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Dinuclear heptacoordinate dibutyltin (IV) complexes derived from Schiff bases and dicarboxylates: Synthesis, cytotoxicity, and antioxidant activity

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ABSTRACT

The synthesis of dinuclear dibutyltin (IV) complexes **1a**–**4d**, prepared in one pot by the reaction of 2-amino-4-R-phenol (R = H, Me, Cl, NO_2), 2-pyridinecarboxaldehyde, dicarboxylic (2,5-pyridinedicarboxylic, terephthalic, isophthalic, and oxalic) acids and dibutyltin oxides, is described. The complexes were characterized using IR, MS and ^{1}H, ^{13}C and ^{119}Sn NMR techniques. The molecular structures of complexes **1a**, **1c** and **4c** were established using X-Ray diffraction, and these complexes exhibited a distorted pentagonal-bipyramidal (BPT) geometry in which the equatorial plane consisted of three oxygen atoms and two nitrogen atoms, and the butyl groups occupied the axial positions. The cytotoxicity of the terephthalic acid derivatives **1a**–**d** in HCT-15 colon cancer, MCF7 breast cancer and PC3 prostate cancer cell lines was investigated *in vitro*. The antioxidant activity of these complexes was also measured using the DPPH (1,1-diphenyl-2-picrylhydrazyl) assay.

1. Introduction

Organotin(IV) complexes have been widely investigated because of their structural diversity and possible applications as cytotoxic, anti-inflammatory, antimicrobial, cardiovascular, insecticidal, and antifungal agents [1–5]. Several ligands have been reported to lead to a variety of complexes, including monomeric, dimeric, trimeric, tetrameric and polymeric complexes with different geometries and coordination modes [6–10]. Special attention has been devoted to Schiff Base ligands, which form organotin complexes with different structural arrangements and interesting biological activities [11-12]. Carboxylates are also important from the biochemical point of view due to their antiproliferative properties [13–17]. Additionally, numerous studies have been undertaken concerning the types of coordination geometries assumed by these complexes. Some examples of dinuclear organotin complexes are the molecular adducts of diorganotin dichloride with *N*-(2-oxidearylideneaminoacidato) [18] and the dinuclear diorganotin(IV) derivatives of pyruvic acid picolinoacylhydrazone, which exhibit supramolecular structures with 1D chains or 2D networks [19]. The Schiff base ligands containing an ONO donor system also afford dinuclear tin(IV) complexes with five- or six-coordinative geometries depending on the type of substituent bonded to the metal center [20], whereas bifunctional tridentate ligands form three classes of organotin(IV) complexes: diorganotin, triorganotin and dinuclear organotin derivatives [21]. Although a number of reports of this class of compounds have been described, few examples of dinuclear organotin complexes containing mixed ligands have been described. Thus, we recently reported the synthesis of a series of mononuclear organotin(IV) complexes with mixed ligand. In that study, we demonstrated that penta- or heptacoordinated complexes can be obtained depending on the reaction conditions and the stoichiometry [22]. As part of our interest in this type of complexes, in this report, we describe the synthesis of dinuclear heptacoordinated dibutyltin(IV) complexes containing mixed ligands and dicarboxylates. In an *in vitro* study, complexes **1a**–**d** exhibited varied antiproliferative activities against three cell lines. These complexes also exhibited antioxidant activity in the DPPH (1,1-diphenyl-2-picrylhydrazyl) assay; specifically, complexes **1b** (IC_{50} = 9.24 μM) and **1c** (IC_{50} = 9.24 μM) were more active than α-tocopherol (IC_{50} = 31.74 μM), which was used as a positive control.

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2. Results and discussion

The complexes were obtained in a one-step reaction from 2-pyridinecarboxaldehyde, 2-amino-4-R-phenol (R = H, CH_3, Cl, NO_2), di-*n*-butyltin(IV) oxide and the corresponding dicarboxylic acid in a 2:2:2:1 M ratio (Scheme 1). The compounds were isolated in yields ranging from 53 to 93%.

2.1. FTIR analysis

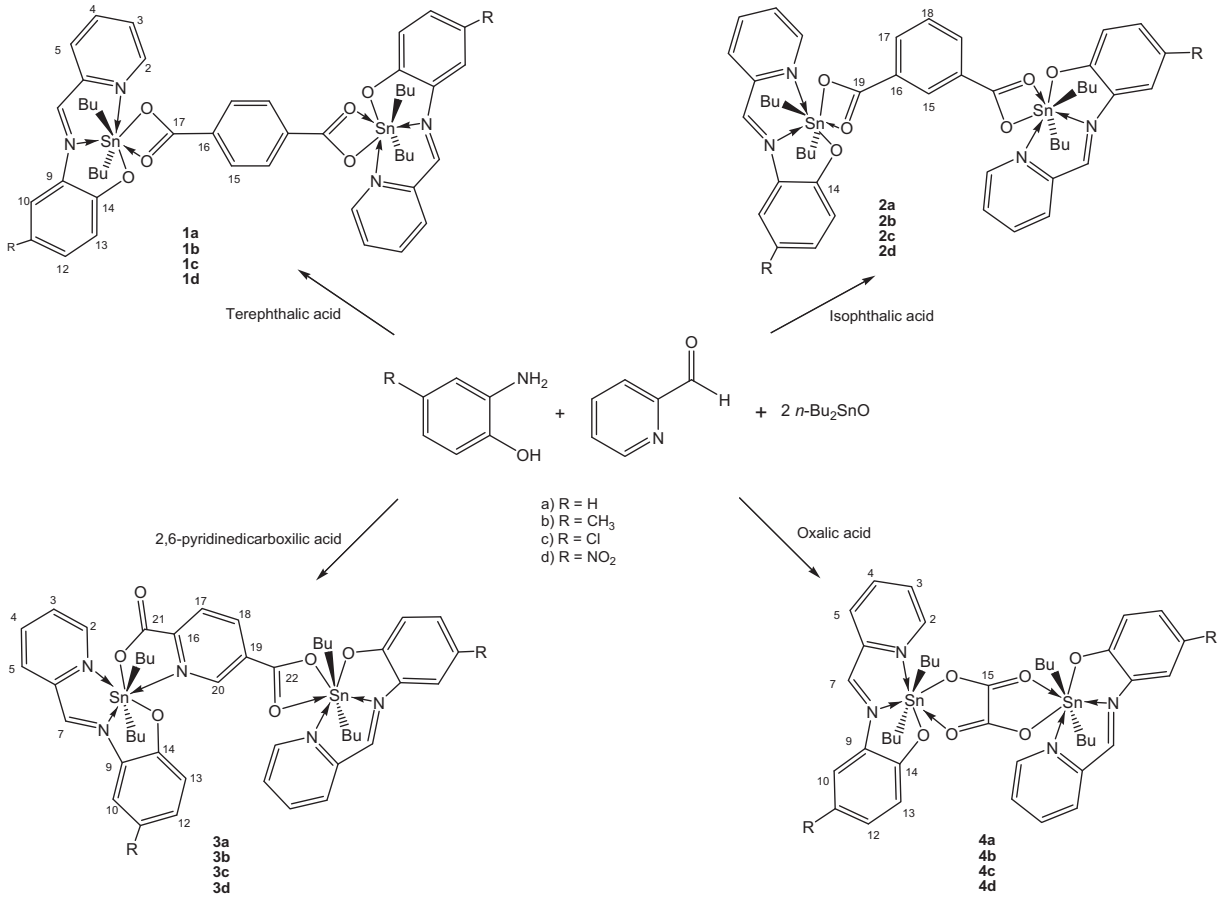
The infrared spectra (FTIR) of complexes **1a**–**4d** exhibited bands in the region of 1588–1612 cm^{-1} that were assigned to the C=N stretching vibrations of the different complexes. These bands are shifted to lower energies compared with the ν(N=C) stretch of the Schiff base ligand [12,22]. This shift has been attributed to the donation of the lone pair of the azomethine nitrogen to the tin atom [11]. The absence of the carboxylic acid and phenol OH groups resulted in the deprotonation of the ligand and the formation of a Sn–O bond. The spectra of complexes **1a**–**d** and **2a**–**d** exhibited two different absorption bands in the range of 1371 cm^{-1} to 1560 cm^{-1}, which correspond to the $\nu_{sym}(COO^-)$ and $\nu_{asym}(COO^-)$ vibrational modes of the carboxyl groups, respectively. The energy difference between the asymmetric and symmetric carboxylate stretching vibrations is in the range of 160–195 cm^{-1}, which is attributed to the formation of a chelating carboxylate with anisobidentate coordination (see Table 1) [23]. However, the spectra for the 2,5-pyridinedicarboxylic acid derivatives **3a**–**d** exhibited two different bands in the ranges of 1648 to 1607 and 1371–1345 cm^{-1} that were assigned to the $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ vibrations.

Table 1
Assignment of characteristic FT-IR vibrations (cm^{-1}).

