^{119}Sn,^{13}C) = 47.7 Hz; C-γa), 26.5 (^3J(^{119}Sn,^{13}C) = 44.6 Hz; C-γb), 22.3 (C-αa), 21.6 (C-αb), 15.2 (C-16), 13.5 (C-δa), 13.4 (C-δb); IR (KBr): $\tilde{\nu}$ = 2958, 2924, 1652, 1584, 1464, 1446, 604, 458 cm^{-1}; MS: *m*/*z* (%): 441 (11) [M^+(^{120}Sn) – CO_2], 439 (4) [M^+(^{118}Sn) – CO_2], 437 (4) [M^+(^{116}Sn) – CO_2], 428 (100), 426 (71), 424 (43), 380 (64), 378 (45), 376 (29), 328 (21), 326 (15), 324 (10), 94 (18); elemental analysis calcd (%) for $C_{20}H_{31}NO_3SSn$: C 49.61, H 6.45, N 2.89;[33] found: C 49.72, H 6.56, N 2.92.

2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-(4′-hydroxybenzyl)-2-stannabenzocyclononen-4-one (5j): Yellow solid, 75.2% yield; m.p. 158 – 159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (br s, 1H; OH), 7.57 (br s, 1H; H-7), 7.36 (dd, J_o = 8.4, 7.5 Hz, 1H; H-11), 6.90 (d, J_o = 7.9 Hz, 2H; H-16), 6.83 (d, J_o = 7.5 Hz, 1H; H-13), 6.77 (d, J_o = 7.9 Hz, 2H; H-17), 6.74 (br d, J_o = 8.4 Hz, 1H; H-10), 6.63 (dd, J_o = 8.4, 7.5 Hz, 1H; H-12), 4.13 (dd, *J* = 8.7, 3.3 Hz, 1H; H-5), 3.37 (dd, *J* = 14.1, 3.3 Hz, 1H; H-14a), 2.93 (dd, *J* = 14.1, 8.7 Hz, 1H; H-14b), 1.63 (m, 2H; H-βa), 1.44 (m, 2H; H-βb), 1.35 (m, 2H; H-αa), 1.32 (m, 2H; H-αb), 1.32 (sext, *J* = 7.3 Hz, 2H; H-γa), 1.20 (sext, *J* = 7.3 Hz, 2H; H-γb), 0.89 (t, *J* = 7.3 Hz, 3H; H-δa), 0.76 (t, *J* = 7.3 Hz, 3H; H-δb); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 174.6 (C-4), 172.7 (C-7), 169.0 (C-9), 156.6 (C-18), 137.9 (C-11), 135.7 (C-13), 131.3 (C-16), 125.6 (C-15), 122.4 (C-10), 117.6 (C-12), 117.1 (C-8), 116.3 (C-17), 70.2 (C-5), 41.3 (C-14), 27.1 (C-βa), 26.9 (C-βb), 26.7 (C-γa), 26.5 (C-γb), 22.0 (C-αa), 21.7 (C-αb), 13.6 (C-δa), 13.5 (C-δb); IR (KBr): $\tilde{\nu}$ = 3198 (OH), 2954, 2924, 2852, 1614, 1560, 1466, 1444, 588 cm^{-1}; MS: *m*/*z* (%): 473 (43) [M^+(^{120}Sn) – CO_2], 471 (32) [M^+(^{118}Sn) – CO_2], 469 (17) [M^+(^{116}Sn) – CO_2], 460 (16), 458 (12), 456 (7), 404 (20), 402 (15), 400 (8), 360 (100), 358 (76), 356 (43), 254 (11), 252 (9), 250 (5), 225 (8), 223 (5), 221 (1), 91 (2); elemental analysis calcd (%) for $C_{24}H_{31}NO_4Sn$: C 55.84, H 6.05, N 2.71; found: C 55.99, H 6.03, N 2.81.

(5*S*)-2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-(indol-3-yl)-2-stannabenzocyclononen-4-one (5k): Yellow solid, 86.5% yield; m.p. 109 – 110 °C; $[\alpha]_D^{25} = -457.7$ (*c* = 0.09, EtOH); $[\alpha]_D^{25} = -380.7$ (*c* = 0.20, MeOH); $[\alpha]_D^{25} = -505.2$ (*c* = 0.21, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.90 (s, 1H; H-17), 7.62 (d, J_o = 8.0 Hz, 1H; H-20), 7.41 (d, J_o = 8.0 Hz, 1H; H-23), 7.34 (t,

$J_o = 8.6$ Hz, 1H; H-11), 7.23 (br s, 1H; H-7), 7.19 (t, $J_o = 8.0$ Hz, 1H; H-22), 7.07 (t, $J_o = 8.0$ Hz, 1H; H-22), 6.87 (s, 1H; H-16), 6.74 (br d, $J_o = 8.6$ Hz, 1H; H-10), 6.58 (m, 1H; H-13), 6.55 (m, 1H; H-12), 4.23 (dd, $J = 9.5$, 3.1 Hz, 1H; H-5), 3.77 (dd, $J = 14.6$, 9.6 Hz, 1H; H-14a), 3.22 (dd, $J = 14.6$ Hz, 3.1 Hz, 1H; H-14b), 1.64 (m, 2H; H-βa), 1.46 (m, 2H; H-βb), 1.38 (m, 2H; H-αa), 1.35 (m, 2H; H-αb), 1.31 (sext, $J = 7.3$ Hz, 2H; H-γa), 1.22 (sext, $J = 7.3$ Hz, 2H; H-γb), 0.93 (t, $J = 7.3$ Hz, 3H; H-δa), 0.79 (t, $J = 7.3$ Hz, 3H; H-δb); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 174.6$ (C-4), 172.5 (C-7), 169.5 (C-9), 137.9 (C-11), 137.0 (C-17), 135.7 (C-13), 127.0 (C-18), 125.3 (C-16), 123.0 (C-22), 122.7 (C-10), 120.5 (C-21), 119.1 (C-20), 117.4 (C-12), 117.3 (C-8), 112.1 (C-23), 109.3 (C-15), 69.0 (C-5), 32.9 (C-14), 27.5 (C-βa), 27.3 (C-βb), 27.1 (C-γa), 26.9 (C-γb), 22.3 (C-αa), 22.0 (C-αb), 14.0 (C-δa), 13.9 (C-δb); IR (KBr): $\tilde{\nu} = 3348$ (NH), 2954, 2920, 2850, 1614, 1588, 1466, 1446, 554 cm^{-1}; MS: m/z (%): 540 (5) [M^+(^{120}Sn)], 538 (5) [M^+(^{118}Sn)], 536 (3) [M^+(^{116}Sn)], 596 (48) [M^+(^{120}Sn) – CO_2], 494 (36) [M^+(^{118}Sn) – CO_2)], 492 (20) [M^+(^{116}Sn) – CO_2)], 483 (65), 481 (48), 479 (27), 439 (10), 437 (7), 435 (4), 427 (7), 425 (6), 423 (5), 383 (100), 381 (77), 379 (45), 354 (16), 352 (13), 350 (7), 298 (39), 296 (35), 294 (19), 277 (27), 275 (20), 273 (11), 250 (13), 248 (8), 246 (5), 240 (18), 238 (14), 236 (9), 225 (5), 223 (4), 221 (1), 91 (2); elemental analysis calcd (%) for $C_{26}H_{32}N_2O_3Sn$: C 57.91, H 5.98, N 5.19; found: C 57.70, H 5.90, N 5.24.

