4.1 INTRODUCTION

Hydrazides have long been of interest to structural chemists for their fascinating chemical features and their ability to form an important class of organic compounds with various applications in organic synthesis. For example, they are useful as starting materials for the synthesis of biologically active heterocycles [Wu *et al.,* 2005]. In the literature, a number of hydrazide Schiff base ligands such as (*E*)-*N*′-(3-chlorobenzylidene)isonicotinohydrazide [Qiu *et al.,* 2006], (*E*)-2-hydroxy-*N*′-(2-naphthylmethylene)benzohydrazide [Qiu *et al.,* 2006b], (*E*)-2-hydroxy-*N*′-[1-(4-methoxyphenyl)ethylidene]benzohydrazide [Qiu *et al.,* 2006c], (*E*)-*N*′-(4-hydroxybenzylidene)benzohydrazide monohydrate [Tai *et al.,* 2007], 4-chloro-*N*′-[(*Z*)-4-(dimethylamino)benzylidene]benzohydrazide monohydrate [Fun *et al.,* 2008], *N'*-[(*E*)-4-bromobenzylidene]-2-(4-isobutylphenyl)propanohydrazide [Fun *et al.,* 2009a] and *N*'-[(*E*)-4-chlorobenzylidene]-2-(4-isobutylphenyl)propanohydrazide [Fun *et al.,* 2009b] have been reported. The molecular structures of these hydrazide ligands are generally stabilized by the presence of both intramolecular and intermolecular O-H….N hydrogen bonding in their structures.

Due to the presence of more than two potential donor sites, the metal complexes of these hydrazone Schiff base ligands have been widely studied. The ligands may coordinate to the metal centre either in the 'keto' or 'enol' form. The coordination of hydrazone Schiff base ligands may involve the nitrogen or oxygen electron-donating atoms, allowing it to act as a multidentate ligand and in some cases, general supramolecular bridging building blocks in their molecular assemblies. In the field of bioinorganic chemistry, many hydrazone ligands have been screened and tested as biologically important species. For example, the interest in salicylaldehyde benzoylhydrazone began when the Schiff base ligand was reported to have mild

bacteriostatic activity. Since then, several substituted salicylaldehyde derivatives of benzoylhydrazone and their metal complexes have been prepared and were tested for various biological activities [Chan *et al.,* 1995, Koh *et al.,* 1998, Ainscough *et al.,* 1995, Ainscough *et al.,* 1999].

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This chapter focuses on the chemistry of diorganotin complexes with tridentate *ONO*- donor Schiff base ligands and a -C=N-N=C- chain in their structures. The precursor compounds used in the preparation of the Schiff base ligand of 3-hydroxy-2-naphthoic hydrazide were salicylaldehydes, substituted salicylaldehydes, 2-hydroxyacetophenone, substituted 2-hydroxyacetophenone, thiosemicarbazides and substituted thiosemicarbazides. Some of the resulting Schiff base ligands were reported to have good antimicrobial activities [Dogan *et al.,* 1998a, Dogan *et al.,* 1998b]. The transition metal complexes of these Schiff base ligands had also been synthesized and had been reported to have good biological activities [Mohd. Ali *et al.,* 2004a, Mohd. Ali *et al.,* 2004b, Pawanoji and Mehta 2009].

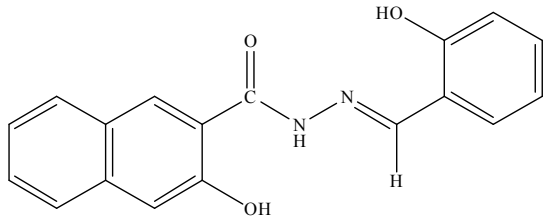
4.2 SYNTHESIS

The following commercial chemicals of reagent grade were used in the synthesis: dimethyltin dichloride, dibutyltin dichloride, diphenyltin dichloride, 3-jhydroxy-2-naphthoic hydrazide, salicylaldehyde, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, 5-nitro-2-hydroxybenzaldehyde, 5-bromo-3-methoxy-2-hydroxybenzaldehyde, 5-bromo-2-hydroxyacetophenone, 5-chloro-2-hydroxyacetophenone, 2-hydroxyacetophenone and triethylamine. Some of the diorganotin starting materials prepared were: dicyclohexyltin dichloride, dicyclohexyltin oxide, dibenzyltin dichloride, di(*o*-chlorobenzyl)tin dichloride and di(*p*-chlorobenzyl)tin dichloride.

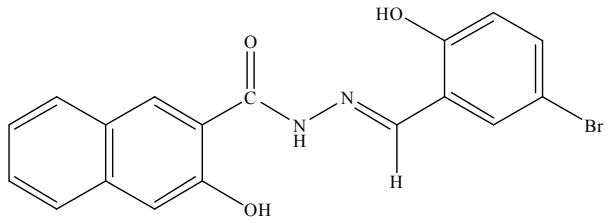
The solvents used in the preparation of the Schiff base ligands and their diorganotin complexes were toluene, absolute ethanol, methanol, chloroform, dichloromethane and hexane. These solvents were distilled before use. The expected structural formulae for the Schiff base ligands are listed in figure 4.1.1

Figure 4.1.1
Structural formula for the NAP Schiff base ligands

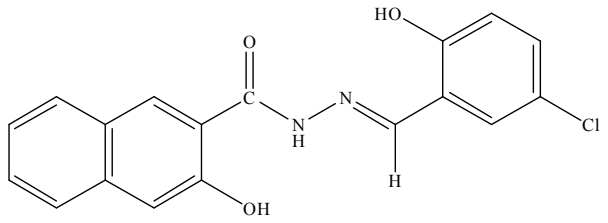
N'-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA**



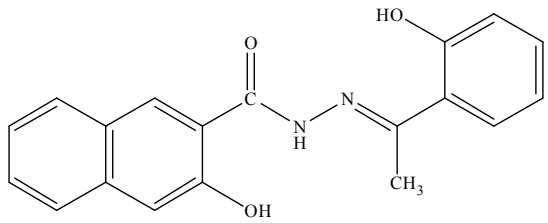
N'-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB**



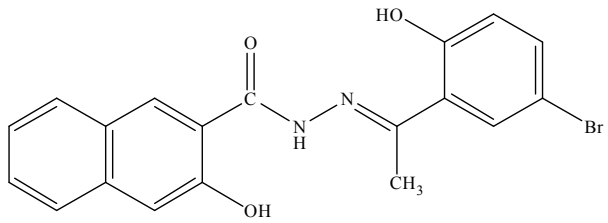
N'-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC**



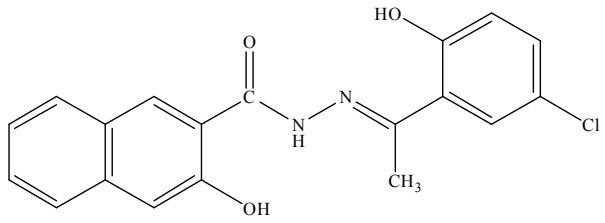
N'-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HD**



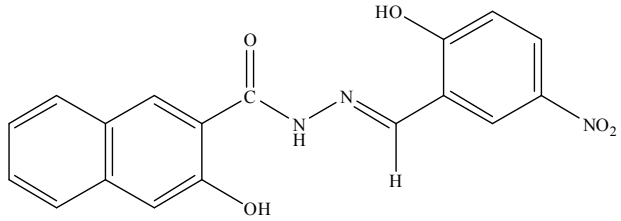
N'-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HE**



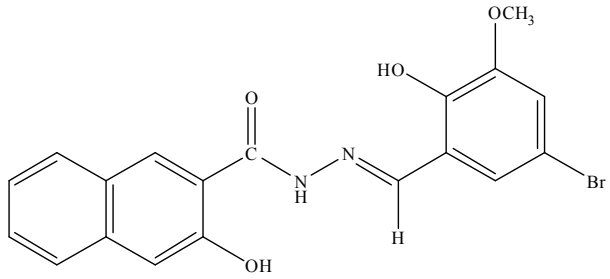
N'-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HF**



N'-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG**



N'-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HH**



4.2.1 Preparation of Ligands

Preparation of N'-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA**

3-Hydroxy-2-naphthoic hydrazide (2.03 g, 0.01 mol) was dissolved in methanol and salicylaldehyde (1.1 mL, 0.01 mol) was slowly added to the solution. The mixture was refluxed for 2 hours and the resulting light yellow solution was filtered. The filtrate was left at room temperature during which light yellow crystals formed and were used without further purification. Yield: 2.67 g (87.0 %) ; m.p. 300-302^{o}C.

Preparation of N'-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB**

3-Hydroxy-2-naphthoic hydrazide (2.03 g, 0.01 mol) and 5-bromosalicylaldehyde (2.05 g, 0.01 mol) were dissolved in methanol and mixed together. The mixture was refluxed for 2 hours and filtered. The filtrate was left at room temperature during which a light yellow solid formed. The ligand was used without further purification. Yield: 3.00 g (77.9 %) ; m.p. 316-318^{o}C.

Preparation of N'-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC**

3-Hydroxy-2-naphthoic hydrazide (2.03 g, 0.01 mol) and 5-chlorosalicylaldehyde (1.57 g, 0.01 mol) were dissolved in 200 mL of methanol. The mixture was refluxed for 2 hours and a yellow solid formed upon cooling to room temperature. The solid was used without further purification. Yield: 2.93 g (86.0 %) ; m.p. 310-312^{o}C.

Preparation of N'-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HD**

3-Hydroxy-2-naphthoic hydrazide (2.03 g, 0.01 mol) was dissolved in methanol and 2-hydroxyacetophenone (1.1 mL, 0.01 mol) was slowly added to the solution. The mixture was refluxed for 2 hours and the resulting light yellow solution was filtered. A light yellow solid formed when the filtrate was left at room temperature. The ligand was used without further purification. Yield: 2.67 g (87.0 %) ; m.p. 316-318^{o}C.

Preparation of N'-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphtho-hydrazide, **HE**

3-Hydroxy-2-naphthoic hydrazide (2.03 g, 0.01 mol) and 5-bromo-2-hydroxyacetophenone (2.15 g, 0.01 mol) were dissolved separately in methanol and mixed together. The solution was refluxed for 2 hours and the resulting beige-coloured solution was filtered. A light yellow solid formed after the filtrate was evaporated slowly. The ligand was used without further purification. Yield: 3.36 g (84.0 %) ; m.p. 210-214^{o}C.

Preparation of N'-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphtho-hydrazide, **HF**

3-Hydroxy-2-naphthoic hydrazide (2.03 g, 0.01 mol) and 5-chloro-2-hydroxyacetophenone (1.71 g, 0.01 mol) were dissolved in methanol, mixed and refluxed for 2 hours. The resulting light yellow solution was filtered whereby a light yellow solid formed upon cooling to room temperature and it was used without further purification. Yield: 3.03 g (85.4 %) ; m.p. 298-300^{o}C.

Preparation of N'-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG**

3-Hydroxy-2-naphthoic hydrazide (2.03 g, 0.01 mol) and 5-nitro-2-hydroxybenzaldehyde (1.67 g, 0.01 mol) were dissolved in 200 mL of methanol. The mixture was refluxed for 2 hours. A yellow solid formed upon cooling to room temperature and was used without further purification. Yield: 2.63 g (74.8 %) ; m.p. 324-326^{o}C.