Compound	ν_{asym}	ν_{sym}	$\delta\nu$
1a	1567	1372	195[a]
1b	1556	1387	169[a]
1c	1548	1369	179[a]
1d	1561	1400	161[a]
2a	1564	1379	185[a]
2b	1545	1381	164[a]
2c	1545	1379	166[a]
2d	1560	1387	173[a]
3a	1639	1345	294[b]
	1607	1373	234[a]
3b	1637	1346	291[b]
	1612	1371	241[a]
3c	1639	1347	291[b]
	1616	1373	243[a]
3d	1648	1355	293[b]
		1381	–
4a	1639	1459	180[c]
4b	1640	1467	173[c]
4c	1641	1460	181[c]
4d	1640	1489	151[c]

Carboxylate coordination mode (a) anisobidentate, (b) monodentate (c) bidentate.

The energy difference between the asymmetric and symmetric carboxylate stretching vibrations indicated that the carboxylates are coordinated to metal center in both the monodentate and anisobidentate coordination modes. These $\Delta\nu$ values are similar to those of the monomeric complex and the 2,5-pyridine tin carboxylates previously described, which verifies the presence of the two



Scheme 1.

coordination modes [6,7,22]. The spectra of the oxalic acid derivatives **4a**–**d** exhibit a $\nu_{asym}(COO^-)$ stretching frequency at approximately 1640 cm^{-1}, and the $\nu_{sym}(COO^-)$ mode appears in the range of 1459–1489 cm^{-1}, which is shifted to a higher energy relative to those observed for complexes **2a**–**3d**. The $\Delta\nu$ value (in the range of 170–180 cm^{-1}) and the band shift of $\nu_{sym}(COO^-)$ indicate that the carboxylate group coordinates to the metal center in a bidentate fashion [23] (Table 1).

2.2. Mass spectrometry (FAB^+)

The mass spectrometry data showed the molecular ions only for complexes **1a**–**c**, **2a**–**d**, **3a**,**3c**–**d**, and **4c** with a low relative abundance; however, for all complexes, the $[M - Bu]^+$ ion and the fragment ions corresponding to the subsequent loss of the butyl and the carboxylate groups $[M^+ - PyCOO^-]$ were also observed. The fragmentation pattern exhibited the characteristic natural isotopic profile in which ^{120}Sn is the most abundant isotope. To confirm the formation of the dinuclear complexes, a comparative analysis of the isotopic distribution of the $[M - 57 - 1]^+$ ion with the calculated isotopic patterns was performed, and a quantitative similitude was observed.

2.3. ^1H NMR

The ^1H NMR spectra of the dinuclear derivatives containing terephthalic and isophthalic acids exhibited signals corresponding to symmetrical species. The ^1H NMR spectra of the derivatives of terephthalic acid (**1a**–**d**) exhibited a single signal between 8.21 and 8.30 ppm corresponding to the aromatic hydrogen H-15. For the complexes containing isophthalic acid derivatives (**2a**–**d**), two doublets signals at approximately 9.1 and 7.5 ppm were detected for protons H-15 and H-18, respectively (the numbering followed in all molecules is indicated in the Supplementary material). The aliphatic region contained only one triplet signal corresponding to the methyl hydrogens of the butyl groups bonded to the tin atom because of the magnetic equivalence of these groups.

For complexes **3a**–**d**, the proton NMR spectra exhibited two groups of signals in the aromatic region for the two metal fragments due to the non-symmetry of 2,5-pyridinedicarboxylate. The chemical shifts for one of these groups of signals are similar to those of the monomeric species that were described previously, which strongly indicates the presence of a heptacoordinated tin heterocyclic ring species in which the carboxylate group is coordinated in a monodentate fashion [22]. In this case, the aliphatic region exhibited two triplet signals for the methyl hydrogens of the butyl groups attached to the metal, thus corroborating the presence of two different chemical environments around the tin atoms in the bimetallic complex. The complete assignment of the individual signals was performed based on the results of 2D experiments.

The ^1H NMR spectra of complexes **4a**–**c** exhibited only one triplet signal arising from the methyl hydrogens of the butyl groups bonded to the metal, as was observed for complexes **1a**–**2d**, thus confirming the symmetry in the molecule. Because complex **4d** was not soluble in common solvents, we were unable to characterize this complex using NMR spectroscopy.

2.4. ^{13}C NMR

The molecular symmetry of complexes **1a**–**2d** is also evident from the ^{13}C NMR spectra. For the terephthalic acid derivatives (**1a**–**1d**), three signals for the *ipso* carbon C-16, the *ortho* carbon C-15 and the carboxylate carbon C-17 were observed. In the case of complexes **2a**–**d**, the isophthalate moieties gave rise to four signals for the *ipso* (C-16), *ortho* (C-15 and C-17) and *meta* (C-18), carbons. All complexes exhibited four signals in the range of 13.4–32.6 ppm corresponding to the butyl groups. This result reveals that the two butyl moieties bonded to the tin atom are equivalent, as was observed in the proton NMR spectra. Thus, for complexes **1a**, **1b** and **2b**, it was also possible to measure the coupling constant $^1J(^{13}C–^{119/117}Sn)$ using these values, and the Lockhart equation [24] was used to calculate the C–Sn–C bond angles, which were determined to be 167.1, 166.2 and 168.9° for complexes **1a**, **1b** and **2b**, respectively.

As was observed for complexes **3a**–**d**, multiple signals for the ligand fragments coordinated to the metal were observed because of the presence of two different coordination modes for the 2,5-pyridinedicarboxylate fragment. Compounds **4a**–**d** exhibited signals for only half of the molecule.

2.5. ^{119}Sn NMR

Typical signals in the range of −347 to −367 ppm for heptacoordinated tin were observed in the ^{119}Sn NMR spectra of compounds **1a**–**2d**. However, in the case of compounds **3a**–**d**, two signals were observed, one in the range of −333 to −357 ppm and the other in the range of −414 to −441 ppm, indicating two different chemical environments around the tin atom. The first signal appears in the same region as those observed for the terephthalic and isophthalic derivatives, which allowed us to successfully assign the signals for each tin atom. For the oxalate derivatives **4a**–**c**, signals with chemical shifts between −413.6 and −415.6 were detected, and these signals are shifted to lower frequencies compared with those of compounds **1a**–**2d**, which strongly suggests a different coordination environment.

2.6. X-ray diffraction

The molecular structures of compounds **1a**, **1c** and **4c** were established using X-ray diffraction. The details of the crystallographic data and a summary of the data parameters for the three complexes are given in Table 2. Selected bond lengths are listed in Table 3, and bond angles were included as Supplementary material. The unit cell of **1c** consists of two halves of crystallographically independent but chemically equivalent molecules. An examination of the molecular structures of these compounds reveals that the two tin atoms are equivalent due to the presence of an inversion center in the molecule; the geometry is a distorted pentagonal bipyramid (BPT) (Figs. 1–3). The equatorial plane consists of three oxygen atoms from the phenoxide and the carboxylate groups, two nitrogen atoms from the azomethine and one nitrogen from the pyridine ring. The butyl groups occupy the axial positions and form a C–Sn–C angle of 167.2(1) to 170.6(3)°. These values are in agreement with those calculated from the NMR solution data (166.2–168.9°), indicating that the geometries of these species are similar. The atoms in the equatorial plane exhibit N(1)–Sn–N(2) and N(2)–Sn–(O1) angles in the range of 66.4–78.4°.

The Sn(1)–O(1) bond lengths are slightly shorter than the van der Waals radii, whereas the Sn–O(3) bond lengths are slightly longer than that found in complexes containing chelating carboxylates [25].The O → Sn bond distances in complexes **1a** and **1c** are 2.519(3) and 2.493(4)/2.528(4) Å, respectively; these values are similar to those of the complexes described in the literature that possess an O–Sn coordination bond [26]. The O → Sn bond length for **4c** (Sn(1)–O(3)) is 2.405(3), which is shorter than those of complexes **1a** and **1c**. This difference may be attributed to the formation of five-membered rings and the presence of a bidentate coordination mode of the carboxylate ligand, which is in contrast with that observed for compounds **1a** and **1c** in which the carboxylate forms four-membered rings, as evidenced from the IR spectra.

Table 2
Crystallographic data for compounds **1a**, **1c** and **4c**.

Complex	**1a**	**1c**	**4c**
Formula	$C_{48}H_{58}N_4O_6Sn_2$	$C_{48}H_{56}Cl_2N_4O_6Sn_2$	$C_{42}H_{52}Cl_2N_4O_6Sn_2$
Formula weight (g mol^{-1})	1024.36	1093.25	1017.16
Crystal size (mm)	0.392 × 0.154 × 0.126	0.204 × 0.108 × 0.044	0.35 × 0.22 × 0.18
Color	Red	Red	Red
Crystal system	Monoclinic	Triclinic	Trigonal
Space group	$P2_1/n$	*P*-1	*R*-3
a (Å)	10.003(1)	9.988(1)	25.3606(11)
b (Å)	18.985(2)	13.186(2)	25.3606(11)
c (Å)	12.273(1)	19.128(2)	20.6259(18)
α (o)	90°	98.760(2)	90°
β (o)	95.245(2)	93.039(2)	90°
γ (o)	90°	104.782(2)	120
V (Å^3)	2320.9(4)	2396.1(5)	11488.5(12)
Z	2	2	9
$D_{calc.}$ (g/cm^3)	1.466	1.449	1.323
No. of collected reflections	25,291	25,901	32,002
No. of independent reflections (R_{int})	4246 (0.0636)	8761 (0.0492)	4698 (0.0786)
No. of observed reflections	4246	8761	4698
No. of parameters	290	563	338
R^a	0.0305	0.0445	0.0464
$R_w{}^b$	0.0412	0.0593	0.0702
GOF	0.962	1.062	0.962