(5*S*)-2,2-Di-*n*-butyl-6-aza-1,3-dioxa-5-phenyl-2-stannabenzocyclononen-4-one (5l): Yellow solid, 86.3% yield; m.p. 84–85 °C; $[\alpha]_D^{25} = -1.3$ ($c = 0.22$, MeOH); $[\alpha]_D^{25} = -2.7$ ($c = 0.232$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.29 (br s, 1H; H-7), 7.42 (ddd, $J_o = 8.8$, 7.7 Hz, $J_m = 1.5$ Hz, 1H; H-11), 7.40 (m, 2H; H-15), 7.38 (m, 2H; H-16), 7.35 (m, 1H; H-17), 7.08 (dd, $J_o =$ 8.1 Hz, $J_m = 1.5$ Hz, 1H; H-13), 6.79 (br d, $J_o = 7.7$ Hz, 1H; H-10), 6.69 (dd, $J_o = 8.8$, 8.1 Hz, 1H; H-12), 5.19 (s, 1H; H-5), 1.66 (m, 2H; H-βa), 1.61 (m, 2H; H-αa), 1.48 (m, 2H; H-αb), 1.46 (m, 2H; H-βb), 1.37 (sext, $J = 7.3$ Hz, 2H; H-γa), 1.33 (sext, $J = 7.3$ Hz, 2H; H-γb), 0.87 (t, $J = 7.3$ Hz, 3H; H-δa), 0.85 (t, $J = 7.3$ Hz, 3H; H-δb); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 174.0$ (C-7), 171.9 (C-4), 169.7 (C-9), 138.2 (C-11), 137.8 (C-14), 135.8 (C-13), 129.3 (C-16), 128.7 (C-17), 127.3 (C-15), 122.6 (C-10), 117.4 (C-8), 117.3 (C-12), 71.3 (^2J(^{119}Sn,^{13}C) = 16.9 Hz; C-5), 27.0 (C-βa), 26.9 (C-βb), 26.7 (^3J(^{119}Sn,^{13}C) = 32.3 Hz, ^2J(^{119}Sn,^{13}C) = 16.9 Hz; C-γa), 26.6 (^3J(^{119}Sn,^{13}C) = 27.7 Hz; C-γb), 22.5 (C-αa), 22.0 (C-αb), 13.5 (C-δa, C-δb); IR (KBr): $\tilde{\nu} = 2956$, 2920, 2850, 1618, 1560, 1468, 1446, 526 cm^{-1}; MS: m/z (%): 443 (27) [M^+(^{120}Sn) – CO_2], 441 (20) [M^+(^{118}Sn) – CO_2], 439 (11) [M^+(^{116}Sn) – CO_2], 374 (3), 372 (2), 370 (1), 330 (100), 328 (80), 326 (47), 225 (20), 223 (15), 221 (5), 91 (15); elemental analysis calcd (%) for $C_{23}H_{29}NO_3Sn$: C 56.82, H 6.01, N 2.88; found: C 56.70, H 6.08, N 2.96.

2,2-Diphenyl-6-aza-1,3-dioxa-2-stannabenzocyclononen-4-one (6a): Yellow solid, 91% yield; m.p. 202–203 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.37 (br s, 1H; H-7), 7.89 (m, 4H, ^3J(^{119}Sn,^{1}H) = 81.1 Hz; H-*o*a, H-*o*b), 7.53 (ddd, $J_o = 8.7$, 8.2 Hz, $J_m = 1.7$ Hz, 1H; H-11), 7.40 (m, 6H; H-*m*a, H-*m*b, H-*p*a, H-*p*b), 7.16 (dd, $J_o = 8.2$ Hz, $J_m = 1.7$ Hz, 1H; H-13), 7.12 (dd, $J_o =$ 8.7 Hz, $J_m = 1.7$ Hz, 1H; H-10), 6.77 (ddd, $J_o = 8.7$, 8.2 Hz, $J_m = 1.7$ Hz, 1H; H-12), 4.34 (br s, 2H; H-5); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 173.2$ (C-7), 170.6 (^2J(^{119}Sn,^{13}C) = 15.6 Hz; C-4), 169.5 (C-9), 138.5 (C-11), 137.8 (C-*i*a, C-*i*b), 136.6 (C-*o*a, C-*o*b), 135.8 (C-13), 131.0 (C-*p*a, C-*p*b), 129.1 (C-*m*a, C-*m*b), 123.0 (C-10), 118.0 (C-12), 117.2 (^3J(^{119}Sn,^{13}C) = 31.1 Hz; C-8), 57.2 (^2J(^{119}Sn,^{13}C) = 19.7 Hz; C-5); IR (KBr): $\tilde{\nu} = 3033$, 2956, 2924, 2854, 1626, 1588, 1468, 1450, 536 cm^{-1}; MS: m/z (%): 407 (100) [M^+(^{120}Sn) – CO_2], 405 (74) [M^+(^{118}Sn) – CO_2], 403 (42) [M^+(^{116}Sn) – CO_2], 351 (37), 349 (28), 347 (16), 330 (43), 328 (33), 326 (19), 303 (45), 301 (39), 299 (16), 253 (17), 251 (13), 249 (8), 197 (83), 195 (63), 193 (37), 167 (51), 161 (54), 133 (29), 120 (47), 118 (36), 116 (20); elemental analysis calcd (%) for $C_{21}H_{17}NO_3Sn$: C 56.04, H 3.81, N 3.11;[33] found: C 56.21, H 3.88, N 3.26. Suitable crystals were obtained using a 1:3 mixture of hexane/dichloromethane.