Preparation of N'-(5-bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HH**

3-Hydroxy-2-naphthoic hydrazide (2.03 g, 0.01 mol) and 5-bromo-3-methoxy-2-hydroxybenzaldehyde (2.32 g, 0.01 mol) were dissolved separately in methanol, mixed together and refluxed for 2 hours. The resulting yellow solution was filtered and left at room temperature during which yellow solid formed. The ligand was used without further purification. Yield: 3.20 g (77.1 %) ; m.p. 288-290^{o}C.

4.2.2 Preparation of organotin complexes

Preparation of [N'-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HA1**

To a suspension of dimethyltin oxide (0.16 g, 1.0 mmol) in dry toluene (40 ml), the ligand **HA** (0.31 g, 1.0 mmol) was added. The mixture was heated under reflux in a Dean and Stark apparatus for 8 hours for azeotropic removal of water formed during the reaction. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was recrystallized from a 1:1 mixture of dichloromethane-hexane. Yield: 0.36 g (78.7 %) ; m.p. 232-234^{o}C.

Preparation of [N'-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HA2**

The ligand, **HA** (0.31 g, 1.0 mmol) and triethylamine (0.14 mL, 1.0 mmol) were added to 100 mL of absolute ethanol and the mixture was heated under reflux for 2 hours. Dibutyltin dichloride (0.30 g, 1.0 mmol) was then added and the mixture was further refluxed for 5 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.43 g (79.2 %) ; m.p. 110-112^{o}C

Preparation of [N'-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diphenyltin(IV), **HA3**

An ethanolic solution containing (0.31 g, 1.0 mmol) ligand **HA** was refluxed with triethylamine (0.14 mL, 1.0 mmol) for 2 hours. Then, an ethanolic solution containing (0.34 g, 1.0 mmol) diphenyltin dichloride was added to the mixture. The mixture was refluxed for another 6 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.44 g (76.9 %) ; m.p. 272-274^{o}C

Preparation of [N'-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HA4**

Dicyclohexyltin oxide (0.30 g, 1.0 mmol) was added to a hot toluene solution containing ligand **HA** (0.31 g, 1.0 mmol). The mixture was heated under reflux in a Dean and Stark apparatus for 8 hours for azeotropic removal of water formed in the reaction. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was recrystallized from a 1:1 mixture of dichloromethane-hexane to give yellow crystals. Yield: 0.43 g (73.2 %) ; m.p. 102-104^{o}C

Preparation of [N'-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibenzyltin(IV), **HA5**

The ligand, **HA** (0.31 g, 1.0 mmol) and triethylamine (0.14 mL, 1.0 mmol) were added to 100 mL of absolute ethanol and the mixture was heated under reflux for 2 hours. Dibenzyltin dichloride (0.37 g, 1.0 mmol) was added into the mixture and was further refluxed for 5 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.41 g (67.1 %) ; m.p. >350^{o}C

Preparation of [N'-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(o-chlorobenzyl)tin(IV), **HA6**

An excess amount of triethylamine (0.14 mL, 1.0 mmol) was added to a ethanolic solution containing ligand **HA** (0.31 g, 1.0 mmol) and refluxed for 2 hours. Next, an ethanolic solution containing (0.44 g, 1.0 mmol) di(*o*-chlorobenzyl)tin

dichloride was added to the mixture, refluxed for 6 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.46 g (67.9 %) ; m.p. 180-182^{o}C

Preparation of [N'-(2-oxidobenzylidene]-3-hydroxy-2-naphthohydrazidato]di(p-chlorobenzyl)tin(IV), **HA7**

An ethanolic solution containing ligand **HA** (0.31 g, 1.0 mmol) was refluxed with triethylamine (0.14 mL, 1.0 mmol) for 2 hours. Next, an ethanolic solution containing di(*p*-chlorobenzyl)tin dichloride (0.44 g, 1.0 mmol) was added to the mixture, refluxed for 6 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.44 g (65.1 %) ; m.p. 139-140^{o}C

The other complexes were prepared with the same procedure as described for the complexes (**HA1**-**HA7**). The yields and melting points of the complexes were tabulated in table 4.3.2.

4.2.3 Physical measurement of the Schiff base ligands and organotin complexes

The melting points of the compounds were determined on an 'Electrothermal' digital melting point apparatus and were uncorrected. Elemental analyses of the complexes were carried out on a Perkin-Elmer EA2400 CHNS Elemental Analyzer in the University of Malaya.

The infrared spectra for the compounds were recorded in the region 400-4000 cm^{-1} with a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and a Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer. The samples were prepared as nujol mulls or KBr pellets. The UV spectra for the ligands and organotin complexes were recorded using a Shimadzu UV-PC1601 UV-visible spectrophotometer in the wavelength range of 190 to 600 nm.

The ^{1}H and ^{13}C NMR spectra for the ligands were recorded in deuterated DMSO at ambient temperature on a JEOL JNM-GSX270 FT NMR SYSTEM spectrometer operating at 270.05 MHz for ^{1}H NMR and 67.80 MHz for ^{13}C NMR. The ^{119}Sn NMR spectra were recorded on a JEOL ECA-400MHz. The chemical shifts were recorded in ppm with reference to Me_4Si for ^{1}H NMR, DMSO for ^{13}C NMR and Me_4Sn for ^{119}Sn NMR. The ^{1}H and ^{13}C NMR spectra were recorded for most ligands and complexes due to their poor solubility in various deuterated solvents. The ^{1}H and ^{13}C NMR spectra of some of the complexes in DMSO gave poor spectra and hence assignment of peaks was not satisfactory.

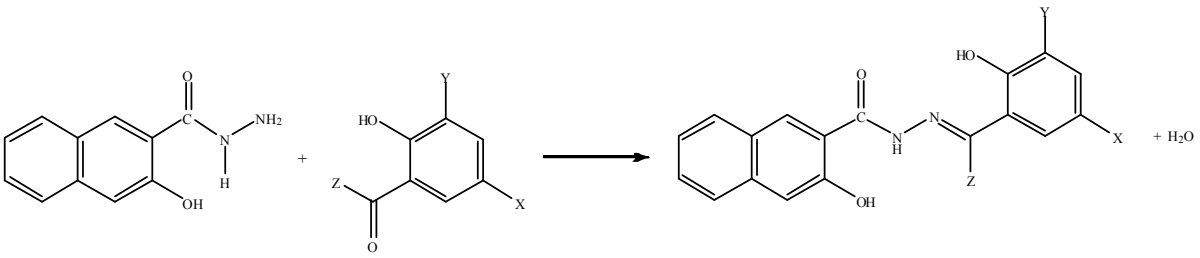
The X-ray crystallographic intensity data were measured using Mo-K_α radiation graphite-crystal monochromator (λ= 0.71073Å) radiation on a Bruker SMART APEX2 CCD diffractometer in University of Malaya. The structure of the compounds were solved by the direct method and refined by the full-matrix least-squares procedure based on F^2 using the SHELXL programme. Supplementary data including observed and calculated structure factors for the complexes are available from the author on request.

4.3 RESULTS AND DISCUSSION

4.3.1 Analytical Data

A total of eight hydrazone Schiff base ligands were prepared from the reactions of 1:1 mole ratio of the 3-hydroxy-2-naphthoic hydrazide with salicylaldehyde, substituted salicylaldehyde, 2-hydroxyacetophenone or substituted 2-hydroxyacetophenone. A general reaction scheme of the preparation of the Schiff base ligands is shown in scheme 4.3.1.

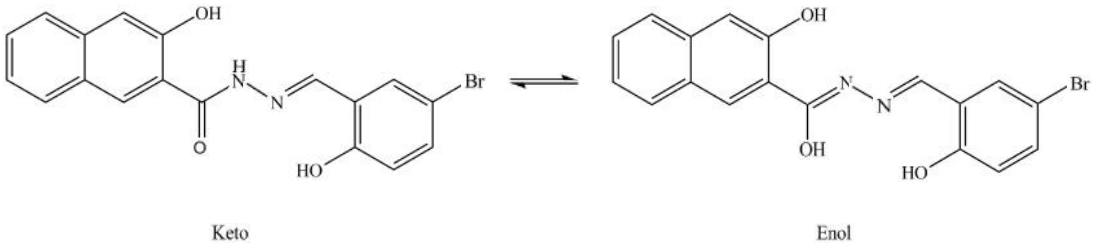
Scheme 4.3.1 Reaction scheme for the preparation of the NAP Schiff base ligands



X = Br, Cl, NO_2 or H
Y = OCH_3 or H
Z = CH_3 or H

The Schiff base ligands were mostly yellow or orange in colour and their melting points were in the range of 210-320^{o}C. They were used without further purification in the preparation of the organotin complexes. The Schiff base ligands could be enolized when in solution as shown in figure 4.3.1 and this had been reported for several similar types of hydrazone ligands [Narang *et al.,* 2000, Yaul *et al.,* 2009].

Figure 4.3.1 Keto-enol isomerization of the hydrazone Schiff base

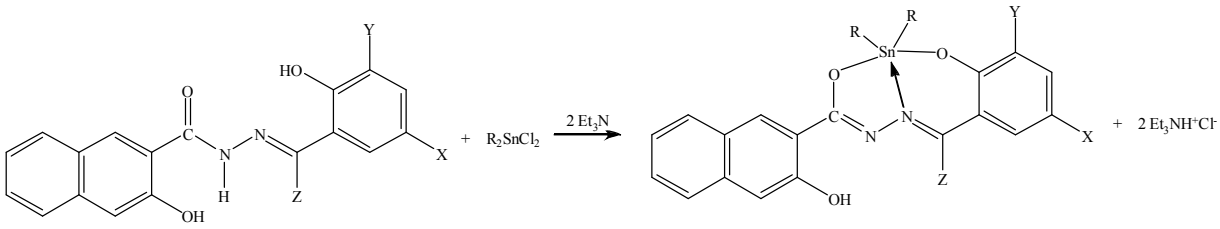


Keto Enol

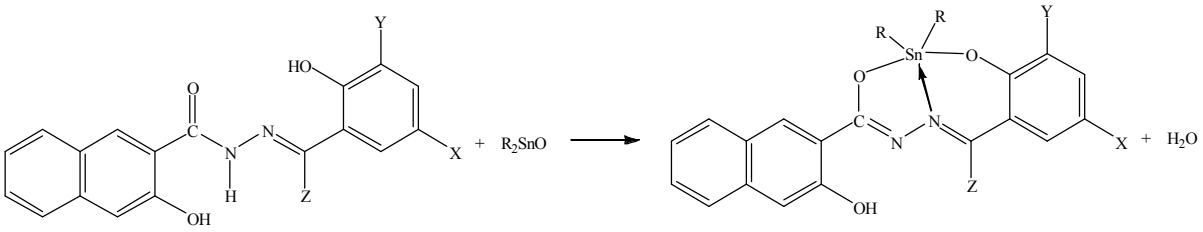
The enolised form of the hydrazone Schiff base ligands contained several potential sites for coordination namely the azomethine nitrogen and three hydroxyl groups [one hydroxyl on the naphthalene ring, the second hydroxyl on the salicylaldehyde or 2-hydroxyacetophenone ring and the third hydroxy attached to the -C=N- moiety]. An important feature of these Schiff base ligands was the presence of several acidic hydroxyl groups which could readily react with either diorganotin oxides or diorganotin halides in the presence of a weak base. In addition, the donation of the lone pair of electrons on the azomethine nitrogen to the tin atom to form a coordinate N $\longrightarrow$Sn bond, tend to stabilize the overall structure.