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $R_w(F_o)^2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

2.7. Cytotoxic studies

The cytotoxic activity of complexes **1a**–**d** was assessed using three tumor cell lines. Table 4 shows the IC_{50} values using HCT-15 colon cancer, MCF7 breast cancer and PC3 prostate cancer cell lines. All of the complexes exhibited higher cytotoxicity than the positive control did. In the MCF7 cell line, compound **1c** was shown to be more cytotoxic than complexes **1a**, **1b**, and **1d** were. In the PC3 cell line, compounds **1a** and **1b** exhibited the poorest cytotoxic properties. A substantial improvement is evident with complex **1d**, which exhibited an IC_{50} value in the micromolar range; thus, complex **1d** is approximately four orders of magnitude more cytotoxic than compounds **1a** and **1b** are. In the HCT15 colon cancer cell line, complex **1d** exhibited better cytotoxicity than complexes **1a** and **1b** did, whereas complex **1a** exhibited lower cytotoxicity. It is evident that compound **1c** displayed higher values of cytotoxicity against MCF7 breast cancer cells than it did against the PC3 prostate and HCT15 colon cell lines, Apparently, the effect of the substituent on the aromatic rings plays a role in the inhibition mechanism, which has also been observed in the heptacoordinate tin compounds derived from pyridine Schiff bases [12]. Although the tested complexes **1a**–**d** exhibited higher cytotoxicity against MCF7 breast cancer cells they are less cytotoxic than the tetra-*n*-butyltin-bis-3,6-dioxaheptanoato and -bis,3,6,9-trioxadecanoato-distannoxane dimers previously described [15].

Table 3
Bond lengths (Å) and angles (°) for complexes **1a**, **1c** and **4c**.

Bond lengths	**1a**	**1c**	**4c**
Sn(1)–O(1)	2.106(2)	2.134(3)	2.162(3)
Sn(2)–O(4)		2.109(3)	
Sn(1)–N(2)	2.339(2)	2.347(3)	2.370(4)
Sn(2)–N(4)		2.356(3)	
Sn(1)–N(1)	2.519(3)	2.493(4)	2.539(4)
Sn(2)–N(3)		*2.528(4)*	
Sn(1)–O(2)	2.288(2)	2.479(3)	2.261(3)
Sn(2)–O(6)		2.571 (3)	
Sn(1)–O(3)	2.595(2)	2.303(3)	2.405(3)
Sn(2)–O(5)		2. 276(3	
Sn(1)–C(19)	2.129(3)	2.128(5)	2.117(6)
Sn(2)–C(45)		2.128(4)	
Sn(1)–C(15)	2.121(3)	2.128(4)	2.107(6)
Sn(2)–C(41)		2.141(4)	
N(2)–C(7)	1.273(3)	1.274(6)	1.281(5)
N(4)–C(33)		1.275(5)	
C(23)–O(2)	1.272(3)	1.253(5)	1.246(5)
C(49)–O(5)		1.272(5)	
C(23)–O(3)	1.247(3)	1.272(5)	
C(49)–O(6)		2.254(5)	

2.8. Antioxidant activity

The antioxidant activity of ligands L1–L4 and complexes **1a**–**d** against the stable free radical 1,1-diphenyl-2-picrylhydrazyl (DPPH) was investigated, as shown in Table 5. The reduction capability of the DPPH radicals was determined from the decrease in its absorbance at 517 nm, which can be induced by antioxidants [27]. The inhibitory effect of the ligands and their corresponding Sn(IV) complexes on OH increased with increases in the sample concentration. All of the complexes exhibited a stronger effect than the free ligands did. Complexes **1a**–**c** were also more active than were α-tocopherol and quercetin, which were used as positive controls. These results agree with those of previous studies [28,29] in which the metal center increased the antioxidant activity in comparison with the free ligand, as was observed for L1–L3 (Table 5). The nitro derivative **1d** did not exhibit activity; conversely, complex **1b** exhibited the highest activity.

3. Conclusions

Dinuclear heptacoordinated species with different crystal structures were obtained. This observation reveals that 2,5-pyridinedicarboxylates give rise to two coordination modes in the molecule. In this case, the preferred structure was observed to include a pyridine nitrogen coordinated to the metal center. The terephthalic and isophthalic acids gave rise to an anisobidentate coordination; however, the oxalic acid derivatives were coordinated in a bidentate mode. The cytotoxicity assay showed that all of the complexes display different antitumor activities against the tumor cells tested. Complex **1d** exhibited the highest cytotoxic activity against PC3 prostate and HCT15 colon cell lines; however, for the MCF7 breast cancer cells, complex **1b** exhibited the best cytotoxicity. The antioxidant activity experiments showed that these complexes possess high antioxidant activity that is capable of stabilizing a radical molecule. These complexes are also more active than are the ligands, indicating that the metal center increases the activity.

4. Experimental

2-Aminophenol, 2-amino-4-methylphenol, 2-amino-4-chlorophenol, 2-amino-4-nitrophenol, 2-pyridinecarboxaldehyde, oxalic acid, 2,5-pyridinedicarboxylic acid, terephthalic acid, isophthalic acid, and dibutyltin oxide were obtained from the Aldrich Chemical Co. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded using a JEOL Eclipse +300 instrument. The reported chemical shifts (ppm) are relative to $(CH_3)_4Si$, and the coupling constants are quoted in Hertz (Hz). The melting points were measured using a Fisher Johns apparatus and are uncorrected. The mass spectra were obtained using a JEOL JMS-AX505 HA mass spectrometer operating in positive mode. The elemental analysis was obtained using an Exeter Analytical CE-440 instrument. The IR spectra were recorded on a

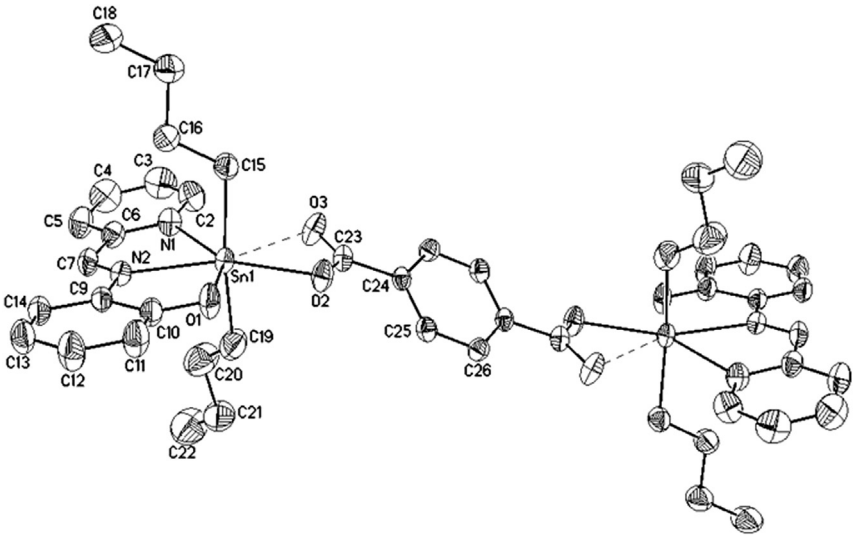


Fig. 1. Perspective view of the molecular structure of complex **1a**, ORTEP (Thermal ellipsoids at 30% of probability).

Bruker Tensor 27 instrument. The X-Ray crystallographic studies were performed using a Bruker Smart Apex CCD diffractometer with a $\lambda_{(Mo\text{-}K\alpha)} = 0.71073$ Å graphite monochromator at $T = 293$ K. All structures were solved using direct methods using a SHELXS [30] program, all non-hydrogen atoms were refined anisotropically using full-matrix, least squares techniques. All hydrogen atoms were placed in idealized positions based on the hybridization with thermal parameters fixed at 1.2 times (for −CH) and 1.5 times (for $-CH_3$) the value of the attached atom. The structure solutions and refinements were performed using SHELXTL v 6.10. [31]. Compound **4c** possesses disordered butyl groups, which were modeled in two and three major contributors. The ratio of the site occupational factor (SOF) for butyl groups was 0.66/0.44 and 0.43/0.35/0.22, respectively.

A cell culture assay for cytotoxicity activity was carried out as described previously [32].

4.1. Reduction of 2,2-diphenyl-1-picrylhydrazyl radical (DPPH)

A test was carried out on 96-well microplates. A 50 μL aliquot of the solution of the test compound was mixed with 150 μL of an ethanolic solution of DPPH (final concentration 100 μM). This mixture was incubated at 37 °C for 30 min, and the absorbance was then measured at 515 nm using a microplate reader ELx 808. The % inhibition of each compound was determined by comparison with a 100 μM DPPH ethanolic blank solution.

The ligands (L1–L4) that were used to compare the antioxidant activity with the corresponding complexes were prepared as follows.