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-methyl-2-stannabenzocyclononen-4-one (6b): Yellow solid, 88.6% yield; m.p. 192–193 °C; $[\alpha]_D^{25} = -216.8$ ($c =$ 0.28, MeOH, immediately after preparation); $[\alpha]_D^{25} = -60.1$ ($c = 0.28$, MeOH, after 3 d); $[\alpha]_D^{25} = -202.7$ ($c = 0.48$, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25} = -202.7$ ($c = 0.481$, $CHCl_3$, after 3 d); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.36$ (br s, 1H; H-7), 7.97 (m, 2H, ^3J(^{119}Sn,^{1}H) = 83.5 Hz; H-*o*b), 7.86 (m, 2H, ^3J(^{119}Sn,^{1}H) = 82.8 Hz; H-*o*a), 7.54 (ddd, $J_o =$ 8.4, 8.0 Hz, $J_m = 1.8$ Hz, 1H; H-11), 7.45 (m, 3H; H-*m*a, H-*p*a), 7.37 (m, 3H; H-*m*b, H-*p*b), 7.20 (dd, $J_o = 7.5$ Hz, $J_m = 1.8$ Hz, 1H; H-13), 7.15 (dd, $J_o =$ 8.4 Hz, $J_m = 1.1$ Hz, 1H; H-10), 6.78 (ddd, $J_o = 8.0$, 7.5 Hz, $J_m = 1.1$ Hz, 1H; H-12), 4.24 (q, $J = 5.8$ Hz, 1H; H-5), 1.53 (d, $J = 7.3$ Hz, 3H; H-14); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 174.3$ (^2J(^{119}Sn,^{13}C) = 19.1 Hz; C-4), 172.4 (C-7), 169.4 (^2J(^{119}Sn,^{13}C) = 29.7 Hz; C-9), 138.5 (C-11), 137.9 (C-*i*a), 137.8 (C-*i*b), 136.8 (C-*o*a), 136.5 (C-*o*b), 135.8 (C-13), 131.1 (C-*p*a), 131.0 (C-*p*b), 129.2 (C-*m*a), 129.1 (C-*m*b), 123.0 (^2J(^{119}Sn,^{13}C) = 7.3 Hz; C-10), 118.0 (C-12), 117.5 (^3J(^{119}Sn,^{13}C) = 31.7 Hz; C-8), 64.1 (C-5), 22.6 (C-14); IR (KBr): $\tilde{\nu} = 2956$, 2924, 2870, 2854, 1622, 1586, 1466, 1444, 542 cm^{-1}; MS: m/z (%): 421 (100) [M^+(^{120}Sn) – CO_2], 419 (74) [M^+(^{118}Sn) – CO_2], 417 (41) [M^+(^{116}Sn) – CO_2], 344 (33), 342 (25), 340 (14), 303 (68), 301 (54), 299 (32), 197 (41), 195 (31), 193 (18), 167 (82), 120 (19), 118 (14), 116 (8); elemental analysis calcd. (%) for $C_{22}H_{19}NO_3Sn$: C 56.94, H 4.13, N 3.02;[33] found: C 57.12, H 4.20, N 3.09. Suitable crystals were obtained using a mixture of dichloromethane/hexane (2:3) to give **6b** in a chiral orthorhombic $P2_12_12_1$ space group. When crystals were obtained using a 2:1:2 hexane/dichloromethane/methanol mixture, **6b-racemic** was obtained in a centrosymmetric monoclinic space group $P2_1/c$.

2,2-Diphenyl-6-aza-1,3-dioxa-5-ethyl-2-stannabenzocyclononen-4-one (6c): Yellow solid, 91.3% yield; m.p. 227–228 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.32$ (br s, 1H; H-7), 7.98 (m, 2H, ^3J(^{119}Sn,^{1}H) = 80.6 Hz; H-*o*b), 7.81 (m, 2H, ^3J(^{119}Sn,^{1}H) = 81.8 Hz; H-*o*a), 7.55 (ddd, $J_o = 8.4$, 8.0 Hz, $J_m =$ 1.8 Hz, 1H; H-11), 7.45 (m, 3H; H-*m*a, H-*p*a), 7.36 (m, 3H; H-*m*b, H-*p*b), 7.22 (dd, $J_o = 7.3$ Hz, $J_m = 1.8$ Hz, 1H; H-13), 7.16 (dd, $J_o = 8.4$ Hz, $J_m =$ 1.1 Hz, 1H; H-10), 6.80 (ddd, $J_o = 8.0$, 7.3 Hz, $J_m = 1.1$ Hz, 1H; H-12), 4.11 (dd, $J = 5.8$, 5.5 Hz, 1H; H-5), 2.04–1.86 (m, 2H; H-14), 0.83 (dd, $J =$ 7.7, 7.4 Hz, 3H; H-15); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 173.7$ (^2J(^{119}Sn,^{13}C) = 14.6 Hz; C-4), 172.8 (C-7), 169.4 (^2J(^{119}Sn,^{13}C) = 28.4 Hz; C-9), 138.3 (C-11), 138.0 (C-*i*a), 137.6 (C-*i*b), 136.6 (C-*o*a), 136.5 (C-*o*b), 135.9 (C-13), 130.9 (C-*p*a), 130.8 (C-*p*b), 129.1 (C-*m*a), 129.0 (C-*m*b), 122.9 (C-10), 118.0 (C-12), 117.4 (^3J(^{119}Sn,^{13}C) = 32.3 Hz; C-8), 69.4 (^2J(^{119}Sn,^{13}C) = 13.8 Hz; C-5), 29.3 (C-14), 9.4 (C-15); IR (KBr): $\tilde{\nu} = 2956$, 2920, 2872, 2852, 1618, 1560, 1466, 1448, 546, 458 cm^{-1}; MS: m/z (%): 435 (100) [M^+(^{120}Sn) – CO_2], 433 (74) [M^+(^{118}Sn) – CO_2], 391 (40) [M^+(^{116}Sn) – CO_2], 358 (14), 356 (11), 354 (6), 303 (33), 301 (26), 299 (15), 167 (34); elemental analysis calcd (%) for $C_{23}H_{21}NO_3Sn$: C 57.78, H 4.43, N 2.93; found: C 58.06, H 4.54, N 2.92. Suitable crystals were obtained using a 1:1:2 mixture of hexane/dichloromethane/methanol.