Generally, diorganotin halides are relatively strong Lewis acids. This explains their ability to form stable complexes with Schiff bases. The ability of the organotin compounds to form complexes largely depended on the electronegativity of the anionic substituents as indicated in the diorganotin halides, $R_2SnCl_2 > R_2SnBr_2 > R_2SnI_2$ [Poller 1972]. In this project, several diorganotin dichlorides and diorganotin oxides were used in the reactions with the prepared hydrazones. A general reaction scheme for the preparation of the complexes is shown in scheme 4.3.2.

Scheme 4.3.2 Reaction scheme for the preparation of the diorganotin NAP Schiff base complexes



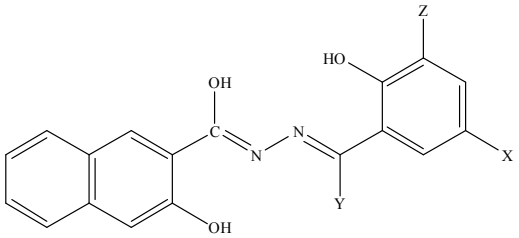
X = Br, Cl, NO_2 or H
Y = OCH_3 or H
Z = CH_3 or H
R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz),



X = Br, Cl, NO_2 or H
Y = OCH_3 or H
Z = CH_3 or H
R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy)

Table 4.3.1
Analytical datas for the NAP ligands

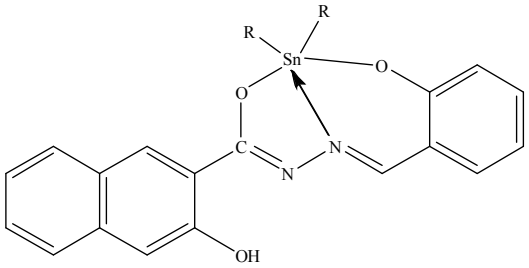
Ligand	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
N'-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA**	Light Yellow	82.1	300-302	71.58 (71.51)	4.46 (4.63)	8.96 (9.26)
N'-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB**	Light Yellow	75.5	316-318	56.05 (56.12)	3.15 (3.37)	7.08 (7.27)
N'-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC**	Light Yellow	77.6	310-312	63.72 (63.44)	3.57 (3.81)	8.06 (8.22)
N'-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HD**	Light Yellow	69.2	296-298	71.71 (71.24)	5.31 (4.99)	8.89 (8.74)
N'-[1-(5-Bromo-2-oxidophenyl)-ethylidene]-3-hydroxy-2-naphtho-hydrazide}, **HE**	Light Yellow	72.4	210-216	56.96 (57.16)	3.75 (3.76)	6.89 (7.01)
N'-[1-(5-Chloro-2-oxidophenyl)-ethylidene]-3-hydroxy-2-naphtho-hydrazide, **HF**	Light Yellow	74.5	298-300	63.96 (64.32)	4.02 (4.23)	7.64 (7.89)
N'-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG**	Yellow	75.3	324-326	61.95 (61.54)	3.56 (3.70)	11.57 (11.95)
N'-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazide, **HH**	Yellow	79.1	288-290	54.81 (54.96)	3.58 (3.61)	6.58 (6.74)



HA: X = H, Y= H, Z = H ; **HB**: X = Br, Y = H, Z = H;
HC: X = Cl, Y = H, Z = H; **HD**: X = H, Y = CH_3, Z = H;
HE: X= Br, Y = CH_3, Z = H; **HF**: X = Cl, Y = CH_3, Z = H;
HG: X = NO_2, Y = H , Z = H; **HH**: X = Br, Y = H, Z = OCH_3

Table 4.3.2a
Analytical data for [(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

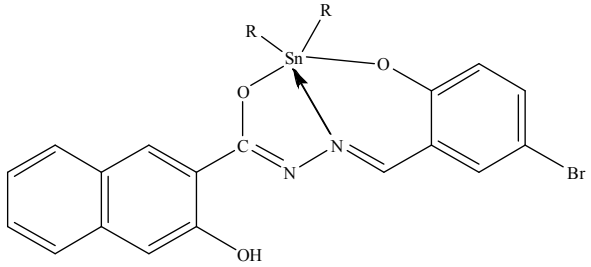
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dimethyltin(IV), **HA1**	Yellow	78.7	232-234	53.07 (53.03)	3.51 (3.97)	5.88 (6.18)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibutyltin(IV), **HA2**	Yellow	79.2	110-112	58.15 (58.16)	5.17 (5.59)	5.05 (5.21)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]diphenyltin(IV), **HA3**	Yellow	76.9	272-274	62.83 (62.42)	4.19 (3.81)	5.01 (4.85)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dicyclohexyltin(IV), **HA4**	Yellow	73.2	102-104	61.54 (61.15)	5.57 (5.77)	4.86 (4.75)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibenzyltin(IV), **HA5**	Yellow	67.1	> 350 (dec.)	63.02 (63.51)	4.24 (4.30)	4.98 (4.63)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*o*-chlorobenzyl)tin(IV), **HA6**	Yellow	67.9	180-182	57.08 (57.01)	3.69 (3.56)	4.10 (4.15)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*p*-chlorobenzyl)tin(IV), **HA7**	Yellow	65.1	139-140	56.67 (57.01)	3.43 (3.56)	3.97 (4.15)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.2b
Analytical data for [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

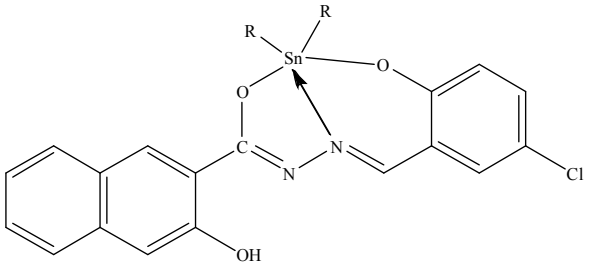
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HB1**	Yellow	80.1	218-220	45.88 (45.16)	3.16 (3.20)	5.40 (5.26)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HB2**	Yellow	81.2	123-124	50.64 (50.71)	4.62 (4.71)	4.26 (4.55)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HB3**	Yellow	73.2	>350 (dec.)	54.42 (54.92)	3.26 (3.20)	4.47 (4.27)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HB4**	Yellow	71.2	156-158	54.48 (53.93)	4.98 (4.94)	4.05 (4.19)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HB5**	Yellow	69.6	144-146	56.55 (56.20)	3.34 (3.66)	4.51 (4.09)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HB6**	Yellow	70.5	140-141	51.08 (51.04)	3.55 (3.05)	3.76 (3.72)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HB7**	Yellow	69.1	80-82	50.77 (51.04)	3.28 (3.05)	3.47 (3.72)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.2c
Analytical data for [*N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

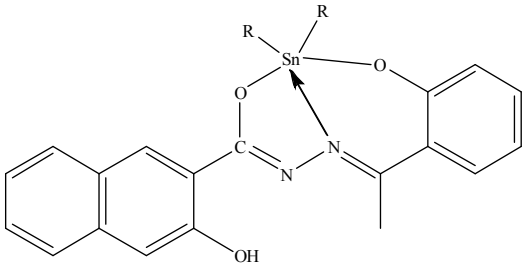
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HC1**	Yellow	82.1	220-222	49.83 (49.28)	3.55 (3.49)	5.89 (5.74)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HC2**	Yellow	80.5	118-120	54.35 (54.65)	5.26 (5.07)	4.95 (4.90)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HC3**	Yellow	77.5	308-310	59.32 (58.91)	3.48 (3.43)	4.66 (4.58)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HC4**	Yellow	76.7	320-322	58.17 (57.77)	5.59 (5.29)	4.33 (4.49)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HC5**	Yellow	73.6	154-156	60.55 (60.09)	3.57 (3.91)	4.07 (4.38)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HC6**	Yellow	75.5	212-213	53.87 (54.27)	3.19 (3.25)	3.74 (3.95)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HC7**	Yellow	67.1	134-136	54.01 (54.27)	3.66 (3.25)	3.90 (3.95)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.2d
Analytical data for {*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

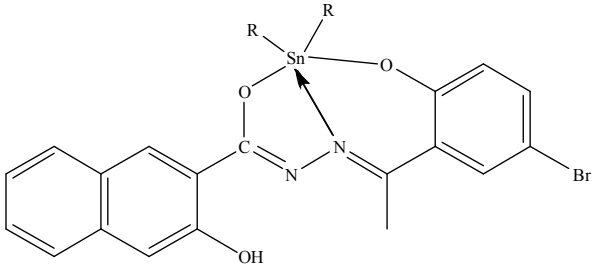
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HD1**	Brown	75.5	180-182	54.19 (54.02)	4.38 (4.28)	6.26 (6.00)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HD2**	Brown	71.2	140-142	58.77 (58.94)	5.61 (5.82)	4.96 (5.09)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HD3**	Brown	74.7	320-322	62.57 (62.98)	4.38 (4.06)	4.49 (4.74)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HD4**	Orange	80.2	206-208	61.55 (61.53)	6.46 (6.28)	4.48 (4.63)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HD5**	Orange	70.2	87-89	64.64 (64.02)	4.34 (4.52)	4.78 (4.52)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HD6**	Orange	72.2	168-170	59.27 (59.33)	4.32 (4.04)	4.27 (4.19)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HD7**	Orange	68.4	138-140	59.82 (59.33)	4.41 (4.04)	3.95 (4.19)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.2e
Analytical data for {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

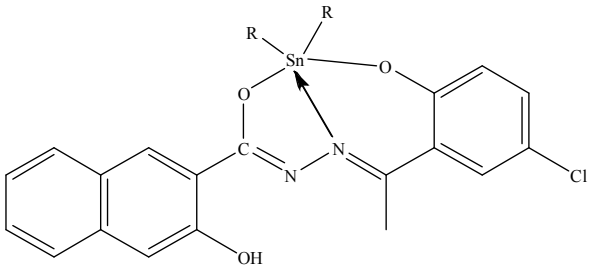
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HE1**	Yellow	81.4	195-196	46.51 (46.20)	3.48 (3.48)	5.30 (5.13)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HE2**	Yellow	79.4	138-139	51.86 (51.40)	4.83 (5.07)	4.63 (4.44)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HE3**	Brown	73.2	148-150	55.84 (55.56)	3.13 (3.43)	3.98 (4.18)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HE4**	Yellow	76.8	158-160	54.48 (54.58)	5.54 (5.13)	4.07 (4.10)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HE5**	Brown	72.1	144-145	56.30 (56.78)	3.91 (4.01)	5.74 (4.01)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HE6**	Brown	74.4	187-189	51.96 (51.67)	3.29 (3.39)	3.53 (3.65)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HE7**	Brown	73.6	188-190	51.32 (51.67)	3.32 (3.39)	3.81 (3.65)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.2f
Analytical data for {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