The corresponding aminophenol and 2-pyridinecarboxaldehyde in a 1:1 ratio were added to a solution of 30 mL of ethanol for L1 or toluene for L2–L4. The reaction mixture was refluxed for 4 h for L1 and for 8 h for L2–L4. The solvent was then evaporated under low

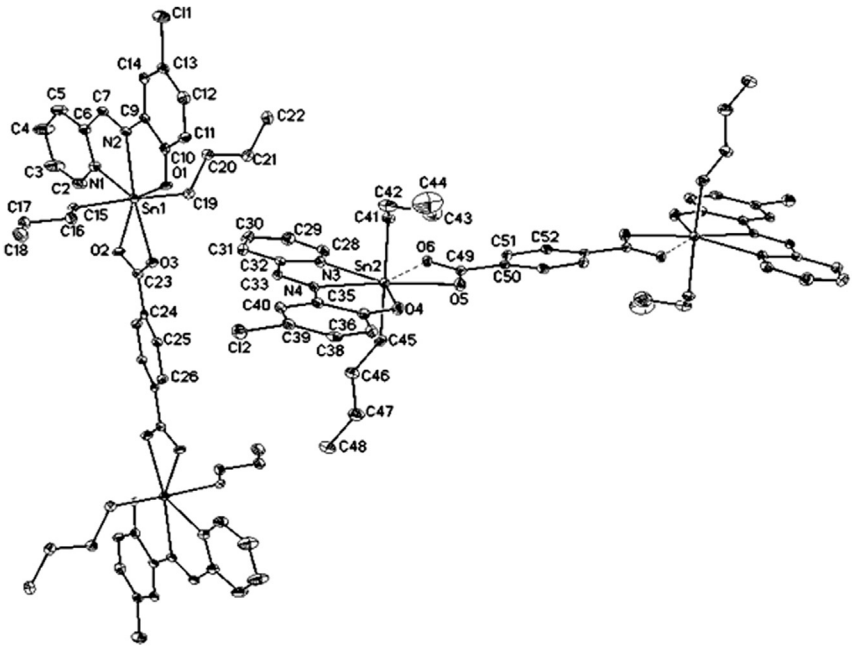


Fig. 2. Perspective view of the molecular structure of complex **1c**, ORTEP (Thermal ellipsoids at 30% of probability).

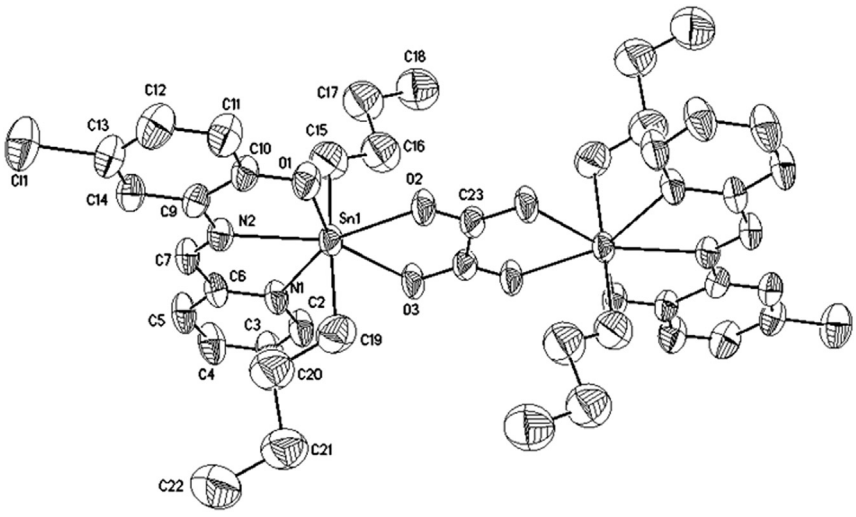


Fig. 3. Perspective view of the molecular structure of complex **4c** ORTEP (Thermal ellipsoids at 30% of probability, the minor component of the disordered butyl group was omitted for clarity).

pressure to yield yellow solids for L1, L3, L4 with melting points (m.p.) of 102–106 °C, 103–104 °C and 205–207°, respectively. A brown solid was obtained for L2 with a m.p. of 133–135 °C.

4.2. Complex ***1a***

To a solution of 0.2 mL (2.090 mmol) of 2-pyridinecarboxaldehyde in 30 mL of methanol, 0.228 g (2.090 mmol) of 2-aminophenol, 0.520 g (2.090 mmol) of di-*n*-butyltin(IV) oxide and 0.174 g (1.045 mmol) of terephthalic acid were added. The reaction mixture was refluxed for 4 h After cooling at room temperature, a precipitate was observed. This precipitate was then filtered to yield 0.996 g (0.975 mmol, 93% yield) of a red solid, m.p. 250 °C (dec); IR (KBr, cm^{-1}): 1567 ($\nu_{asym}CO_2$), 1372 ($\nu_{sym}CO_2$), 1586 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.60 (12H, t, J = 7.2 Hz, $Sn(CH_2)_2\underline{CH_3}$), 0.99–1.45 (24H, m, $Sn(\underline{CH_2})_3CH_2$), 6.68 (2H, ddd, J = 8.3, 7.0, 1.2 Hz, H-11), 7.19 (2H, dd, J = 8.5, 1.2 Hz, H-13), 7.31 (2H, ddd, J = 8.5, 7.0, 1.4 Hz, H-12), 7.54 (2H, dd, J = 8.3, 1.4 Hz, H-10), 7.61 (2H, ddd, J = 7.5, 5.0, 0.8 Hz, H-3), 7.79 (2H, d, J = 7.7 Hz, H-5), 8.04 (2H, ddd, J = 7.7, 7.5, 1.7 Hz, H-4), 8.30 (4H, s, H-15), 8.78 (2H, s, H-7), 9.25 (2H, d, J = 5.0 Hz, H-2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.6 (C-δ), 26.3 (C-γ), 27.6 (C-β), 31.8 ($^1J^{119Sn/117Sn-13C}$ = 1030/975 Hz, C-α), 115.9 (C-10), 116.0 (C-13), 122.4 (C-11), 126.2 (C-3), 126.7 (C-5), 129.7 (C-15), 130.3 (C-9), 133.6 (C-12), 136.3 (C-16), 139.1 (C-4), 142.7 (C-7), 148.6 (C-6), 149.7 (C-2), 164.3 (C-14), 175.5 (C-17); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −347.7; MS (FAB^+) [m/z] (%): [M^+, 1026] (1); [$(M - Bu)^+$, 969] (15), [431] (100); Anal. Calc. for $C_{48}H_{58}O_6N_4Sn_2$: C 56.28, H 5.71, N 5.47, Found: C 56.05, H 5.65, N 5.48.

4.3. Complex ***1b***

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde and 0.129 g (1.045 mmol) of 2-amino-4-methylphenol in 15 mL of methanol, 0.261 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.086 g (0.523 mmol) of terephthalic acid were added. The reaction mixture was stirred at room temperature for 1 h until a precipitate was observed. The mixture was then filtered to give 0.4502 g (0.427 mmol, 82% yield) of a red solid, m.p. 230 °C (dec); IR (KBr, cm^{-1}): 1556 ($\nu_{asym}CO_2$), 1387 ($\nu_{sym}CO_2$), 1598 (νC=N); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.60 (12H, t, J = 7.2 Hz, $Sn(CH_2)_3\underline{CH_3}$), 0.97–1.50 (24H, m, $Sn(\underline{CH_2})_3CH_3$), 2.30 (6H, s, CH_3), 6.95 (2H, d, J = 8.5 Hz, H-13), 7.14 (2H, dd, J = 8.5, 1.7 Hz, H-12), 7.40 (2H, s, H-10), 7.58 (2H, ddd, J = 7.6, 5.0, 1.0 Hz, H-3), 7.84 (2H, d, J = 7.7 Hz, H-5), 8.04 (2H, ddd, J = 7.7, 7.6, 1.5 Hz, H-4), 8.21 (4H, s, H-15), 8.83 (2H, s, H-7), 9.21 (2H, d, J = 5.0 Hz, H-2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 13.6 (C-δ), 20.7 (CH_3), 26.6 (C-γ), 27.9 (C-β), 32.0 ($^1J^{119Sn/117Sn-13C}$ = 1020/965 Hz, C-α), 116.3 (C-10), 121.5 (C-13), 125.6 (C-11), 126.9 (C-3), 127.2 (C-5), 129.7 (C-15), 130.1 (C-9), 135.1 (C-12), 136.9 (C-16), 139.6 (C-4), 143.3 (C-7), 148.8 (C-6), 149.7 (C-2), 162.4 (C-14), 175.1 (C-17); ^{119}Sn NMR (CD_2Cl_2, 112 MHz) δ: −351.7; MS (FAB^+) [m/z] (%): [M^+, 1053] (2); [$(M - Bu)^+$, 997] (10), [445] (100); Anal. Calc. for $C_{50}H_{62}O_6N_4Sn_2$: C 57.06, H 5.94, N 5.32, Found: C 57.01, H 5.96, N 5.33.

4.4. Complex ***1c***

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.151 g (1.051 mmol) of 2-amino-4-chlorophenol, 0.261 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.087 g (0.523 mmol) of terephthalic acid were added. The reaction mixture was stirred for 2 h at room temperature until a precipitate was observed, which was then filtered to give 0.455 g (0.427 mmol, 80% yield) of a red solid, m.p. 214–217 °C; IR (KBr, cm^{-1}): 1548 ($\nu_{asym}CO_2$), 1369 ($\nu_{sym}CO_2$), 1591 (νC=N); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.68 (12H, t, J = 7.2 Hz, $Sn(CH_2)_3\underline{CH_3}$), 0.97–1.38 (24H, m, $(\underline{CH_2})_3CH_3$), 7.00 (2H, d, J = 9.0 Hz, H-13), 7.25 (2H, dd,

Table 4
IC_{50} μM of complexes **1a**–**d**.