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-isopropyl-2-stannabenzocyclononen-4-one (6d): Yellow solid, 89.1% yield; m.p. 208–209 °C; $[\alpha]_D^{25} = -357.4$ ($c = 0.22$, MeOH); $[\alpha]_D^{25} = -330.1$ ($c = 0.22$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.27$ (br s, 1H; H-7), 8.01 (m, 2H, ^3J(^{119}Sn,^{1}H) = 81.7 Hz; H-*o*a), 7.23 (m, 2H, ^3J(^{119}Sn,^{1}H) = 79.5 Hz; H-*o*b), 7.55 (ddd, $J_o = 8.4$, 7.0 Hz, 1H; H-11), 7.45 (m, 3H; H-*m*a, H-*p*a), 7.34 (m, 3H; H-*m*b, H-*p*b), 7.22 (dd, $J_o = 8.0$ Hz, $J_m = 1.5$ Hz, 1H; H-13), 7.16 (br d, $J_o = 8.4$ Hz, 1H; H-10), 6.80 (dd, $J_o = 8.0$, 7.7 Hz, 1H; H-12), 3.95 (d, $J = 4.4$ Hz, 1H; H-5), 2.26 (dhept, $J = 7.0$, 4.4 Hz, 1H; H-14), 0.94 (d, $J = 7.0$ Hz, 3H; H-15a), 0.84 (d, $J = 7.0$ Hz, 3H; H-15b); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 173.5$ (^2J(^{119}Sn,^{13}C) = 14.9 Hz; C-4), 173.2 (C-7), 169.7 (^2J(^{119}Sn,^{13}C) = 28.0 Hz; C-9), 138.4 (C-11), 137.9 (C-*i*a), 137.8 (C-*i*b), 136.7 (C-*o*a), 136.6 (C-*o*b), 136.2 (C-13), 131.0 (C-*p*a), 130.8 (C-*p*b), 129.1 (C-*m*a, C-*m*b), 123.1 (C-10), 118.2 (C-12), 117.4 (^3J(^{119}Sn,^{13}C) = 33.1 Hz; C-8), 74.2 (^2J(^{119}Sn,^{13}C) = 12.8 Hz; C-5), 35.0 (C-14), 19.1 (C-15b), 18.6 (C-15a); IR (KBr): $\tilde{\nu} =$ 2956, 2922, 2872, 2856, 1614, 1540, 1468, 1444, 586, 458 cm^{-1}; MS m/z (%): 449 (100) [M^+(^{120}Sn) – CO_2], 447 (73) [M^+(^{118}Sn) – CO_2], 445 (40) [M^+(^{116}Sn) – CO_2], 434 (76), 432 (55), 430 (31), 372 (10), 370 (8), 368 (4), 303 (30), 301 (23), 299 (14), 167 (29); elemental analysis calcd (%) for $C_{24}H_{23}NO_3Sn$: C 58.57, H 4.71, N 2.85; found: C 58.68, H 4.76, N 2.90. Suitable crystals were obtained using a 3:2 mixture of hexane/dichloromethane or a 1:1:1 mixture of hexane/dichloromethane/methanol.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-isobutyl-2-stannabenzocyclononen-4-one (6e): Yellow solid, 84.9% yield; m.p. 198–200 °C; $[\alpha]_D^{25} = -168.5$ ($c =$ 0.28, MeOH, immediately after preparation); $[\alpha]_D^{25} = -168.9$ ($c = 0.28$, MeOH, after 3 d); $[\alpha]_D^{25} = -204.9$ ($c = 0.267$, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25} = -204.3$ ($c = 0.267$, $CHCl_3$, after 3 d); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.23$ (br s, 1H; H-7), 7.98 (m, 2H, ^3J(^{119}Sn,^{1}H) = 81.6 Hz; H-*o*b), 7.82 (m, 2H, ^3J(^{119}Sn,^{1}H) = 81.8 Hz; H-*o*b), 7.55 (dd, $J_o =$ 8.8, 7.3 Hz, 1H; H-11), 7.47 (m, 3H; H-*m*a, H-*p*a), 7.37 (m, 3H; H-*m*b, H-*p*b), 7.21 (d, $J_o = 7.8$ Hz, 1H; H-13), 7.15 (d, $J_o = 8.8$ Hz, 1H; H-10), 6.81 (dd, $J_o =$ 7.8, 7.3 Hz, 1H; H-12), 4.18 (dd, $J = 8.8$, 5.9 Hz, 1H; H-5), 1.80 (m, 1H; H-14a), 1.64 (m, 2H; H-15), 1.51 (m, 1H; H-14b), 0.90 (d, $J = 6.4$ Hz, 3H; H-16a), 0.81 (d, $J = 6.4$ Hz, 3H; H-16b); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta =$ 174.0 (^2J(^{119}Sn,^{13}C) = 21.6 Hz; C-4), 171.7 (C-7), 169.4 (^2J(^{119}Sn,^{13}C) = 28.5 Hz; C-9), 138.2 (C-11), 137.7 (C-*i*a), 137.6 (C-*i*b), 136.7 (C-*o*a), 136.3 (C-*o*b), 135.7 (C-13), 130.9 (C-*p*a), 130.8 (C-*p*b), 129.1 (C-*m*a), 129.0 (C-*m*b),

123.0 (C-10), 117.9 (C-12), 117.3 ($^3J(^{119}Sn,^{13}C)=32.6$ Hz; C-8), 67.8 ($^2J(^{119}Sn,^{13}C)=15.7$ Hz; C-5), 44.8 (C-14), 23.9 (C-15), 22.9 (C-16b), 22.0 (C-16a); IR (KBr): $\tilde{\nu}=2954$, 2924, 2866, 1620, 1586, 1468, 1446, 596 cm^{-1}; MS: *m*/*z* (%): 463 (56) [$M^+(^{120}Sn)-CO_2$], 461 (41) [$M^+(^{118}Sn)-CO_2$], 459 (22) [$M^+(^{116}Sn)-CO_2$], 420 (100), 418 (74), 416 (40), 303 (7), 301 (6), 299 (4), 197 (7), 195 (6), 193 (3), 167 (14); elemental analysis calcd (%) for $C_{25}H_{25}NO_3Sn$: C 59.32, H 4.98, N 2.77;[33] found: C 59.48, H 5.10, N 2.87.