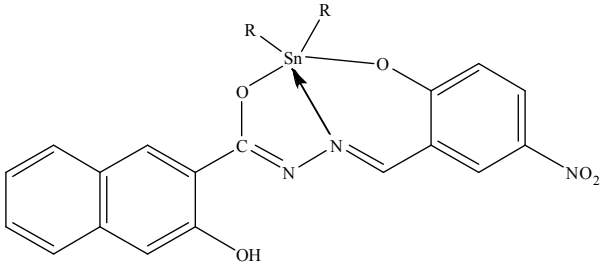
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HF1**	Yellow	80.5	234-236	50.19 (50.30)	3.85 (3.79)	5.82 (5.58)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HF2**	Yellow	82.5	135-136	55.91 (55.39)	5.40 (5.29)	4.59 (4.78)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HF3**	Yellow	78.7	168-170	59.90 (59.50)	3.66 (3.68)	4.12 (4.47)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HF4**	Yellow	78.4	158-160	58.78 (58.40)	5.91 (5.49)	3.98 (4.39)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HF5**	Yellow	75.3	140-142	59.98 (60.64)	3.91 (4.13)	4.58 (4.28)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HF6**	Yellow	75.6	158-160	55.18 (54.85)	3.12 (3.46)	3.74 (3.87)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HF7**	Yellow	77.7	190-191	55.29 (54.85)	3.17 (3.46)	3.44 (3.87)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.2g
Analytical data for [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

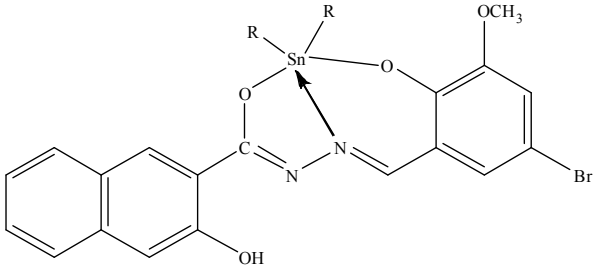
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HG1**	Yellow Green	78.2	275-277	55.12 (54.96)	3.79 (4.24)	6.87 (7.12)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HG2**	Yellow	74.4	156-158	53.87 (53.66)	4.94 (4.98)	7.24 (7.22)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HG3**	Yellow	76.2	>350 (dec.)	57.55 (57.91)	3.47 (3.37)	6.69 (6.75)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HG4**	Yellow	75.5	207-209	57.16 (56.83)	5.77 (5.20)	6.67 (6.62)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HG5**	Yellow	73.3	> 350 (dec.)	59.22 (59.12)	3.63 (3.85)	6.52 (6.46)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HG6**	Yellow	76.9	202-204	53.79 (53.44)	3.32 (3.20)	5.51 (5.84)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HG7**	Yellow	77.5	218-220	53.84 (53.44)	3.23 (3.20)	6.14 (5.84)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.2h
Analytical data for [*N'*-(5-bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

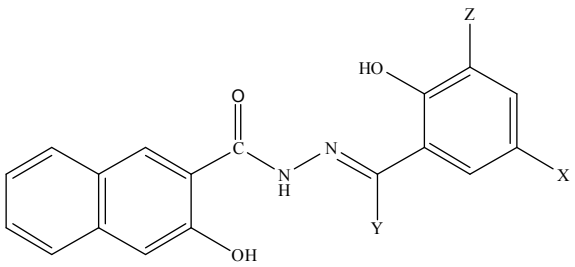
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)		
				C	H	N
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HH1**	Yellow	80.5	265-267	44.30 (44.73)	3.39 (3.37)	4.66 (4.96)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HH2**	Yellow	74.5	119-120	50.32 (50.20)	4.44 (4.80)	4.22 (4.33)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HH3**	Yellow	74.2	267-270	53.83 (54.26)	3.32 (3.35)	4.01 (4.08)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HH4**	Yellow	77.8	262-264	53.84 (53.33)	5.36 (5.01)	4.34 (4.01)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HH5**	Yellow	62.2	118-120	55.61 (55.50)	3.64 (3.78)	4.21 (3.92)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HH6**	Yellow	60.9	128-130	51.18 (50.61)	3.32 (3.19)	4.00 (3.58)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HH7**	Yellow	60.1	> 350 (dec.)	50.86 (50.61)	3.01 (3.19)	3.21 (3.58)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

4.3.2 IR Spectral data

Table 4.3.3 summarizes the characteristic infrared stretching frequencies for ligands **HA-HH** while the stretching vibration frequencies for the diorganotin complexes are listed in table 4.3.4.



HA: X = H, Y= H, Z = H ; **HB**: X = Br, Y = H, Z = H;
HC: X = Cl, Y = H, Z = H; **HD**: X = H, Y = CH_3, Z = H;
HE: X= Br, Y = CH_3, Z = H; **HF**: X = Cl, Y = CH_3, Z = H;
HG: X = NO_2, Y = H , Z = H; **HH**: X = Br, Y = H, Z = OCH_3

The secondary amine and hydroxyl stretching frequencies of the free ligands were expected in the 3100-3400 cm^{-1} region in all the Schiff base ligands. However, these absorption bands were not clearly observed as there was overlapping between the hydroxyl and the secondary amine stretching bands. In the complexes, a characteristic absorption at 3300-3500 cm^{-1} was observed which indicated that some of the phenolic hydroxyl groups did not participate in the coordination to the centre metal atom [Dey *et al.,* 1989, Yin and Chen 2006a].

All the Schiff base ligands exhibited C=N and -O=C-N- stretching frequencies in the region of 1620-1660 cm^{-1} as derived from the two azomethine groups. This was within the range reported for the similar group of Schiff base ligands [Yin *et al.,* 2005b, Yin and Chen 2006b, Dey *et al.,* 2002]. This finding confirmed the involvement of the azomethine nitrogen in coordination with the tin atom which weakened the C=N bond and led to the lowering of the C=N stretching frequencies in the diorganotin complexes. Therefore, the values of *ν*(-N=C-C=N-) were found in the region between 1590-1620

cm^{-1}. This was due to decrease in the electron density in the azomethine nitrogen and carbonyl moieties.

The phenolic C-O stretching frequency for the ligands and organotin complexes was recorded in the 1000-1200 cm^{-1} region [Signorini *et al.,* 1996, Faniran *et al.,* 1974, Bellamy 1958]. The shifting of the phenolic C-O stretching bands in the diorganotin complexes to different stretching frequencies could be explained by the coordination of two of the hydroxyl groups to the tin centre.

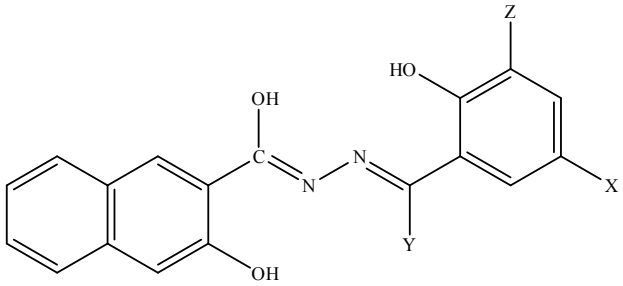
For the diorganotin complexes, the presence of two new bands could be observed in the region of 400-800 cm^{-1}. The medium absorption in the region of 680-710 cm^{-1} had been assigned to the Sn-O stretching mode of vibration. The weak absorption in the region of 460-480 cm^{-1} had been assigned to the Sn-N stretching vibration. All these values were within the range reported for a number of diorganotin derivatives [Yin *et al.*, 2005b, Singh *et al.*, 1999].

Ligand **HH** and its complexes which comprised of a *m*-methoxy substituent in the phenyl ring, exhibited an asymmetrical and symmetrical C-O-C vibration stretching vibrational 1050-1100 cm^{-1}.

Table 4.3.3
Infrared spectral data for the NAP ligands

Ligand	ν(N-H, O-H)	ν(C=O)	ν(C=N)	ν(C-O)	ν_a(C-O-C), ν_s(C-O-C)
N'-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA**	3189b	1645s	1622s	1168m	-
N'-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB**	3240b	1642s	1629s	1175m	-
N'-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC**	3187b	1647s	1630s	1176m	-
N'-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HD**	3284b	1654s	1620s	1173m	-
N'-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HE**	3286b	1656s,	1649s	1176m	-
N'-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HF**	3279b	1655s	1648s	1181m	-
N'-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG**	3233b	1638s,	1631s	1176m	-
N'-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HH**	3227b	1638s	1625s	1170m	1072m, 1020w

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

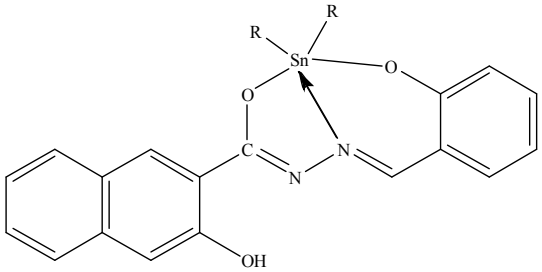


HA: X = H, Y= H, Z = H ; **HB**: X = Br, Y = H, Z = H;
HC: X = Cl, Y = H, Z = H; **HD**: X = H, Y = CH_3, Z = H;
HE: X= Br, Y = CH_3, Z = H; **HF**: X = Cl, Y = CH_3, Z = H;
HG: X = NO_2, Y = H , Z = H; **HH**: X = Br, Y = H, Z = OCH_3

Table 4.3.4a
Infrared spectral data for [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(C=N-N=C)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HA1**	3424b	1638s	1598s	1173m	700w	463w
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HA2**	3424b	1638s	1609s	1171m	707m	461m
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HA3**	3402b	1638s	1600s	1171m	696m	464w
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HA4**	3400w	1638s	1606s	1170m	696w	475m
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HA5**	3423b	1638s	1601s	1172m	695w	472w
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HA6**	3424b	1637s	1608s	1172m	671m	476m
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HA7**	3400b	1638s	1600s	1171m	690w	475w

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

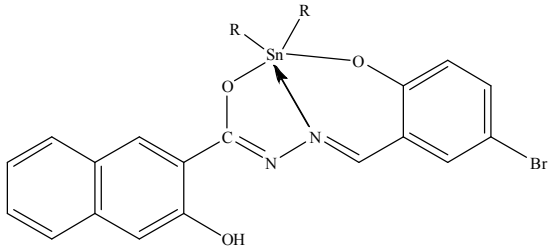


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.4b
Infrared spectral data for [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(C=N-N=C)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HB1**	3431b	1638s	1601s	1182m	696m	478m
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HB2**	3422b	1638s	1602m	1172m	697w	476w
[(*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HB3**	3386b	1638s	1602s	1183m	697m	474w
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HB4**	3400b	1638s	1601s	1172m	698w	472w
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HB5**	3422b	1639s	1617s	1183m	698m	476m
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HB6**	3402b	1638s	1604s	1183m	695m	477m
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HB7**	3392b	1639s	1616s	1170m	695m	475m