Complex	PC3	HCT15	MCF-7
1a	8.6 ± 0.7	6.5 ± 0.7	4.3 ± 0.5
1b	3.3 ± 0.2	2.0 ± 0.2	0.7 ± 0.01
1c	7.1 ± 0.4	2.7 ± 0.2	3.7 ± 0.1
1d	2.6 ± 0.1	1.0 ± 0.1	1.5 ± 0.1
Cis-platin	15.90 ± 2.1	13.48 ± 0.7	25.8 ± 3.7

Table 5
Antioxidant activity IC_{50} μM of ligands L1-L4 and complexes **1a**–**d**.

Compound	IC_{50}(μM)	Complex	IC_{50}(μM)
L1	26.29 ± 2.89	**1a**	21.18 ± 2.68
L2	21.10 ± 2.37	**1b**	9.24 ± 1.12
L3	36.26 ± 2.59	**1c**	14.02 ± 3.14
L4	30.22 ± 0.72	**1d**	114.91 ± 20.04
Quercetine	10.89 ± 0.47		
α-tocopherol	31.74 ± 1.04		

J = 9.0, 2.4 Hz, H-12), 7.57 (2H, d, J = 2.4 Hz, H-10), 7.67 (2H, ddd, J = 7.8, 4.8, 0.9 Hz, H-3), 7.82 (2H, d, J = 7.8 Hz, H-5), 8.09 (2H, ddd, J = 7.8, 7.8, 1.5 Hz, H-4), 8.21 (4H, s, H-15), 8.80 (2H, s, H-7), 9.23 (2H, d, J = 4.8 Hz, H-2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 13.6 (C-δ), 26.6 (C-γ), 27.9 (C-β), 32.2 (C-α), 116.4 (C-10), 120.6 (C-11), 123.0 (C-13), 127.1 (C-3), 127.7 (C-5), 129.8 (C-15), 131.0 (C-9), 133.4 (C-12), 136.7 (C-16), 139.8 (C-4), 144.8 (C-7), 148.4 (C-6), 150.0 (C-2), 163.2 (C-14), 175.4 (C-17); ^{119}Sn NMR (CD_2Cl_2, 112 MHz) δ: −355.2; MS (FAB$^+$) [m/z] (%): [(M − H)$^+$, 1093] (2); [(M − Bu)$^+$, 1037] (10), [465] (100); Anal. Calc for $C_{48}H_{56}O_6N_4Sn_2Cl_2$: C 52.73, H 5.16, N 5.12, Found: C 52.09, H 5.15, N 4.95.

4.5. Complex **1d**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.162 g (1.05 mmol) of 2-amino-4-nitrophenol, 0.262 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.087 g (0.525 mmol) of terephthalic acid were added. The reaction mixture was stirred for 1 h 40 min until a precipitate was observed, which was then filtered to give 0.510 g (0.457 mmol, 87% yield) of a red solid, m.p. 217 °C; IR (KBr, cm^{-1}): 1561 ($\nu_{asym}CO_2$), 1400 ($\nu_{sym}CO_2$), 1590 (νC=N); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.61 (12H, t, J = 7.2 Hz, Sn(CH_2)$_3CH_3$), 0.99–1.38 (24H, m, Sn(CH_2)$_3CH_3$), 7.06 (2H, d, J = 9.4 Hz, H-13), 7.76 (2H, ddd, J = 7.7, 5.0, 0.9 Hz, H-3), 7.98 (2H, d, J = 7.7 Hz, H-5), 8.18 (2H, ddd, J = 7.7, 7.7, 1.5 Hz, H-4), 8.20 (2H, dd, J = 9.4, 2.6 Hz, H-12), 8.25 (4H, s, H-15), 8.60 (2H, d, J = 2.6 Hz, H-10), 9.06 (2H, s, H-7), 9.30 (2H, d, J = 5.0 Hz, H-2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 13.5 (C-δ), 26.5 (C-γ), 27.9 (C-β), 32.6 (C-α), 113.9 (C-13), 121.5 (C-12), 127.9 (C-3), 128.4 (C-5), 128.6 (C-10), 129.8 (C-9), 129.9 (C-15), 136.4 (C-11), 136.7 (C-16), 140.3 (C-4), 147.3 (C-7), 147.8 (C-6), 150.2 (C-2), 170.0 (C-14), 176.0 (C-17); ^{119}Sn NMR (CD_2Cl_2, 112 MHz) δ: −366.9; MS (FAB+) [m/z] (%): [(M − Bu − 1)+, 1058] (10), [476] (100); Anal. Calc. for $C_{48}H_{56}O_{10}N_6Sn_2$: C 51.73, H 5.06, N 7.54, Found: C 51.23, H 5.13, N 7.04.

4.6. Complex **2a**

To a solution of 0.2 mL (2.090 mmol) of 2-pyridinecarboxaldehyde in 30 mL of methanol, 0.228 g (2.090 mmol) of 2-aminophenol, 0.520 g (2.090 mmol) of di-*n*-butyltin(IV) oxide and 0.174 g (1.045 mmol) of isophthalic acid were added. The reaction mixture was refluxed for 1 h. After cooling at room temperature, a precipitate was observed, which was filtered to give 0.931 g (0.908 mmol, 87% yield) of an orange solid, m.p. 242–245 °C; IR (KBr, cm^{-1}): 1564 ($\nu_{asym}CO_2$), 1379 ($\nu_{sym}CO_2$), 1586 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.59 (12H, t, J = 7.2 Hz, Sn(CH_2)$_3$<u>CH_3</u>), 0.98–1.42 (24H, m, Sn(<u>CH_2</u>)$_3CH_3$), 6.67 (2H, ddd, J = 8.2, 7.0, 1.2 Hz, H-11), 7.18 (2H, dd, J = 8.4, 1.2 Hz, H-13), 7.31 (2H, ddd, J = 8.4, 7.0, 1.5 Hz, H-12), 7.50 (1H, d, J = 7.6 Hz, H-18), 7.54 (2H, dd, J = 8.2, 1.5 Hz, H-10), 7.64 (2H, ddd, J = 7.6, 5.0, 1.0 Hz, H-3), 7.81 (2H, d, J = 7.7 Hz, H-5), 8.06 (2H, ddd, J = 7.7, 7.6, 1.7 Hz, H-4), 8.39 (2H, dd, J = 7.6, 1.5 Hz, H-17), 8.80 (2H, s, H-7), 9.12 (1H, t, J = 1.5 Hz, H-15), 9.35 (2H, d, J = 5.0 Hz, H-2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.6 (C-δ), 26.3 (C-γ), 27.6 (C-β), 32.0 (C-α), 115.8 (C-10), 115.9 (C-13), 122.3 (C-11), 126.2 (C-3), 126.5 (C-5), 127.6 (C-18), 130.3 (C-15), 131.8 (C-9), 133.2 (C-12), 133.5 (C-16), 133.6 (C-17), 139.1 (C-4), 142.2 (C-7), 148.5 (C-6), 149.9 (C-2), 164.5 (C-14), 175.6 (C-19); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −347.7; MS (FAB$^+$) [m/z] (%): [M$^+$, 1026] (2); [(M − Bu − 1)$^+$, 968] (5), [431] (100); Anal. Calc for $C_{48}H_{58}O_6N_4Sn_2$: C 56.28, H 5.71, N 5.47, Found: C 55.95, H 5.61, N 5.45.

4.7. Complex **2b**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.129 g (1.045 mmol) of 2-amino-4-methylphenol, 0.262 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.086 g (0.523 mmol) of isophthalic acid were added. The reaction mixture was stirred for 1 h 30 min until a precipitate was observed. The mixture was then filtered to give 0.478 g (0.454 mmol, 87% yield) of a red solid, m.p. 226–230 °C; IR (KBr, cm^{-1}): 1545 ($\nu_{asym}CO_2$), 1381 ($\nu_{sym}CO_2$), 1604 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.59 (12H, t, J = 7.2 Hz, Sn(CH_2)$_3$<u>CH_3</u>), 0.97–1.42 (24H, m, Sn(<u>CH_2</u>)$_3CH_3$), 3.30 (6H, s, Ar–CH_3), 7.09 (2H, d, J = 8.7 Hz, H-13), 7.14 (2H, dd, J = 8.7, 1.5 Hz, H-12), 7.35 (2H, s, H-10), 7.50 (1H, d, J = 7.7 Hz, H-18), 7.62 (2H, dd, J = 7.5, 5.3 Hz, H-3), 7.81 (2H, d, J = 7.7 Hz, H-5), 8.06 (2H, ddd, J = 7.7, 7.5, 1.7 Hz, H-4), 8.39 (2H, dd, J = 7.7, 1.7 Hz, H-17), 8.78 (2H, s, H-7), 9.12 (1H, s, H-15), 9.32 (2H, d, J = 5.3 Hz, H-2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.4 (C-δ), 20.6 (CH_3), 26.2 (C-γ), 27.4 (C-β), 31.8 ($^1J^{119Sn/117Sn-13C}$ = 1045.3/1008.4 Hz, C-α), 115.7 (C-10), 121.8 (C-13), 125.0 (C-11), 125.9 (C-3), 126.4 (C-5), 127.5 (C-18), 129.6 (C-9), 131.7 (C-15), 133.1 (C-16), 133.5 (C-17), 134.9 (C-12), 139.1 (C-4), 141.7 (C-7), 148.5 (C-6), 149.7 (C-2), 162.4 (C-14), 175.4 (C-19); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −355.1; MS (FAB$^+$) [m/z] (%): [M$^+$, 1054] (1); [(M − Bu)$^+$, 997] (10), [445] (100); Anal. Calc. for $C_{50}H_{62}O_6N_4Sn_2$: C 57.06, H 5.94, N 5.32, Found: C 57.09, H 5.96, N 5.37.