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-*sec*-butyl-2-stannabenzocyclononen-4-one (6f): Yellow solid, 93.1% yield; m.p. 93–95 °C; $[\alpha]_D^{25}=-309.2$ (*c* = 0.26, MeOH, immediately after preparation); $[\alpha]_D^{25}=-309.8$ (*c* = 0.26, MeOH, after 3 d); $[\alpha]_D^{25}=-296.5$ (*c* = 0.240, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25}=-304.2$ (*c* = 0.240, $CHCl_3$, after 3 d); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.30$ (br s, 1H; H-7), 8.03 (m, 2H, $^3J(^{119}Sn,^1H)=83.9$ Hz; H-*o*b), 7.75 (m, 2H, $^3J(^{119}Sn,^1H)=79.5$ Hz; H-*o*b), 7.56 (dd, $J_o=8.4$, 7.3 Hz, 1H; H-11), 7.45 (m, 3H; H-*m*a, H-*p*a), 7.35 (m, 3H; H-*m*b, H-*p*b), 7.22 (d, $J_o=7.7$ Hz, 1H; H-13), 7.16 (d, $J_o=8.4$ Hz, 1H; H-10), 6.81 (dd, $J_o=7.7$, 7.3 Hz, 1H; H-12), 4.05 (d, $J=4.0$ Hz, 1H; H-5), 1.92 (m, 1H; H-14), 1.59 (m, 1H; H-15a), 1.15 (m, 1H; H-15b), 0.89 (d, $J=6.6$ Hz, 3H; H-17), 0.80 (t, $J=7.0$ Hz, 3H; H-16); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=173.7$ (C-4), 173.2 (C-7), 169.9 (C-9), 138.7 (C-11), 138.2 (C-*i*a), 138.0 (C-*i*b), 137.0 (C-*o*a), 136.9 (C-*o*b), 135.7 (C-13), 131.2 (C-*p*a), 131.1 (C-*p*b), 129.4 (C-*m*a), 129.3 (C-*m*b), 123.3 (C-10), 118.4 (C-12), 117.7 (C-8), 73.5 (C-5), 43.0 (C-14), 26.0 (C-15), 15.6 (C-17), 12.2 (C-16); IR (KBr): $\tilde{\nu}=2952$, 2920, 2868, 2854, 1614, 1540, 1466, 1446, 522, 458 cm^{-1}; MS: *m*/*z* (%): 463 (83) [$M^+(^{120}Sn)-CO_2$], 461 (61) [$M^+(^{118}Sn)-CO_2$], 459 (33) [$M^+(^{116}Sn)-CO_2$], 434 (100), 432 (74), 431 (31), 386 (9), 384 (7), 382 (4), 303 (20), 301 (15), 299 (9), 167 (26), 154 (19), 86 (30); elemental analysis calcd (%) for $C_{25}H_{25}NO_3Sn$: C 59.32, H 4.98, N 2.77; found: C 59.44, H 5.03, N 2.84. Suitable crystals were obtained using a 1:1 mixture of hexane/dichloromethane.

2,2-Diphenyl-6-aza-1,3-dioxa-5-*n*-hexyl-2-stannabenzocyclononen-4-one (6g): Yellow solid, 92.7% yield; m.p. 133–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.31$ (br s, 1H; H-7), 7.99 (m, 2H, $^3J(^{119}Sn,^1H)=82.4$ Hz; H-*o*b), 7.82 (m, 2H, $^3J(^{119}Sn,^1H)=81.1$ Hz; H-*o*b), 7.56 (ddd, $J_o=8.7$, 8.2 Hz, $J_m=1.7$ Hz, 1H; H-11), 7.46 (m, 3H; H-*m*a, H-*p*a), 7.37 (m, 3H; H-*m*b, H-*p*b), 7.22 (dd, $J_o=7.9$ Hz, $J_m=1.7$ Hz, 1H; H-13), 7.17 (dd, $J_o=8.2$ Hz, $J_m=1.0$ Hz, 1H; H-10), 6.81 (ddd, $J_o=8.7$, 7.9 Hz, $J_m=1.0$ Hz, 1H; H-12), 4.17 (t, $J=5.7$ Hz, 1H; H-5), 1.88 (m, 2H; H-14), 1.16 (m, 2H; H-17), 1.08 (m, 2H; H-18), 0.96 (m, 2H; H-15), 0.75 (t, $J=6.8$ Hz, 3H; H-19); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta=173.8$ ($^2J(^{119}Sn,^{13}C)=15.2$ Hz; C-4), 172.4 (C-7), 169.4 ($^2J(^{119}Sn,^{13}C)=29.0$ Hz; C-9), 138.3 (C-11), 137.9 (C-*i*a), 137.7 (C-*i*b), 136.7 (C-*o*a), 136.5 (C-*o*b), 135.8 (C-13), 130.9 (C-*p*a), 130.8 (C-*p*b), 129.1 (C-*m*a), 128.9 (C-*m*b), 123.0 ($^3J(^{119}Sn,^{13}C)=6.6$ Hz; C-10), 118.0 (C-12), 117.4 ($^3J(^{119}Sn,^{13}C)=32.2$ Hz; C-8), 68.7 ($^2J(^{119}Sn,^{13}C)=15.0$ Hz; C-5), 36.2 (C-14), 31.3 (C-15), 28.9 (C-16), 24.7 (C-17), 22.3 (C-18), 14.1 (C-19); IR (KBr): $\tilde{\nu}=2956$, 2926, 2856, 2360, 2344, 2332, 1618, 1560, 1466, 1448, 558 cm^{-1}; MS: *m*/*z* (%): 491 (100) [$M^+(^{120}Sn)-CO_2$], 489 (73) [$M^+(^{118}Sn)-CO_2$], 487 (39) [$M^+(^{116}Sn)-CO_2$], 420 (89), 418 (68), 416 (39), 393 (23), 391 (18), 389 (10), 303 (28), 301 (22), 299 (13), 167 (21); elemental analysis calcd (%) for $C_{27}H_{31}NO_3Sn\cdot CH_2Cl_2$: C 54.32, H 5.05, N 2.26; found: C 54.40, H 5.12, N 2.29. Suitable crystals were obtained using a 4:1 mixture of hexane/dichloromethane.