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

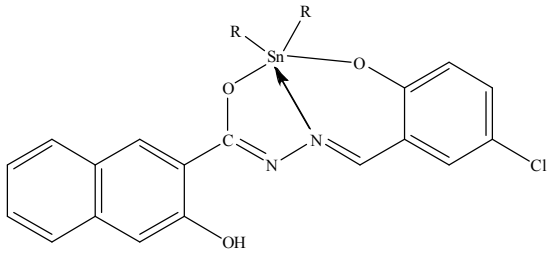


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.4c
Infrared spectral data for [*N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(C=N-N=C)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HC1**	3431b	1638s	1604s	1182m	713m	478m
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HC2**	3430b	1638s	1610s	1183m	714w	478w
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HC3**	3428b	1639s	1610s	1183m	697m	473m
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HC4**	3400b	1640s	1602s	1183m	714w	465m
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HC5**	3428b	1640s	1615s	1184m	698m	477m
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HC6**	3380b	1640s	1606s	1183m	709w	477w
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HC7**	3422b	1639s	1617s	1170m	711w	477m

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

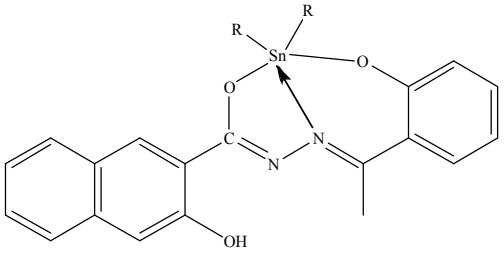


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.4d
Infrared spectral data for {*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(C=N-N=C)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HD1**	3395b	1639s	1595m	1173m	739w	475w
{*N'*- [1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HD2**	3381b	1625s	1590m	1170m	740m	471m
{*N'*- [1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HD3**	3400b	1638s	1600m	1173m	736m	480m
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HD4**	3424b	1638s	1594m	1170m	739m	474w
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HD5**	3399b	1639s	1597m	1170m	695m	476w
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HD6**	3403b	1638s	1598m	1170m	707w	477w
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HD7**	3384b	1639s	1590m	1173m	706w	471w

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

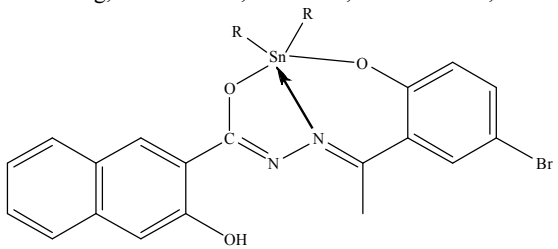


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.4e
Infrared spectral data for {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(C=N-N=C)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HE1**	3431b	1638s	1578m	1171m	676w	476w
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HE2**	3400b	1639s	1577s	1171m	679m	476m
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HE3**	3386b	1639s	1581s	1172m	696w	457w
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HE4**	3402b	1638s	1593s	1170m	679w	481w
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HE5**	3400b	1638s	1592m	1171m	678w	476m
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HE6**	3402b	1638s	1578m	1171m	677w	478m
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HE7**	3424b	1639s	1578m	1172m	677w	480m

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

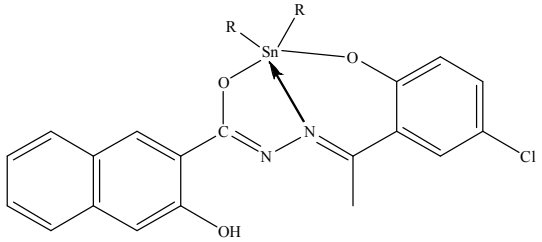


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.4f
Infrared spectral data for {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(C=N-N=C)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HF1**	3400b	1638s	1597m	1172m	696w	475w
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HF2**	3400b	1639s	1596m	1172m	695m	476m
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HF3**	3405b	1638s	1598m	1172m	697m	484m
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HF4**	3424b	1639s	1598m	1170m	671w	476w
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HF5**	3387b	1639s	1593m	1172m	695m	475w
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HF6**	3387b	1627s	1594m	1170m	679w	477w
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HF7**	3400b	1639s	1596m	1172m	696w	478w

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

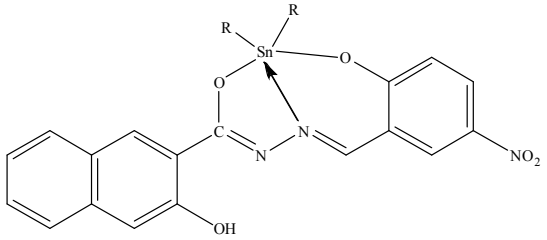


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.4g
Infrared spectral data for [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(C=N-N=C)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HG1**	3409b	1639s	1608s	1174m	703m	466m
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HG2**	3394b	1639s	1607s	1170m	704m	463m
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HG3**	3411b	1638s	1610s	1171m	699m	471m
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HG4**	3424b	1639s	1607s	1170m	704m	475w
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HG5**	3449b	1638s	1609s	1170m	699m	476m
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HG6**	3424b	1639s	1607s	1172m	705w	478m
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HG7**	3449b	1639s	1608s	1171m	706w	477m

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

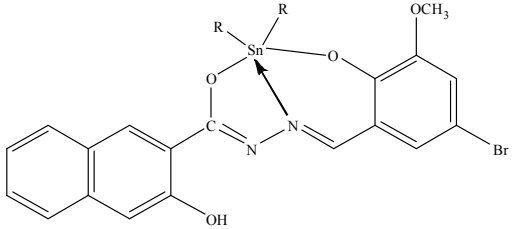


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.4h
Infrared spectral data for [*N'*-(5-bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(C=N-N=C)	*v*(C-O)	v_a(C-O-C), v_s(C-O-C)	*v*(Sn-O)	*v*(Sn-N)
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HH1**	3449b	1642s	1607s	1168m	1092m, 1050m	696w	467m
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HH2**	3399b	1640s	1613s	1170m	1088m, 1045m	694w	475m
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphthohydrazidato]-diphenyltin(IV), **HH3**	3423b	1640s	1601s	1171m	1074s, 1051s	697m	475m
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HH4**	3400b	1639s	1598m	1170m	1073m, 1053m	671w	478m
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphthohydrazidato]-dibenzyltin(IV), **HH5**	3334b	1639s	1611m	1171m	1090w, 1049m	694m	474w
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]-di(*o*-chlorobenzyl)tin(IV), **HH6**	3394b	1640s	1602m	1171m	1050m	695m	474m
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]-di(*p*-chlorobenzyl)tin(IV), **HH7**	3394b	1639s	1610m	1172m	1052m	695w	474w

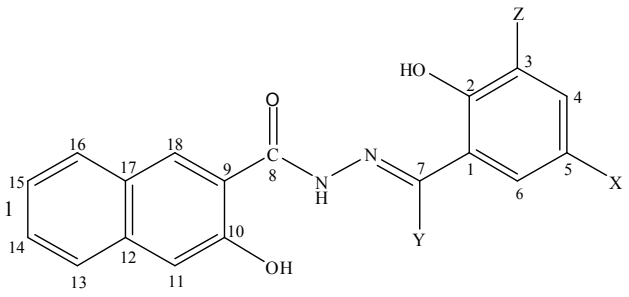
[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

4.3.3 NMR Spectral Data

The ^{1}H and ^{13}C NMR spectra for the free ligands and complexes were recorded in deuterated DMSO due to the poor solubility of most of the complexes in common deuterated solvents such as $CDCl_3$, CD_3OD, CD_3CN and others. The ^{1}H NMR chemical shifts for the ligands are listed in table 4.3.5 while the ^{13}C NMR chemical shifts for the ligands are listed in table 4.3.6. The ^{1}H NMR chemical shifts for the complexes are listed in table 4.3.7, the ^{13}C NMR chemical shifts for the complexes are listed in table 4.3.8 and the ^{119}Sn NMR chemical shifts are listed in table 4.3.9.



HA: X = H, Y= H, Z = H ; **HB**: X = Br, Y = H, Z = H;
HC: X = Cl, Y = H, Z = H; **HD**: X = H, Y = CH_3, Z = H;
HE: X= Br, Y = CH_3, Z = H; **HF**: X = Cl, Y = CH_3, Z = H;
HG: X = NO_2, Y = H , Z = H; **HH**: X = Br, Y = H, Z = OCH_3

^{1}H NMR Spectra

The presence of three sharp resonance signals in the range of 11.00-14.00 ppm for the ligands **HA-HH** was due to the characteristic phenolic protons and the amine protons. The methine protons of the azomethine group, -N=C(H)- occurred as a singlet peak in the range of 8.00-9.00 ppm for ligands **HA**, **HB**, **HC, HG** and **HH**. The chemical shifts for the phenyl groups in ligands **HA-HH** exhibited a group of multiplets in the range of 5.50-7.90 ppm and another singlet between 8.35-8.60 ppm. These observations were also found in the spectra for the diorganotin complexes.

For ligands **HD**, **HE** and **HF**, the chemical shift of the methyl substituent on the azomethine carbon was found at the range of 2.66-2.79 ppm. The protons of the methoxy group in ligand **HH** occurred as a singlet at 3.96 ppm.

The decrease in the intensity of the OH proton signal in the diorganotin complexes suggested the bonding of the tin atom to the oxygen atom of the Schiff base ligand was through the replacement of one of the phenolic protons. The absence of an NH proton signal in the ^{1}H NMR spectra of the organotin complexes suggested that the enolized form of the Schiff base ligand had reacted with the diorganotins through the displacement of the proton in the azomethine group.

The chemical shift values of the aromatic and aliphatic protons of the complexes were located in the expected region of the spectra. These chemical shift values were useful for the confirmation of the presence of the alkyl and aryl groups in the complexes.

^{13}C NMR spectra

The chemical shifts of the azomethine carbon in the ligands occured in the range of 155-170 ppm. Among the Schiff base ligands, ligands **HD**, **HE**, **HF** and **HG** showed the highest C(7) chemical shift, which was between 156-163 ppm. The carbonyl carbon, C(8) was more deshielded than C(7) and its chemical shift was higher, between 162-168 ppm.

The chemical shift of C(5) was the highest in ligands **HB**, **HC**, **HE**, **HF**, **HG** and **HH** which was between 170-177 ppm. This was due to the presence of the electron-withdrawing group; bromine, chlorine and nitro on C(5) in the phenyl ring.

Among these ligands, the nitro substituted Schiff base ligand, **HG** showed the highest chemical shift value at 176.4 ppm.

The methyl group attached to C(7) in **HD**, **HE** and **HF** was found in the chemical shift region between 13-25 ppm. The chemical shifts of the aryl carbons of the salicylaldehyde and naphthalene rings were between 110-158 ppm and these values were consistent with those of the aromatic carbons in Schiff base ligands [Yin *et al.,* 2005b, Yin *et al.,* 2006a].

In the ^{13}C NMR spectra of the complexes; as a result of the poor solubility of some of the complexes in all the deuterated solvents including DMSO, rigorous assignments of the carbon peaks could not be done especially on the *J*-coupling of the organotin fragments.

The chemical shifts of the C(7) and C(8) of the organotin were also in the range of 160-170 ppm. Compared to chemical shift values of the ligands, C(7) and C(8) were found to have shifted to lower values by 5-10 ppm. The chemical shift of C(5) was also found in the similar region as the Schiff base ligands.