4.8. Complex **2c**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.151 g (1.051 mmol) of 2-amino-4-chlorophenol, 0.261 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.087 g (0.523 mmol) of isophthalic acid were added. The reaction mixture was stirred for 45 min until a precipitate was observed. The mixture was then filtered to give 0.424 g (0.389 mmol, 74% yield) of a red solid, m.p. 207–212 °C; IR (KBr, cm^{-1}): 1545 ($\nu_{asym}CO_2$), 1379 ($\nu_{sym}CO_2$), 1600 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.60 (12H, t, J = 7.2 Hz, Sn(CH_2)$_3$<u>CH_3</u>), 1.01–1.41 (24H, m, Sn(<u>CH_2</u>)$_3CH_3$), 7.11 (2H, d, J = 9.0 Hz, H-13), 7.25 (2H, dd, J = 9.0, 2.5 Hz, H-12), 7.50 (1H, d, J = 7.8 Hz, H-18), 7.53 (2H, d, J = 2.7 Hz, H-10), 7.68 (2H, dd, J = 7.2, 5.1 Hz, H-3), 7.85 (2H, d, J = 7.8 Hz, H-5), 8.10 (2H, ddd, J = 7.8, 7.2, 1.5 Hz, H-4), 8.38 (2H, dd, J = 7.8, 1.5 Hz, H-17), 8.76 (2H, s, H-7), 9.10 (1H, s, H-15), 9.34 (2H, d, J = 5.1 Hz, H-2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 13.5 (C-δ), 26.2 (C-γ), 27.5 (C-β), 32.0 (C-α), 115.8 (C-10), 120.4 (C-11), 123.2 (C-13), 126.5 (C-3), 126.8 (C-5), 127.6 (C-18), 130.4 (C-15), 131.8 (C-9), 133.2 (C-16), 133.3 (C-12), 133.3 (C-17), 139.3 (C-4), 143.2 (C-7), 148.1 (C-6), 149.9 (C-2), 163.2 (C-14), 175.7 (C-19); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −357.8; MS (FAB$^+$) [m/z] (%): [(M + H)$^+$, 1095] (0.2); [(M − Bu)$^+$, 1037] (3), [465] (100); Anal. Calc. for $C_{48}H_{56}O_6N_4Sn_2Cl_2$: C 52.73, H 5.16, N 5.12, Found: C 52.03, H 5.17, N 4.91.

4.9. Complex **2d**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.162 g (1.05 mmol) of 2-amino-4-nitrophenol, 0.262 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.087 g (0.525 mmol) of isophthalic acid were added. The reaction mixture was stirred for 2 h until a precipitate was observed. The mixture was then filtered to give 0.473 g (0.424 mmol, 81% yield) of a red solid, m.p. 208–211 °C; IR (KBr, cm^{-1}): 1560 ($\nu_{asym}CO_2$), 1387 ($\nu_{sym}CO_2$), 1592 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.61 (12H, t, J = 7.2 Hz, Sn(CH_2)$_3CH_3$), 1.00–1.40 (24H, m, Sn(CH_2)$_3CH_3$), 7.16 (2H, d, J = 9.4 Hz, H-13), 7.56 (1H, d, J = 7.7 Hz, H-18), 7.80 (2H, ddd, J = 7.4, 5.1, 0.7 Hz, H-3), 8.04 (2H, d, J = 7.7 Hz, H-5), 8.22 (2H, ddd, J = 7.7, 7.4, 1.5 Hz, H-4), 8.23 (2H, dd, J = 9.4, 2.6 Hz, H-12), 8.42 (2H, dd, J = 7.7, 1.2 Hz, H-17), 8.65 (2H, d, J = 2.6 Hz, H-10), 9.09 (2H, s, H-7), 9.12 (1H, d, J = 1.2 Hz, H-15), 9.41 (2H, d, J = 5.1 Hz, H-2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.4 (C-δ), 26.1 (C-γ), 27.6 (C-β), 32.4 (C-α), 113.6 (C-13), 121.7 (C-12), 127.4 (C-18), 127.8 (C-3), 128.5 (C-5,10),

129.3 (C-15), 131.9 (C-9), 132.7 (C-16), 133.6 (C-17), 136.3 (C-11), 139.9 (C-4), 146.2 (C-7), 147.6 (C-6), 150.2 (C-2), 169.9 (C-14), 176.3 (C-19); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −369.3; MS (FAB+) [*m*/*z*] (%): [M^+, 1116] (1); [$(M - Bu - 1)^+$, 1058] (4), [476] (100); Anal. Calc. for $C_{48}H_{56}O_{10}N_6Sn_2$: C 51.73, H 5.06, N 7.54, Found: C 51.29, H 5.16, N 7.34.

4.10. Complex **3a**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 30 mL of methanol, 0.114 g (1.045 mmol) of 2-aminophenol, 0.260 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.090 g (0.582 mmol) of 2,5-pyridinedicarboxylic acid were added. The reaction mixture was refluxed for 1 h 30 min, which was followed by the distillation of 10 mL of solvent. After cooling at room temperature, a precipitate was observed, which was filtered to give 0.400 g (0.389 mmol, 74% yield) of an orange solid, m.p. 237–242 °C; IR (KBr, cm^{-1}): 1639, 1607 ($\nu_{asym}CO_2$), 1345, 1373 ($\nu_{sym}CO_2$), 1590 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.49 (6H, t, J = 7.1 Hz, $Sn(CH_2)_3\underline{CH_3}$), 0.62 (6H, t, J = 7.2 Hz, $Sn(CH_2)_3\underline{CH_3}$), 0.84–1.57 (24H, m, $Sn(\underline{CH_2})_3CH_3$), 6.64 (1H, ddd, J = 8.3, 6.9, 1.2 Hz, H-11), 6.71 (1H, ddd, J = 8.1, 7.2, 1.2 Hz, H-11′), 7.20 (1H, dd, J = 8.4, 1.2 Hz, H-13), 7.31 (1H, dd, J = 8.5, 1.2 Hz, H-13′), 7.32 (2H, ddd, J = 8.4, 6.9, 1.2 Hz, H-12), 7.34 (2H, ddd, J = 8.5, 7.2, 1.4 Hz, H-12′), 7.57 (1H, dd, J = 8.3, 1.5 Hz, H-10), 7.57 (1H, ddd, J = 7.3, 5.2, 1.1 Hz, H-3), 7.58 (1H, dd, J = 8.1, 1.4 Hz, H-10′), 7.67 (1H, ddd, J = 7.6, 4.9, 1.0 Hz, H-3′), 7.74 (1H, d, J = 7.6 Hz, H-5), 7.87 (1H, d, J = 7.8 Hz, H-5′), 8.04 (1H, ddd, J = 7.6, 7.3, 1.7 Hz, H-4), 8.10 (1H, ddd, J = 7.8, 7.6, 1.5 Hz, H-4′), 8.57 (1H, d, J = 7.8, H-17), 8.81 (1H, s, H-7), 8.82 (1H, dd, J = 7.8, 1.9 Hz, H-20), 8.88 (1H, s, H-7'b), 9.30 (1H, d, J = 5.2 Hz, H-2), 9.84 (1H, d, J = 4.9 Hz, H-2′), 10.34 (1H, s, H-15); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.4 (C-δ), 13.6 (C-δ), 26.2 (C-γ), 26.3 (C-γ), 27.5 (C-β), 27.8 (C-β), 31.6 (C-α), 32.6 (C-α), 114.9 (C-10), 116.0 (C-10′), 116.1 (C-13), 116.4 (C-13′), 122.2 (C-11), 122.5 (C-11′), 125.0 (C-17), 126.0 (C-3), 126.1 (C-3′), 126.5 (C-5), 126.9 (C-5′), 130.2 (C-9), 130.4 (C-9′), 132.6 (C-19), 133.1 (C-12), 133.8 (C-12′), 138.9 (C-4), 139.3 (C-4′), 141.2 (C-18), 142.1 (C-7), 143.2 (C-7′), 148.4 (C-6), 148.5 (C-6′), 149.6 (C-2), 150.0 (C-2′), 151.3 (C-20), 151.8 (C-16), 164.1 (C-14), 165.1 (C-14′), 166.9 (C-22), 172.7 (C-21); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −335.8, −440.7; MS (FAB$^+$) [*m*/*z*] (%): [M^+, 1027] (1); [$(M - Bu)^+$, 970] (5), [431] (100); Anal. Calc. for : $C_{47}H_{57}O_6N_5Sn_2$ C 55.05, H 5.60, N 6.83, Found: C 54.91, H 5.56, N 6.82.