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-benzyl-2-stannabenzocyclononen-4-one (6h): Yellow solid, 90.8% yield; m.p. 194–196 °C; $[\alpha]_D^{25}=-437.2$ (*c* = 0.22, MeOH, immediately after preparation); $[\alpha]_D^{25}=-442.6$ (*c* = 0.22, MeOH, after 3 days); $[\alpha]_D^{25}=-485.4$ (*c* = 0.29, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25}=-496.3$ (*c* = 0.294, $CHCl_3$, after 3 d); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.99$ (m, 2H; H-*o*b), 7.83 (m, 2H; H-*o*a), 7.51 (m, 1H; H-11), 7.48 (m, 3H; H-*m*a, H-*p*a), 7.37 (m, 3H; H-*m*b, H-*p*b), 7.26 (br s, 1H; H-7), 7.13 (m, 2H; H-16), 7.12 (m, 2H; H-10, H-18), 6.93 (m, 2H; H-17), 6.72 (dd, $J_o=7.8$ Hz, $J_m=2.0$ Hz, 1H; H-13), 6.67 (dd, $J_o=7.8$, 7.1 Hz, $J_m=1.1$ Hz, 1H; H-12), 4.19 (dd, $J=10.3$, 3.4 Hz, 1H; H-5), 3.50 (dd, $J=13.7$, 3.4 Hz, 1H; H-14a), 2.71 (dd, $J=13.7$, 10.2 Hz, 1H; H-14b); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=173.2$ (C-4), 172.3 (C-7), 169.3 (C-9), 138.1 (C-11), 137.9 (C-*i*a), 137.5 (C-*i*b), 136.7 (C-*o*a), 136.4 (C-*o*b), 135.6 (C-13), 135.0 (C-15), 130.9 (C-*p*a), 130.8 (C-*p*b), 130.1 (C-17), 129.2 (C-*m*a), 129.0 (C-*m*b, C-16), 127.5 (C-18), 122.7 (C-10), 117.8 (C-12), 116.9 (C-8), 70.5 (C-5), 41.6 (C-14); IR (KBr): $\tilde{\nu}=2956$, 2924, 2870, 2852, 2670, 1616, 1540, 1470, 1444, 540 cm^{-1}; MS: *m*/*z* (%): 497 (100) [$M^+(^{120}Sn)-CO_2$], 495 (75) [$M^+(^{118}Sn)-CO_2$], 493 (40) [$M^+(^{116}Sn)-CO_2$], 420 (35), 418 (26), 416 (14), 393 (34), 391 (27), 389 (16), 303 (32), 301 (25), 299 (15), 167 (27), 132 (14); elemental analysis calcd. (%) for $C_{28}H_{23}NO_3Sn$: C 62.26, H 4.29, N 2.59;[33] found: C 62.47, H 4.33, N 2.71.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-(2-methylsulfanylethyl)-2-stannabenzocyclononen-4-one (6i): Yellow solid, 88.1% yield; m.p. 151–149 °C; $[\alpha]_D^{25}=-412.0$ (*c* = 0.26, MeOH, immediately after preparation); $[\alpha]_D^{25}=-412.0$ (*c* = 0.262, MeOH, after 3 d); $[\alpha]_D^{25}=-428.9$ (*c* = 0.266, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25}=-428.9$ (*c* = 0.266, $CHCl_3$, after 3 d); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.43$ (br s, 1H; H-7), 7.98 (m, 2H; H-*o*b), 7.81 (m, 2H; H-*o*a), 7.55 (ddd, $J_o=8.1$, 7.0 Hz, $J_m=1.7$ Hz, 1H; H-11), 7.45 (m, 3H; H-*m*a, H-*p*a), 7.35 (m, 3H; H-*m*b, H-*p*b), 7.22 (dd, $J_o=7.9$ Hz, $J_m=1.7$ Hz, 1H; H-13), 7.16 (dd, $J_o=8.1$ Hz, $J_m=1.0$ Hz, 1H; H-10), 6.79 (ddd, $J_o=7.9$, 7.0 Hz, $J_m=1.0$ Hz; 1H, H-12), 4.39 (dd, $J=6.9$, 5.5 Hz, 1H; H-5), 2.52 (m, 1H; H-15a), 2.35 (m, 1H; H-15b), 2.19 (m, 1H; H-14a), 2.07 (m, 1H; H-14b), 1.86 (s, 3H; H-16); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta=173.3$ ($^2J(^{119}Sn,^{13}C)=15.1$ Hz; C-4), 173.0 (C-7), 169.4 ($^2J(^{119}Sn,^{13}C)=29.4$ Hz; C-9), 138.4 (C-11), 137.8 (C-*i*a), 137.6 (C-*i*b), 136.5 (C-*o*a), 136.3 (C-*o*b), 135.9 (C-13), 130.9 (C-*p*a), 130.8 (C-*p*b), 129.1 (C-*m*a), 129.0 (C-*m*b), 122.9 (C-10), 118.0 (C-12), 117.3 ($^3J(^{119}Sn,^{13}C)=32.5$ Hz; C-8), 66.7 ($^2J(^{119}Sn,^{13}C)=16.2$ Hz; C-5), 34.6 (C-14), 29.3 (C-15), 15.1 (C-16); IR (KBr): $\tilde{\nu}=2958$, 2924, 1652, 1584, 1464, 1446, 604, 458 cm^{-1}; MS: *m*/*z* (%): 481 (24) [$M^+(^{120}Sn)-CO_2$], 479 (18) [$M^+(^{118}Sn)-CO_2$], 477 (10) [$M^+(^{116}Sn)-CO_2$], 451 (51), 449 (38), 447 (21), 420 (100), 418 (73), 416 (40), 197 (9), 195 (7), 193 (4); elemental analysis calcd for $C_{24}H_{23}NO_3SSn$: C 54.99, H 4.42, N 2.67;[33] found: C 55.18, H 4.61, N 2.69.