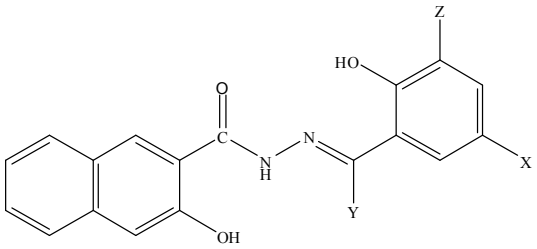
The ^{13}C NMR spectra for the complexes showed a slight chemical shift value for all carbon resonances as compared to the free ligands, as a consequence of the electron density transfer from the ligand to the acceptor. The aromatic carbons of the ligand as well as the diorganotin complexes appeared within the expected range and were in close agreement with the reported literature values [Yin *et al.*, 2005b, Yin *et al.*, 2006a, Yin *et al.*, 2007, Yin *et al.*, 2008, Hong *et al.*, 2010].

^{119}Sn NMR Spectra

The ^{119}Sn NMR chemical shifts have long been used as an indicator to predict the coordination environment of tin atom in the complexes [Holeček *et al*., 1983a, Holeček *et al*., 1983b, Nádvorník *et al*., 1984, Lyčka *et al*., 1985, Lyčka *et al*., 1987, Holeček *et al*., 1988]. In this study, the ^{119}Sn NMR chemical shifts of the dimethyltin complexes were found between -157 to 160 ppm, dibutyltin complexes at around -196 ppm, diphenyltin complexes at -340 ppm and dicyclohexyltin complexes at -262 ppm. In general, the ^{119}Sn NMR chemical shifts of the alkyltins were formed in the upfield region, followed by the cycloalkyltin and aryltin which had the largest downfield shift. However, the ^{119}Sn NMR chemical shift values for the dibenzyltin, di(*o*-chlorobenzyl)tin and di(*p*-chlorobenzyl)tin were found in a wider range, from -200 to -550 ppm. One of the reasons could be due to the complexes not being in a five-coordinated coordination due to many other factors such as the presence of a solvate solvent in the coordination sphere. However, the ^{119}Sn NMR chemical shift values were found to be in the similar range as those reported for the respective diorganotin compounds indicating most of these diorganotin complexes were in a five-coordinated tin geometry.

Table 4.3.5
^{1}H NMR chemical shifts for the NAP ligands

Ligand	Assignments[a] [δ(^{1}H)/ppm]				
	Aryl	-N=C(H)	-OH	-NH-	-N=C(CH$_3$)- or OMe$_3$
N'-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA**	6.78-6.90 (m, 1H), 7.33-7.92 (m, 7H), 8.45 (s, 1H)	8.67 (s, 1H)	11.25 (s, 2H)	12.14 (s, 1H)	-
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide], **HB**	6.90-6.93 (m, 1H), 7.32-7.91 (m, 7H), 8.43 (s, 1H)	8.62 (s, 1H)	11.24 (s, 2H)	12.20 (s, 1H)	-
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide], **HC**	6.95-6.98 (m, 1H), 7.32-7.92 (m,7H), 8.43 (s, 1H)	8.63 (s, 1H)	11.23 (s, 2H)	12.20 (s, 1H)	-
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide}, **HD**	6.88-6.94 (m, 1H), 7.25-7.94 (m, 7H), 8.39 (m, 1H)	-	11.00 (s, 2H)	12.92 (s, 1H)	2.43 (s, 3H)
{*N'*-[1-(5-Bromo-2-oxidophenyl)-ethylidene]-3-hydroxy-2-naphthohydrazide}, **HE**	6.78-6.90 (m, 1H), 7.25-7.83 (m, 7H), 8.39 (m, 1H)	-	11.35 (s, 2H)	12.92 (s, 1H)	2.44 (s, 3H)
{*N'*-[1-(5-Chloro-2-oxidophenyl)-ethylidene]-3-hydroxy-2-naphthohydrazide}, **HF**	6.80-6.94 (m, 1H), 7.31-7.98 (m, 7H), 8.34 (s, 1H)	-	11.40 (s, 2H)	13.02 (s, 1H)	2.57 (s, 3H)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide], **HG**	7.10-7.14 (m, 1H), 7.32-7.92 (m, 7H), 8.59 (s, 1H)	8.74 (s, 1H)	10.50 (s, 2H)	12.30 (s, 1H)	-
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazide], **HH**	7.17-7.91 (m, 7H), 8.42 (s, 1H)	8.63 (s, 1H)	10.83 (s, 1H), 11.19 (s, 1H)	12.17 (s, 1H)	3.84 (s, 3H)

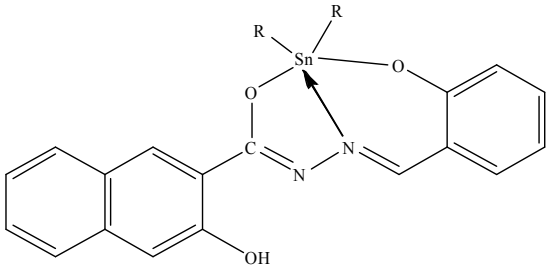


HA: X = H, Y= H, Z = H ; **HB**: X = Br, Y = H, Z = H;
HC: X = Cl, Y = H, Z = H; **HD**: X = H, Y = CH_3, Z = H;
HE: X= Br, Y = CH_3, Z = H; **HF**: X = Cl, Y = CH_3, Z = H;
HG: X = NO_2, Y = H , Z = H; **HH**: X = Br, Y = H, Z = OCH_3

Table 4.3.6a
^{1}H NMR chemical shifts for [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]			
	Aryl	-N=C(H)	-OH	R groups
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dimethyltin(IV), **HA1**	6.73-6.80 (m, 1H), 7.15-7.82 (m, 8H), 8.49 (s, 1H)	8.64 (s, 1H)	11.61 (s, 1H)	0.92 (s, 6H)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibutyltin(IV), **HA2**	6.73-6.82 (m, 1H), 7.18-7.85 (m, 8H), 8.50 (s, 1H)	8.67 (s, 1H)	11.73 (s, 1H)	0.86-1.74 (m, 18H)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]diphenyltin(IV), **HA3**	6.80-6.85 (m, 1H), 7.12-7.97 (m, 8H), 8.69 (s, 1H)	8.79 (s, 1H)	11.53 (s, 1H)	7.12-7.97 (m, 10H)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dicyclohexyltin(IV), **HA4**	6.65-6.80 (m, 1H), 7.23-7.67 (m, 8H), 8.43 (s, 1H)	8.95 (s, 1H)	12.02 (s, 1H)	0.77-2.46 (m, 22H)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibenzyltin(IV), **HA5**	6.79-6.92 (m, 1H), 7.21-7.92 (m, 8H), 8.43 (s, 1H)	8.65 (s, 1H)	11.64 (s, 1H)	2.48-3.15 (m, 4H), 7.21-7.92 (m, 10H)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*o*-chlorobenzyl)tin(IV), **HA6**	6.95-6.96 (m, 1H), 7.18-7.65 (m, 8H), 8.37 (s, 1H)	8.49 (s, 1H)	11.29 (s, 1H)	3.02-3.14 (m, 4H), 7.18-7.65 (m, 8H)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*p*-chlorobenzyl)tin(IV), **HA7**	6.59-6.78 (m, 1H), 7.05-7.91 (m, 8H), 8.26 (s, 1H)	8.37 (s, 1H)	11.66 (s, 1H)	3.50-3.59 (m, 4H), 7.05-7.91 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

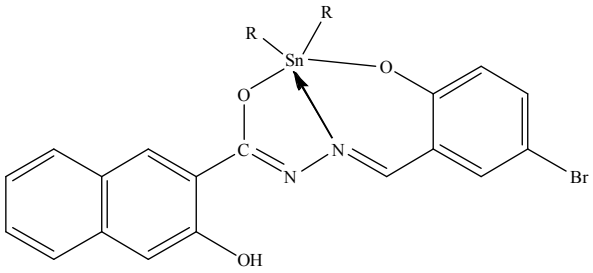


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl(Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.6b
^{1}H NMR chemical shifts for [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]			
	Aryl	-N=C(H)	-OH	R groups
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HB1**	6.67-6.70 (m, 1H), 7.26-7.82 (m, 7H), 8.49 (s, 1H)	8.59 (s, 1H)	11.48 (s, 1H)	0.79 (s, 6H)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HB2**	6.68-6.71 (m, 1H), 7.28-7.84 (m, 7H), 8.50 (s, 1H)	8.58 (s, 1H)	11.58 (s, 1H)	0.86-1.70 (m, 18H)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HB3**	7.01-7.04 (m, 1H), 7.31-7.68 (m, 7H), 8.57 (s, 1H)	8.78 (s, 1H)	11.39 (s, 1H)	7.31-7.68 (m, 10H)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HB4**	6.70-6.73 (m, 1H), 7.27-7.87 (m, 7H), 8.53 (s, 1H)	8.57 (s, 1H)	11.67 (s, 1H)	1.40-2.25 (m, 22H)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HB5**	6.69-7.87 (m, 8H), 8.56 (s, 1H)	8.92 (s, 1H)	11.53 (s, 1H)	2.71-2.96 (m, 4H), 6.69-7.87 (m, 10H)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HB6**	6.90-7.82 (m, 8H), 8.05 (s, 1H)	8.35 (s, 1H)	11.17 (s, 1H)	2.98-3.16 (m, 4H), 6.90-7.82 (m, 8H)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HB7**	6.55-7.87 (m, 8H), 8.31 (s, 1H)	8.64 (s, 1H)	11.80 (s, 1H)	2.97-3.01 (m, 4H), 6.55-7.87 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

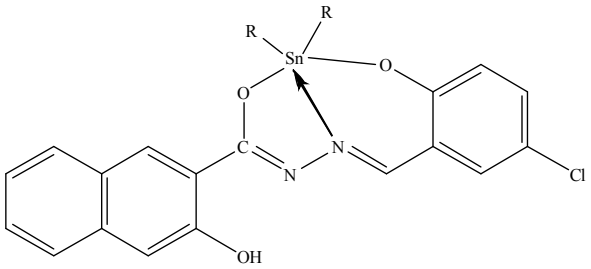


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.6c
^{1}H NMR chemical shifts for [*N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]			
	Aryl	-N=C(H)	-OH	R groups
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HC1**	6.71-6.75 (m, 1H), 7.13-7.82 (m, 7H), 8.49 (s, 1H)	8.56 (s, 1H)	11.49 (s, 1H)	0.79 (s, 6H)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HC2**	6.71-6.75 (m, 1H), 7.10-7.83 (m, 7H), 8.50 (s, 1H),	8.54 (s, 1H)	11.60 (s, 1H)	0.86-1.80 (m, 18H)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HC3**	7.04-7.94 (m, 8H), 8.53 (s, 1H),	8.77 (s, 1H)	11.38 (s, 1H)	7.04-7.94 (m, 10H)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HC4**	6.69-7.94 (m, 8H), 8.47(s, 1H),	8.94 (s, 1H)	12.05 (s, 1H)	1.18-2.02 (m, 22H)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HC5**	6.95-7.05 (m, 1H), 7.50-8.02 (m, 7H), 8.48 (s, 1H)	8.98 (s, 1H)	12.14 (s, 1H)	2.75-2.85 (m, 4H), 7.50-8.02 (m, 10H)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HC6**	7.26-7.88 (m, 8H), 8.17 (s, 1H)	8.66 (s, 1H)	11.81 (s, 1H)	2.98-3.09 (m, 4H), 7.26-7.88 (m, 8H)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HC7**	6.74-6.76 (m, 1H), 7.26-7.88 (m, 7H), 8.17 (s, 1H)	8.66 (s, 1H)	11.81 (s, 1H)	2.97-3.05 (m, 4H), 7.26-7.88 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