4.11. Complex **3b**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.129 g (1.045 mmol) of 2-amino-4-methylphenol, 0.261 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.088 g (0.523 mmol) of 2,5-pyridinedicarboxylic acid were added. The reaction mixture was stirred for 1 h until a precipitate was observed. The mixture was then filtered to give 0.475 g (0.450 mmol, 91% yield) of a red solid, m.p. 242 °C (dec); IR (KBr, cm^{-1}): 1637, 1612 ($\nu_{asym}CO_2$), 1346, 1371 ($\nu_{sym}CO_2$), 1612 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.49 (6H, t, J = 7.1 Hz, $Sn(CH_2)_3\underline{CH_3}$), 0.61 (6H, t, J = 7.2 Hz, $Sn(CH_2)_3\underline{CH_3}$), 0.82–1.56 (24H, m, $Sn(\underline{CH_2})_3CH_3$), 2.32 (6H, s, Ar–$CH_3$), 7.12 (1H, d, J = 8.7 Hz, H-13), 7.15–7.20 (3H, m, H-13′, 12, 12′), 7.37 (1H, s, 10), 7.39 (1H, s, 10′), 7.55 (1H, ddd, J = 7.6, 5.2, 0.8 Hz, H-3), 7.64 (1H, dd, J = 6.9, 5.1 Hz, H-3′), 7.73 (1H, d, J = 7.7 Hz, H-5), 7.85 (1H, d, J = 7.7 Hz, H-5′), 7.99 (1H, ddd, J = 7.7, 7.6, 1.5 Hz, H-4), 8.09 (1H, ddd, J = 7.7, 6.9, 1.4 Hz, H-4′), 8.56 (1H, d, J = 8.0 Hz, H-17), 8.77 (1H, s, H-7), 8.81 (1H, dd, J = 8.0, 1.8 Hz, H-18), 8.85 (1H, s, H-7′), 9.28 (1H, d, J = 5.2 Hz, H-2), 9.83 (1H, d, J = 5.1 Hz, H-2′), 10.32 (1H, s, H-20); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.3 (C-δ), 13.4 (C-δ), 20.7 (CH_3), 26.1 (C-γ), 26.2 (C-γ), 27.4 (C-β), 27.6 (C-β), 31.3 (C-α), 32.4 (C-α), 115.7 (C-10), 115.9 (C-10′), 121.6 (C-13), 122.1 (C-13′), 124.0 (C-11), 124.8 (C-11′), 125.6 (C-17), 125.7 (C-3), 125.9 (C-3′), 126.2 (C-5), 126.7 (C-5′), 129.6 (C-9), 129.7 (C-9), 132.5 (C-19), 134.5 (C-12), 135.1 (C-12′), 138.8 (C-4), 139.2 (C-4′), 141.0 (C-7), 141.4 (C-7′), 148.4 (C-6), 148.5 (C-6′), 149.3 (C-2), 149.9 (C-2′), 151.1 (C-20), 151.7 (C-16), 162.0 (C-14), 163.0 (C-14′), 166.9 (C-22), 172.5 (C-121); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −333.2, −438.3; MS (FAB$^+$) [*m*/*z*] (%): [$(M - Bu)^+$, 998] (6), [445] (100); Anal. Calc. for $C_{49}H_{61}O_6N_5Sn_2$: C 55.87, H 5.84, N 6.65, Found: C 55.77, H 5.81, N 6.59.

4.12. Complex **3c**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.152 g (1.051 mmol) of 2-amino-4-chlorophenol, 0.262 g (1.045 mmol) of di-*n*-butyltin (IV) oxide and 0.088 g (0.523 mmol) of 2,5-pyridinedicarboxylic acid were added. The reaction mixture was stirred for 50 min until a precipitate was observed. The mixture was then filtered to give 0.404 g (0.370 mmol, 71% yield) of a red solid, m.p. 224–228 °C (dec); IR (KBr, cm^{-1}): 1639, 1616 ($\nu_{asym}CO_2$), 1347, 1373 ($\nu_{sym}CO_2$), 1590 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.49 (6H, t, J = 7.2 Hz, $Sn(CH_2)_3CH_3$), 0.62 (6H, t, J = 7.2 Hz, $Sn(CH_2)_3CH_3$), 0.8–1.6 (24H, m, $Sn(CH_2)_3CH_3$), 7.14 (1H, d, J = 9.3, Hz, H-13), 7.14 (1H, d, J = 9.3, Hz, H-13′), 7.25 (1H, dd, J = 9.3, 2.4 Hz, H-12′), 7.29 (1H, dd, J = 9.3, 2.6 Hz, H-12), 7.55 (1H, d, J = 2.4 Hz, H-10′), 7.57 (1H, d, J = 2.6 Hz, H-10), 7.67 (1H, dd, J = 6.6, 5.1 Hz, H-3′), 7.69 (1H, dd, J = 7.2, 4.8 Hz, H-3), 7.76 (1H, d, J = 7.5 Hz, H-5′), 7.89 (1H, d, J = 7.5 Hz, H-5), 8.03 (1H, ddd, J = 7.5, 6.6, 1.5 Hz, H-4′), 8.13 (1H, ddd, J = 7.5, 7.2, 1.5 Hz, H-4), 8.57 (1H, d, J = 8.1 Hz, H-18), 8.75 (1H, s, H-7′), 8.81 (1H, dd, J = 8.1,1.8 Hz, H-17), 8.82 (1H, s, H-7), 9.28 (1H, d, J = 4.8 Hz, H-2), 9.84 (1H, d, J = 5.1 Hz, H-2′), 10.28 (1H, s, H-20); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.5 (C-δ), 13.6 (C-δ), 26.2 (C-γ), 26.3 (C-γ), 27.6 (C-β), 27.8 (C-β), 31.6 (C-α), 32.7 (C-α), 115.0 (C-10), 116.0 (C-10′), 116.2 (C-13), 116.4 (C-13′), 122.2 (C-11), 122.5 (C-11′), 125.0 (C-17), 126.0 (C-3), 126.1 (C-3′), 126.5 (C-5), 126.9 (C-5′), 130.2 (C-9), 130.5 (C-9′), 132.6 (C-19), 133.1 (C-12), 133.8 (C-12′), 139.0 (C-4), 139.4 (C-4′), 141.2 (C-18), 142.1 (C-7), 143.2 (C-7′), 148.4 (C-6), 148.6 (C-6′), 149.6 (C-2), 150.0 (C-2′), 151.3 (C-20), 151.9 (C-16), 164.1 (C-14), 165.1 (C-14′), 166.9 (C-22), 172.7 (C-21); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −335.0, 439.8; MS (FAB+) [*m*/*z*] (%): [M^+, 1095] (2); [$(M - Bu)^+$, 1038] (10), [465] (100); Anal. Calc for $C_{47}H_{55}O_6N_5Sn_2Cl_2$: C 51.59, H 5.07, N 6.40, Found: C 51.02, H 5.05, N 6.07.

4.13. Complex **3d**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.162 g (1.05 mmol) of 2-amino-4-nitrophenol, 0.262 g (1.045 mmol) of di-*n*-butyltin (IV) oxide and 0.087 g (0.525 mmol) of 2,5-pyridinedicarboxylic acid were added. The reaction mixture was stirred for 1 h 40 min until a precipitate was observed. The mixture was then filtered to give 0.510 g (0.457 mmol, 87% yield) of a red solid, m.p. 217 °C (dec); IR (KBr, cm^{-1}): 1648 ($\nu_{asym}CO_2$), 1355, 1381 ($\nu_{sym}CO_2$), 1589 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.51 (6H, t, J = 6.9 Hz, $Sn(CH_2)_3CH_3$), 0.64 (6H, t, J = 7.2 Hz, $Sn(CH_2)_3CH_3$), 0.86–1.56 (24H, m, $Sn(CH_2)_3CH_3$), 7.17 (1H, d, J = 9.4 Hz, H-13), 7.21 (1H, d, J = 9.4 Hz, H-13′), 7.73 (1H, dd, J = 7.0, 5.4 Hz, H-3), 7.82 (1H, dd, J = 7.0, 5.1 Hz, H-3′), 7.98 (1H, d, J = 7.6 Hz, H-5), 8.14 (1H, d, J = 7.7 Hz, H-5′), 8.15 (1H, ddd, J = 7.6, 7.0, 1.5 Hz, H-4), 8.27 (1H, ddd, J = 7.7, 7.0, 1.5 Hz, H-4′), 8.28 (2H, dd, J = 9.4, 2.6 Hz, H-12), 8.62 (1H, d, J = 8.0 Hz, H-18), 8.68 (1H, d, J = 2.6 Hz, H-10), 8.73 (1H, d, J = 2.4 Hz, H-10′), 8.86 (1H, dd, J = 8.0, 1.9 Hz, H-17), 9.10 (1H, s, H-7), 9.22 (1H, s, H-7′), 9.37 (1H, d, J = 5.4 Hz, H-2), 9.89 (1H, d, J = 5.1 Hz, H-2′), 10.28 (1H, d, J = 1.9 Hz, H-20); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 12.9 (C-δ), 13.0 (C-δ), 25.4 (C-γ), 25.5 (C-γ), 27.0 (C-β), 27.1 (C-β), 31.5 (C-α), 32.1 (C-α), 114.0 (C-

13), 120.3 (C-12), 120.6 (C-12′), 124.5 (C-17), 126.8 (C-3), 127.3 (C-3), 127.3 (C-5), 127.4 (C-5′), 128.0 (C-10), 128.7 (C-10′), 129.3 (C-9), 129.5 (C-9′), 131.8 (C-19), 135.0 (C-11), 136.0 (C-11′), 139.6 (C-4), 140.0 (C-4′), 140.8 (C-18), 147.1 (C-7), 147.4 (C-7′), 148.5 (C-6), 148.8 (C-6′), 149.0 (C-2), 149.8 (C-2′), 150.1 (C-20), 151.0 (C-16), 165.6 (C-14), 168.7 (C-14′), 169.6 (C-22), 172.3 (C-21); ^{119}Sn NMR (DMSO-d_6, 112 MHz) δ: −356.8, −447.6; MS (FAB+) [m/z] (%): [M^+, 1117] (1); [(M − Bu − 1)$^+$, 1059] (7), [476] (100); Anal. Calc. for $C_{47}H_{55}O_{10}N_7Sn_2$: C 50.61, H 4.97, N 8.79, Found: C 50.01, H 5.00, N 8.49.