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-(4′-hydroxybenzyl)-2-stannabenzocyclononen-4-one (6j): Yellow solid, 87.4% yield; m.p. 203–204 °C; $[\alpha]_D^{25}=-2.8$ (*c* = 0.18, MeOH, immediately after preparation); $[\alpha]_D^{25}=-1.5$ (*c* = 0.21, $CHCl_3$, immediately after preparation); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.34$ (br s, 1H; H-7), 7.92 (m, 2H; H-*o*b), 7.78 (m, 2H; H-*o*a), 7.48 (ddd, $J_o=8.4$, 8.1 Hz, $J_m=1.5$ Hz, 1H; H-11), 7.46 (m, 3H; H-*m*a, H-*p*a), 7.36 (m, 3H; H-*m*b, H-*p*b), 7.09 (d, $J_o=8.4$ Hz, 1H; H-10), 6.77 (dd, $J_o=8.1$ Hz, $J_m=1.5$ Hz, 1H; H-13), 6.75 (d, $J_o=8.4$ Hz, 2H; H-16), 6.67 (d, $J_o=8.1$ Hz, 1H; H-12), 6.65 (d, $J_o=8.4$ Hz, 2H; H-17), 4.13 (dd, $J=10.2$, 3.3 Hz, 1H; H-5), 3.35 (dd, $J=13.9$, 3.3 Hz, 1H; H-14a), 2.63 (dd, $J=13.9$, 10.3 Hz, 1H; H-14b); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta=174.2$ (C-4), 172.2 (C-7), 169.2 (C-9), 155.7 (C-18), 138.1 (C-11), 137.8 (C-*i*a), 137.2 (C-*i*b), 136.6 (C-*o*a), 136.3 (C-*o*b), 135.7 (C-13), 131.2 (C-16), 130.9 (C-*p*a), 130.8 (C-*p*b), 129.2 (C-*m*a), 129.0 (C-*m*b), 126.1 (C-15), 122.7 (C-10), 117.9 (C-12), 116.9 ($^3J(^{119}Sn,^{13}C)=27.7$ Hz; C-8), 116.0 (C-17), 70.6 (C-5), 40.9 (C-14); IR (KBr): $\tilde{\nu}=3198$ (OH), 2954, 2924, 2852, 1614, 1560, 1466, 1444, 588 cm^{-1}; MS: *m*/*z* (%): 513 (100) [$M^+(^{120}Sn)-CO_2$], 511 (74) [$M^+(^{118}Sn)-CO_2$], 509 (42) [$M^+(^{116}Sn)-CO_2$], 436 (40), 434 (31), 432 (17), 393 (39), 391 (31), 389 (16), 303 (42), 301 (34), 299 (23), 225 (15), 223 (9), 221 (1), 197 (12), 167 (40), 132 (39), 78 (73); elemental analysis calcd (%) for $C_{28}H_{25}NO_4Sn$: C 60.47, H 4.17, N 2.52; found: C 60.32, H 4.12, N 2.49.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-(indol-3-yl)-2-stannabenzocyclononen-4-one (6k): Yellow solid, 90.0% yield; m.p. 147–148 °C; $[\alpha]_D^{25}=-620.4$ (*c* = 0.26, MeOH, immediately after preparation); $[\alpha]_D^{25}=-605.5$ (*c* = 0.26, MeOH, after 3 d); $[\alpha]_D^{25}=-686.4$ (*c* = 0.257, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25}=-695.7$ (*c* = 0.257, $CHCl_3$, after 3 d); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=8.40$ (s, 1H; H-17), 7.94 (m, 2H; H-*o*b), 7.82 (m, 2H; H-*o*a), 7.51 (d, $J_o=8.0$ Hz, 1H; H-20), 7.44 (m, 1H; H-11), 7.46 (m, 4H; H-*m*a, H-*p*a, H-23), 7.36 (m, 3H; H-*m*b, H-*p*b), 7.28 (m, 1H; H-22), 7.08 (br s, 1H; H-7), 7.07 (m, 1H; H-21), 7.03 (m, 1H; H-10), 6.62 (m, 1H; H-16), 6.58 (dd, $J_o=7.9$, 7.0 Hz, 1H; H-12), 6.49 (dd, $J_o=7.9$, $J_m=1.5$ Hz, 1H; H-13), 4.26 (dd, $J=10.2$, 3.3 Hz, 1H; H-5), 3.68 (dd, m, $J=14.3$, 3.3 Hz, 1H; H-14a), 2.83 (dd, $J=14.3$, 10.2 Hz, 1H; H-14a); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=174.2$ ($^2J(^{119}Sn,^{13}C)=14.6$ Hz; C-4), 171.9 (C-7), 169.0 ($^2J(^{119}Sn,^{13}C)=29.4$ Hz; C-9), 138.1 (C-11), 137.9 (C-*i*a), 137.8 (C-*i*b), 136.6 (C-*o*a, C-18), 136.4 (C-*o*b), 135.5 (C-13), 130.9 (C-*p*a), 130.8 (C-*p*b), 129.2 (C-*m*a), 129.0 (C-*m*b), 126.5 (C-19), 125.0 (C-16), 122.6 (C-10, C-22), 120.1 (C-21), 118.5 (C-20), 117.7 (C-12), 116.9 ($^3J(^{119}Sn,^{13}C)=32.6$ Hz; C-8), 111.9 (C-23), 108.6 (C-15), 68.8 ($^2J(^{119}Sn,^{13}C)=15.8$ Hz; C-5), 32.1 (C-14); IR (KBr): $\tilde{\nu}=3348$ (NH), 2954, 2920, 2850, 1614, 1588, 1466, 1446, 554 cm^{-1}; MS: *m*/*z* (%): 580 (5) [$M^+(^{120}Sn)$], 578 (4) [$M^+(^{118}Sn)$], 576 (3) [$M^+(^{116}Sn)$], 536 (81) [$M^+(^{120}Sn)-CO_2$], 534 (61) [$M^+(^{118}Sn)-CO_2$], 532 (33) [$M^+(^{116}Sn)-CO_2$], 503 (57), 501 (42), 499 (24), 451 (92), 449 (68), 447 (38), 394 (69), 392 (56), 390 (32), 277 (34), 275 (27), 273 (16), 250 (20), 248 (15), 246 (9), 167 (17), 143 (22), 130 (100), 78 (20); elemental analysis calcd (%) for $C_{30}H_{26}N_2O_3Sn$: C 61.99, H 4.51, N 4.82; found: C 62.07, H 4.73, N 4.93.