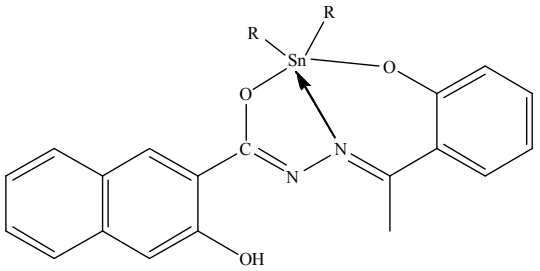


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.6d
^{1}H NMR chemical shifts for {*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]			
	Aryl	-O<u>H</u>	-N=C(C<u>H</u>$_3$)- or OMe$_3$	R groups
{*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HD1**	6.80-6.89 (m, 1H), 7.15-7.84 (m, 8H), 8.55 (s, 1H)	11.92 (s, 1H)	2.86 (s, 3H)	0.88 (s, 6H)
{*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HD2**	6.76-6.85 (m, 1H), 7.07-7.83 (m, 8H), 8.40 (s, 1H)	12.00 (s, 1H)	2.73 (s, 3H)	0.65-1.60 (m, 18H)
{*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HD3**	6.82-6.99 (m, 1H), 7.10-7.80 (m, 8H), 8.40 (s, 1H)	12.02 (s, 1H)	2.90 (s, 3H)	7.10-7.80 (m, 10H)
{*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HD4**	6.74-6.90 (m, 1H), 7.17-7.81 (m, 8H), 8.56 (s, 1H)	12.04 (s, 1H)	2.83 (s, 3H)	1.26-2.26 (m, 22H)
{*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HD5**	6.80-6.98 (m, 1H), 7.14-7.88 (m, 8H), 8.40 (s, 1H)	11.95 (s, 1H)	2.89 (s, 3H)	2.91-3.08 (m, 4H), 7.14-7.88 (m, 10H)
{*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HD6**	6.90-7.04 (m, 1H), 7.19-7.88 (m, 8H), 8.38 (s, 1H)	12.00 (s, 1H)	2.89 (s, 3H)	2.89-3.06 (m, 4H), 7.19-7.88 (m, 8H)
{*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HD7**	6.68-6.91 (m, 1H), 7.06- 7.72 (m, 8H), 8.32 (s, 1H)	12.12 (s,1H)	2.89 (s, 3H)	2.86-2.94 (m, 4H), 7.06-7.72 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

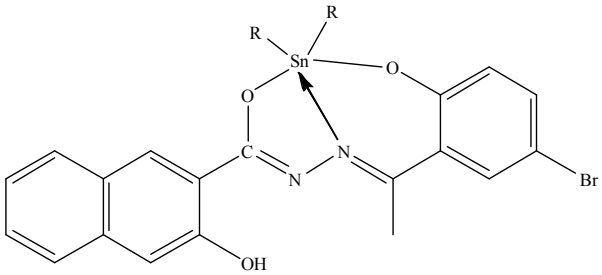


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.6e
^{1}H NMR chemical shifts for {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]			
	Aryl	-O<u>H</u>	-N=C(C<u>H</u>$_3$)- or OMe$_3$	R groups
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HE1**	6.74-6.76 (m, 1H), 7.25- 7.67 (m, 7H), 8.51 (s, 1H)	11.76 (s, 1H)	2.79 (s, 3H)	0.82 (s, 6H)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HE2**	6.80-6.85 (m, 1H), 7.30-7.47 (m, 7H), 8.51 (s, 1H)	11.87 (s, 1H)	2.80 (s, 3H)	0.85-1.63 (m, 18H)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HE3**	6.88-6.95 (m, 1H), 7.23-7.78 (m, 7H), 8.36 (s, 1H)	11.46 (s, 1H)	2.70 (s, 3H)	7.23-7.78 (m, 10H)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HE4**	6.76- 6.80 (m 1H), 7.28-7.89 (m, 7H), 8.56 (s, 1H)	11.97 (s, 1H)	2.80 (s, 3H)	0.85-2.20 (m, 22H)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HE5**	6.66-6.86 (m, 1H), 7.04-7.90 (m, 7H), 8.38 (s, 1H)	12.07 (s, 1H)	2.67 (s, 3H)	2.71-3.00 (m, 4H), 7.04-7.90 (m, 10H)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HE6**	6.43-6.59 (m, 1H), 6.95-7.97 (m, 7H), 8.45 (s, 1H)	11.49 (s, 1H)	2.66 (s, 3H)	2.99-3.28 (m, 4H), 6.95-7.97 (m, 8H)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HE7**	6.43-6.56 (m, 1H), 7.03-7.97 (m, 7H), 8.40 (m, 1H)	11.50 (s, 1H)	2.66 (s, 3H)	3.03-3.10 (m, 4H), 7.03-7.97 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

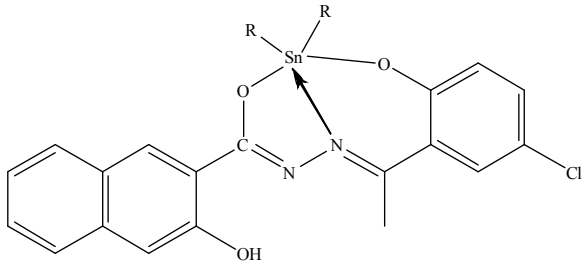


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.6f
^{1}H NMR chemical shifts for {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]			
	Aryl	-O<u>H</u>	-N=C(C<u>H</u>$_3$)- or OMe$_3$	R groups
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HF1**	6.79-6.82 (m, 1H), 7.25-7.67 (m, 7H), 8.51 (s, 1H)	11.77 (s, 1H)	2.79 (s, 3H)	0.82 (s, 6H)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HF2**	6.81-6.82 (m, 1H), 7.24-7.46 (m, 7H), 8.51 (s, 1H)	11.86 (s, 1H)	2.79 (s, 3H)	0.86-1.62 (m, 18H)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HF3**	7.14-8.00 (m, 8H), 8.54 (s, 1H)	11.70 (s, 1H)	2.86 (s, 3H)	7.14-8.00 (m, 10H)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HF4**	6.75-6.77 (m, 1H), 7.25-7.60 (m, 7H), 8.51 (s, 1H)	11.85 (s, 1H)	2.80 (s, 3H)	0.86-1.62 (m, 22H)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HF5**	6.74-6.77 (m, 1H), 6.94-7.86 (m, 7H), 8.40 (s, 1H)	11.45 (s, 1H)	2.47 (s, 3H)	2.92-3.03 (m, 4H), 6.94-7.86 (m, 10H)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HF6**	6.87-8.01 (m, 8H), 8.32 (s, 1H)	11.42 (s, 1H)	2.57 (s, 3H)	3.01-3.11 (m, 4H), 6.87-8.01 (m, 8H)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HF7**	6.70-7.88 (m, 8H), 8.28 (s, 1H)	11.35 (s, 1H)	2.59 (s, 3H)	2.91-2.93 (m, 4H), 6.70-7.88 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

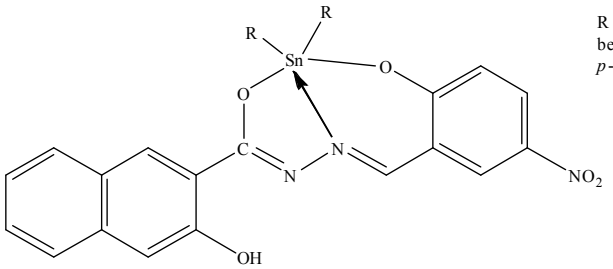


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.6g
^{1}H NMR chemical shifts for the [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]			
	Aryl	-N=C(H)	-OH	R groups
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HG1**	6.75-6.78 (m, 1H), 7.16-8.17 (m, 7H), 8.57 (s, 1H)	8.64 (s, 1H)	11.30 (s, 1H)	1.02 (s, 6H)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HG2**	6.79-6.83 (m, 1H), 7.26-8.19 (m, 7H), 8.51 (s, 1H)	8.74 (s, 1H)	11.37 (s, 1H)	0.87-1.82 (m, 18H)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HG3**	6.91-6.95 (m, 1H), 7.15-7.93 (m, 7H), 8.28 (s, 1H)	8.73 (s, 1H)	11.20 (s, 1H)	7.15-7.93 (m, 10H)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HG4**	6.81-6.85 (m, 1H), 7.26-7.87 (m, 7H), 8.54 (s, 1H)	8.73 (s, 1H)	11.45 (s, 1H)	0.85-2.35 (m, 22H)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HG5**	6.66-6.76 (m, 1H), 7.02-8.20 (m, 7H) 8.50-8.56 (s, 1H)	8.72 (s, 1H)	11.83 (s, 1H)	2.81-2.91 (m, 4H), 7.02-8.20 (m, 10H)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HG6**	6.60-6.78 (m, 1H), 6.97-8.00 (m, 7H), 8.39 (s, 1H)	8.44 (s, 1H)	11.67 (s, 1H)	2.92-2.97 (m, 4H), 6.97-8.00 (m, 8H)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HG7**	6.80-8.85 (m, 1H), 7.02-8.12 (m, 7H), 8.30 (s, 1H)	8.49 (s, 1H)	11.67 (s, 1H)	3.00-3.29 (m, 4H), 7.02-8.12 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

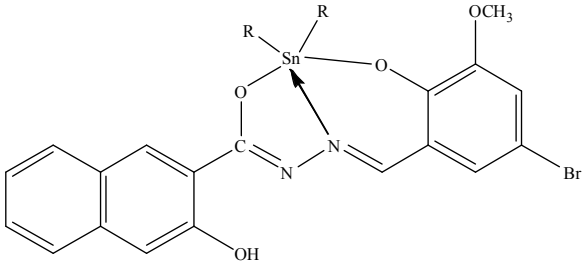


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.6h
^{1}H NMR chemical shifts for the [*N'*-(5-bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complexes	Assignments[a] [δ(^{1}H)/ppm]				
	Aryl	-N=C(H)	-OH	-N=C(CH_3)- or OMe_3	R groups
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HH1**	6.91-6.92 (m, 1H), 6.98-7.64 (m, 6H), 8.48 (s, 1H)	8.52 (s, 1H)	11.39 (s, 1H)	3.85 (s, 3H)	0.97 (s, 6H)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HH2**	6.95-7.00 (m, 1H), 7.02-7.87 (m, 6H), 8.44 (s, 1H)	8.85 (s, 1H)	12.16 (s, 1H)	3.67 (s, 3H)	0.66-1.50 (m, 18H)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HH3**	6.92-6.93 (m, 1H), 7.05- 7.94 (m, 6H), 8.53 (s, 1H)	8.76 (s, 1H)	11.32 (s, 1H)	3.96 (s, 3H)	7.05- 7.94 (m, 10H)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HH4**	6.95-7.00 (m, 1H), 7.13-7.89 (m, 6H), 8.44 (s, 1H)	8.79 (s, 1H)	11.50 (s, 1H)	3.82 (s, 3H)	0.75-2.27 (m, 22H)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HH5**	6.70-6.80 (m, 1H), 7.00-8.04 (m, 6H), 8.30 (s, 1H)	8.44 (s, 1H)	11.64 (s, 1H)	3.78 (s, 3H)	1.10-1.18 (m, 4H), 7.00-8.04 (m, 10H)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)-tin(IV), **HH6**	6.70-6.81 (m, 1H), 7.00-7.90 (m. 6H), 8.31 (s, 1H)	8.39 (s, 1H)	11.57 (s, 1H)	3.84 (s, 3H)	1.14-1.24 (m, 4H), 7.00-7.90 (m. 8H)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)-tin(IV), **HH7**	6.70-6.76 (m, 1H), 7.13-7.85 (m, 6H), 8.37 (s, 1H)	8.56 (s, 1H)	11.32 (s, 1H)	3.91 (s, 3H)	1.10-1.16 (m, 4H), 7.13-7.85 (m, 8H)