4.14. Complex **4a**

To a solution of 0.2 mL (2.090 mmol) of 2-pyridinecarboxaldehyde in 30 mL of methanol, 0.228 g (2.090 mmol) of 2-aminophenol, 0.520 g (2.090 mmol) of di-*n*-butyltin(IV) oxide and 0.094 g (1.045 mmol) of oxalic acid were added. The reaction mixture was stirred for 1 h until a precipitate was observed, and it was then filtered to give 0.920 g (0.968 mmol, 93% yield) of an orange solid, m.p. 253–257 °C (dec); IR (KBr, cm^{-1}): 1639 ($\nu_{asym}CO_2$), 1459 ($\nu_{sym}CO_2$), 1590 (νC=N); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.59 (6H, t, J = 7.2 Hz, Sn(CH_2)$_3$$\underline{CH_3}$), 0.97–1.30 (12H, m, Sn($\underline{CH_2}$)$_3$$CH_3$), 6.68 (1H, ddd, J = 8.2, 7.0, 1.2 Hz, H-11), 7.26 (1H, ddd, J = 8.4, 7.0, 1.4 Hz, H-12), 7.31 (1H, dd, J = 8.4, 1.2 Hz, H-13), 7.52 (1H, dd, J = 8.2, 1.4 Hz, H-10), 7.54 (1H, ddd, J = 7.5, 5.0, 1.0 Hz, H-3), 7.75 (1H, d, J = 7.7 Hz, H-5), 8.04 (1H, ddd, J = 7.7, 7.5, 1.7 Hz, H-4), 8.78 (1H, s, H-7), 9.63 (1H, d, J = 5.0 Hz, H-2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.5 (C-δ), 26.3 (C-γ), 27.9 (C-β), 31.8 (C-α), 115.3 (C-10), 115.9 (C-13), 122.4 (C-11), 126.1 (C-3), 126.4 (C-5), 130.4 (C-9), 133.3 (C-12), 138.9 (C-4), 142.8 (C-7), 148.6 (C-6), 150.9 (C-2), 164.9 (C-14), 169.9 (C-15); ^{119}Sn NMR ($CDCl_3$, 112 MHz) δ: −415.6; MS (FAB$^+$) [m/z] (%): [(M − Bu − 1)$^+$, 892] (3), [431] (100); Anal. Calc. for $C_{42}H_{54}O_6N_4Sn_2$: C 53.19, H 5.74, N 5.91, Found: C 51.43, H 5.65, N 5.60.

4.15. Complex **4b**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.130 g (1.045 mmol) of 2-amino-4-methylphenol, 0.262 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.048 g (0.523 mmol) of oxalic acid were added. The reaction mixture was stirred for 5 min until a precipitate was observed and then filtered. To separate the tin oxide from the remainder of the reaction mixture, the solid was dissolved in CH_2Cl_2 and filtered again. The solution was dried to yield 0.267 g (0.275 mmol, 53% yield) of a red solid, m.p. 265–268 °C; IR (KBr, cm^{-1}): 1640 ($\nu_{asym}CO_2$), 1467 ($\nu_{sym}CO_2$), 1604 (νC=N); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.61 (6H, t, J = 7.2 Hz, Sn(CH_2)$_3$$\underline{CH_3}$), 0.97–1.26 (12H, m, Sn($\underline{CH_2}$)$_3$$CH_3$), 2.30 (3H, s, Ar–$CH_3$), 6.90 (1H, d, J = 8.5 Hz, H-13), 7.11 (1H, dd, J = 8.5, 1.9 Hz, H-12), 7.36 (1H, d, J = 1.9 Hz, H-10), 7.59 (1H, ddd, J = 7.6, 5.1, 1.0 Hz, H-3), 7.78 (1H, d, J = 7.7 Hz, H-5), 8.04 (1H, ddd, J = 7.7, 7.6, 1.7 Hz, H-4), 8.79 (1H, s, H-7), 9.54 (1H, d, J = 5.1 Hz, H-2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 13.6 (C-δ), 20.7 (CH_3), 26.7 (C-γ), 28.2 (C-β), 32.3 (C-α), 116.1 (C-10), 121.7 (C-13), 124.8 (C-11), 126.4 (C-3), 126.9 (C-5), 130.6 (C-9), 134.8 (C-12), 139.2 (C-4), 143.2 (C-7), 149.0 (C-6), 150.8 (C-2), 163.2 (C-14), 167.2 (C-15); ^{119}Sn NMR (CD_2Cl_2, 112 MHz) δ: −413.6; MS (FAB$^+$) [m/z] (%): [(M − Bu)$^+$, 921] (0.5), [445] (100); Anal. Calc. for $C_{44}H_{58}O_6N_4Sn_2$: C 54.13, H 5.99, N 5.74, Found: C 54.52, H 6.09, N 5.70.

4.16. Complex **4c**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.151 g (1.051 mmol) of 2-amino-4-chlorophenol, 0.262 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.047 g (0.523 mmol) of oxalic acid were added. The reaction mixture was stirred for 1 h, and the solvent was then eliminated under vacuum. The solid was crystallized from CH_2Cl_2/Hexane to give 0.351 g (0.345 mmol, 66% yield) of an orange solid, m.p. 247–250 °C (dec); IR (KBr, cm^{-1}): 1641 ($\nu_{asym}CO_2$), 1460 ($\nu_{sym}CO_2$), 1588 (νC=N); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.61 (6H, t, J = 7.2 Hz, Sn(CH_2)$_3$$\underline{CH_3}$), 0.97–1.38 (12H, m, Sn($\underline{CH_2}$)$_3$$CH_3$), 7.00 (1H, d, J = 9.0 Hz, H-13), 7.25 (1H, dd, J = 9.0, 2.4 Hz, H-12), 7.57 (1H, d, J = 2.4 Hz, H-10), 7.67 (1H, ddd, J = 7.8, 4.8, 0.9 Hz, H-3), 7.82 (1H, d, J = 7.8 Hz, H-5), 8.09 (1H, ddd, J = 7.8, 7.8, 1.5 Hz, H-4), 8.80 (1H, s, H-7), 9.23 (1H, d, J = 4.8 Hz, H-2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ: 13.6 (C-δ), 26.6 (C-γ), 28.2 (C-β), 32.4 (C-α), 116.3 (C-10), 119.9 (C-11), 123.0 (C-13), 127.0 (C-3), 127.5 (C-5), 131.2 (C-9), 133.4 (C-12), 139.5 (C-4), 145.1 (C-7), 148.5 (C-6), 150.9 (C-2), 163.8 (C-14); ^{119}Sn NMR (CD_2Cl_2, 112 MHz) δ: −414.9; MS (FAB$^+$) [m/z] (%): [M^+, 1018] (0.2); [(M − Bu)$^+$, 961] (0.6), [465] (100); Anal. Calc. for $C_{42}H_{52}O_6N_4Sn_2Cl_2$: C 49.51, H 5.11, N 5.50, Found: C 51.54, H 5.30, N 5.34.

4.17. Complex **4d**

To a solution of 0.1 mL (1.045 mmol) of 2-pyridinecarboxaldehyde in 15 mL of methanol, 0.162 g (1.051 mmol) of 2-amino-4-nitrophenol, 0.262 g (1.045 mmol) of di-*n*-butyltin(IV) oxide and 0.047 g (0.525 mmol) of oxalic acid were added. The reaction mixture was stirred for 15 min until a precipitate was observed. The mixture was then filtered to give 0.400 g (0.345 mmol, 74% yield) of a yellow solid, m.p. 265 °C (dec); IR (KBr, cm^{-1}): 1640 ($\nu_{asym}CO_2$), 1489 ($\nu_{sym}CO_2$), 1588 (νC=N); MS (FAB$^+$) [m/z] (%): [(M − Bu − 1)$^+$, 982] (1), [476] (100); Anal. Calc. for $C_{42}H_{52}O_{10}N_6Sn_2$: C 48.58, H 5.05, N 8.09, Found: C 48.24, H 5.14, N 7.87.

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Appendix A. Supplementary material

CCDC 870877, 870878 and 870879 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.03.038.

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