(5*S*)-2,2-Diphenyl-6-aza-1,3-dioxa-5-phenyl-2-stannabenzocyclononen-4-one (6l): Yellow solid, 92% yield; m.p. 124 °C (subl.); $[\alpha]_D^{25} = -211.7$ ($c = 0.27$, MeOH, immediately after preparation); $[\alpha]_D^{25} = -4.0$ ($c = 0.273$, MeOH, after 3 d); $[\alpha]_D^{25} = -199.6$ ($c = 0.267$, $CHCl_3$, immediately after preparation); $[\alpha]_D^{25} = -201.9$ ($c = 0.267$, $CHCl_3$, after 3 d); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.28$ (br s, 1H; H-7), 7.99 (m, 2H, $^3J(^{119}Sn,^1H) = 78.8$ Hz; H-*o*a), 7.94 (m, 2H, $^3J(^{119}Sn,^1H) = 81.0$ Hz; H-*o*a), 7.56 (ddd, $J_o = 8.5$, 7.0 Hz, $J_m = 1.7$ Hz, 1H; H-11), 7.47 (m, 3H; H-*m*a, H-*p*a), 7.43 (m, 3H; H-*m*b, H-*p*b), 7.42 (m, 2H; H-15), 7.24 (m, 1H; H-17), 7.22 (m, 2H; H-16), 7.16 (d, $J_o = 8.5$ Hz, 1H; H-10), 7.07 (dd, $J_o = 7.8$ Hz, $J_m = 1.7$ Hz, 1H; H-13), 6.76 (dd, $J_o = 7.8$, 7.0 Hz, 1H; H-12), 5.20 (s, 1H; H-5); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 172.0$ ($^2J(^{119}Sn,^{13}C) = 16.6$ Hz; C-4), 174.8 (C-7), 169.6 ($^2J(^{119}Sn,^{13}C) = 29.8$ Hz; C-9), 138.7 (C-11), 138.1 (C-14), 138.0 (C-*i*a), 137.8 (C-*i*b), 136.7 (C-*o*a), 136.6 (C-*o*b), 136.2 (C-13), 131.0 (C-*p*a), 130.9 (C-*p*b), 129.3 (C-16), 129.1 (C-*m*a), 129.0 (C-*m*b), 128.7 (C-17), 127.9 (C-15), 122.9 (C-10), 118.0 (C-12), 117.5 ($^3J(^{119}Sn,^{13}C) = 32.0$ Hz; C-8), 71.0 ($^2J(^{119}Sn,^{13}C) = 16.1$ Hz; C-5); IR (KBr): $\tilde{\nu} = 2956$, 2920, 2850, 1618, 1560, 1468, 1446, 526 cm^{-1}; MS: *m*/*z* (%): 483 (100) [$M^+(^{120}Sn) - CO_2$], 481 (74) [$M^+(^{118}Sn) - CO_2$], 479 (40) [$M^+(^{116}Sn) - CO_2$], 406 (24), 404 (18), 402 (11), 303 (53), 301 (42), 299 (24), 167 (51); elemental analysis calcd (%) for $C_{27}H_{23}NO_3Sn$: C 61.64, H 4.02, N 2.66; found: C 61.88, H 4.10, N 2.66. Suitable crystals were obtained using a 1:1:2 mixture of hexane/dichloromethane/methanol.

X-ray structures of 5a, d, f, 6a, b, b-racemic, c, d, f, g and l: X-ray diffraction studies were performed on an Enraf-Nonius CAD4 diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å, graphite monochromator, $T = 293$ K, $\omega/2\theta$ scan mode) and an Enraf-Nonius FR590 Kappa-CCD diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å, graphite monochromator, $T = 293$ K, CCD rotating images). The crystals were mounted in Lindeman tubes. Absorption corrections were performed with SHELXS,[60] or by MULSCAN semi-empirical correction (PLATON)[61] procedures. The data were corrected for Lorentz and polarization effects. The SHELXS-97 program was applied for structure solution, while SHELXL-97 version 34 was used for refinement and data output;[60] both were applied in the WIN-GX program set,[62] and the corresponding molecular graphs were prepared with the ORTEP 3 program.[63] All non-hydrogen atoms were refined anisotropically. Some of the hydrogen atoms were determined by difference Fourier maps and these were refined with one overall isotopic thermal parameter; the remaining hydrogen atoms were geometrically modelled and calculated.

CCDC-189790 (**5a**), -160058 (**5d**), -189791 (**5f**), -189792 (**6a**), -189793 (**6b**), -189794 (**6b-racemic**), -189795 (**6c**), -189796 (**6d**), -189797 (**6f**), -189798 (**6g**), and -189799 (**6l**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Acknowledgement

Financial support and scholarships to H. I. Beltrán and L. S. Zamudio-Rivera from the Consejo Nacional de Ciencia y Teconología (CONACyT, México) are acknowledged. The authors would like to thank Q. F. I. Dolores Castillo for recording the IR spectra, Q. I. Victor González and Q. F. B. Ma. Luisa Rodríguez for recording the NMR spectra, Q. I. Geiser Cuellar for measuring the mass spectra, the IMP (Instituto Mexicano del Petróleo) for performing the elemental analyses, and Dra. Maria de Jesus Rosales Hoz and I. F. Marco Antonio Leyva for providing facilities and helpful information about CCDC software.

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Received: July 19, 2002
Revised: January 31, 2003 [F4260]