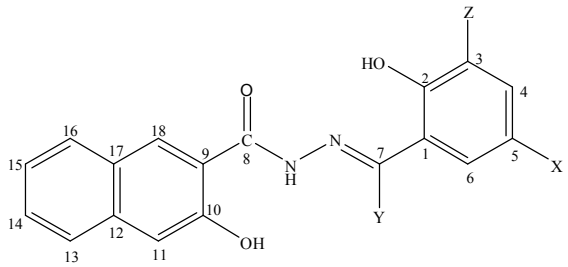
[a] s = singlet, d = doublet, t = triplet, m = multiplet



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.7
^{13}C NMR chemical shifts for the NAP ligands

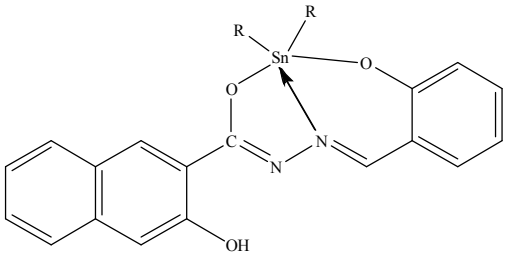
Ligands	^{13}C NMR chemical shifts [$\delta(^{13}C)$/ppm]
N'-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA**	110.7, 116.6, 118.8, 119.6, 120.2, 124.0, 126.0, 126.9, 128.5, 128.8, 129.7, 130.5, 131.8, 136.1, 149.0, 154.1, 157.7 (C_7), 163.8 (C_8)
N'-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB**	110.6, 110.7, 118.8, 120.2, 121.3, 124.0, 125.9, 126.8, 128.4, 128.8, 130.5, 133.9, 136.0, 146.2, 154.0, 156.5 (C_7), 163.8 (C_2), 171.2 (C_8)
N'-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC**	110.6, 110.8, 118.4, 120.3, 123.2, 124.0, 126.0, 126.9, 128.4, 128.8, 130.5, 133.3, 136.0, 146.4, 154.0, 156.2 (C_7), 163.8 (C_2), 171.9 (C_8)
N'-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HD**	13.6 , 110.9, 118.6, 119.8, 121.2, 124.0, 126.0, 126.9, 128.5, 129.0, 129.4, 130.5, 131.9, 136.0, 136.2, 153.1, 154.9, 162.5 (C_7), 167.1 (C_8)
N'-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HE**	22.6, 110.6, 119.0, 120.1, 121.4, 123.3, 125.8, 126.4, 127.9, 128.3, 128.9, 130.5, 131.6, 132.6, 134.3, 155.0, 161.0 (C_7), 164.5 (C_2), 173.5 (C_8)
N'-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HF**	25.2, 110.9, 118.6, 120.6, 121.2, 124.0, 126.0, 126.9, 128.5, 129.0, 129.5, 130.6, 131.1, 132.5, 134.4, 154.9, 162.2 (C_7), 167.1 (C_2), 173.9 (C_8)
N'-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG**	110.6, 117.3, 118.7, 120.0, 120.4, 124.0, 126.0, 126.9, 128.4, 128.8, 130.5, 136.0, 140.0, 145.0, 154.0, 162.7 (C_7), 164.0 (C_2), 176.4 (C_8)
N'-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphthohydrazide, **HH**	56.5 (O-$\underline{C}H_3$), 110.4, 110.7, 116.3, 120.4, 121.8, 124.1, 126.1, 127.0, 128.5, 128.9, 130.5, 136.1, 146.4, 149.4, 154.1, 157.8 (C_7), 163.9 (C_2), 173.6 (C_8)



HA: X = H, Y= H, Z = H ; **HB**: X = Br, Y = H, Z = H;
HC: X = Cl, Y = H, Z = H; **HD**: X = H, Y = CH_3, Z = H;
HE: X= Br, Y = CH_3, Z = H; **HF**: X = Cl, Y = CH_3, Z = H;
HG: X = NO_2, Y = H , Z = H; **HH**: X = Br, Y = H, Z = OCH_3

Table 4.3.8a
^{13}C NMR chemical shifts for the [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

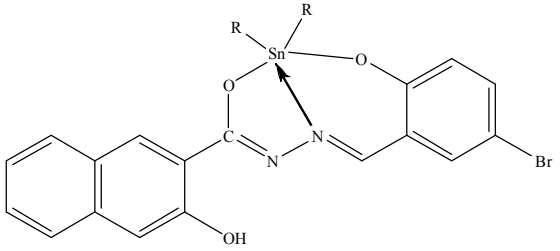
Complex	Assignments [$\delta(^{13}C)$/ppm]
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dimethyltin(IV), **HA1**	1.8 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 559 Hz] δ(Sn-Me), 111.1, 116.3, 117.6, 118.0, 121.8, 123.3, 126.1, 127.3, 128.0, 128.8, 130.8, 134.4, 135.9, 136.7, 155.4, 161.7, 166.6 (C_7), 169.7 (C_8)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibutyltin(IV), **HA2**	13.5, 22.7 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 610 Hz], 26.5 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 78 Hz], 27.0 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 32 Hz] δ(Sn-Bu), 111.0, 116.3, 117.3, 118.2, 121.8, 123.3, 126.1, 127.3, 127.9, 128.8, 130.7, 134.3, 135.9, 136.6, 155.5, 161.5, 167.2 (C_7), 169.9 (C_8)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]diphenyltin(IV), **HA3**	111.3, 116.4, 117.8, 118.0, 122.3, 123.5, 123.7, 126.2, 127.4, 127.7, 128.1, 128.9 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 87 Hz], 129.1, 130.9, 131.0, 134.6, 136.2, 136.3 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 26 Hz], 136.8, 138.4 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 760 Hz], 155.5, 161.8, 167.5 (C_7), 169.8 (C_8)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dicyclohexyltin(IV), **HA4**	26.7, 28.5 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 72 Hz], 30.0 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 42 Hz], 42.8 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 604 Hz] δ(Sn-Cyh), 111.0, 117.1, 117.3, 119.0, 121.6, 124.0, 126.3, 127.3, 128.6, 128.9, 129.2, 130.3, 135.5, 136.0, 155.6, 162.3, 167.8 (C_7), 169.6 (C_8)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibenzyltin(IV), **HA5**	26.0 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 685 Hz] δ(Sn-CH_2), 111.0, 116.6, 118.3, 119.3, 123.0, 123.4, 125.2, 126.1, 127.6, 128.5, 129.5, 130.5, 131.3, 135.1, 136.0, 137.97, 142.1, 152.8, 154.1, 155.1, 157.6, 164.3, 167.2 (C_7), 170.0 (C_8)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*o*-chlorobenzyl)tin(IV), **HA6**	29.7[$^{1}J(^{119}Sn\text{-}^{13}C)$ = 609 Hz] δ(Sn-CH_2), 110.9, 111.0, 116.3, 117.7, 121.8, 123.3, 126.2, 126.7, 126.9, 127.3, 128.0, 128.2, 128.5, 128.9, 129.0, 130.3[$^{2}J(^{119}Sn\text{-}^{13}C)$ = 49 Hz], 133.2, 134.0, 135.7, 136.7, 155.4, 161.7, 167.2 (C_7), 169.5 (C_8)
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*p*-chlorobenzyl)tin(IV), **HA7**	35.55 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 730 Hz] δ(Sn-CH_2), 110.5, 116.8, 117.8, 119.1, 121.2, 123.7, 126.2, 127.1, 127.6, 127.7, 128.3, 128.8, 129.0, 130.3 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 63 Hz], 131.5, 134.7, 134.9, 136.3, 138.4, 138.6, 155.5, 160.1, 166.8 (C_7), 168.9 (C_8)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.8b
^{13}C NMR chemical shifts for [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

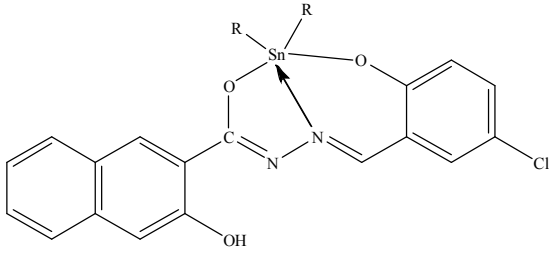
Complex	Assignments [δ(^{13}C)/ppm]
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HB1**	1.9 [^{1}J(^{119}Sn-^{13}C) = 581 Hz] δ(Sn-Me), 108.5, 111.2, 111.7, 123.4, 123.8, 126.1, 127.3, 128.1, 128.8, 131.0, 135.5, 136.8, 138.3, 155.4, 160.2 (C_7), 165.5 (C_2), 170.1 (C_8)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HB2**	13.6, 22.8 [^{1}J(^{119}Sn-^{13}C) = 565 Hz], 26.4 [^{3}J(^{119}Sn-^{13}C) = 77 Hz], 26.7 [^{2}J(^{119}Sn-^{13}C) = 28 Hz] δ(Sn-Bu), 108.1, 111.1, 111.8, 118.0, 123.4, 123.8, 126.1, 127.3, 128.0, 128.6, 130.9, 135.5, 136.8, 138.2, 155.4, 160.0 (C_7), 166.1(C_2), 170.3 (C_8)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HB3**	108.4, 110.9, 117.2, 117.3, 123.1, 123.7, 125.7, 126.9, 127.8, 128.5 [^{3}J(^{119}Sn-^{13}C) = 87 Hz], 129.2, 130.6, 130.7, 135.3, 135.6, 136.4 [^{2}J(^{119}Sn-^{13}C) = 22 Hz], 137.5, 138.1 [^{1}J(^{119}Sn-^{13}C) = 697 Hz], 154.9, 159.8 (C_7), 165.7 (C_2), 169.7 (C_8)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HB4**	26.4 (C_δ), 28.4 [^{3}J(^{119}Sn-^{13}C) = 76 Hz] (C_γ), 29.9 [^{2}J(^{119}Sn-^{13}C) = 22 Hz] (C_β), 41.0 [^{1}J(^{119}Sn-^{13}C) = 584 Hz] δ(Sn-Cyh), 107.8, 111.1, 117.8, 118.1, 122.3, 123.8, 126.1, 127.3, 128.0, 128.8, 130.8, 135.5, 136.7, 138.1, 155.5, 159.7 (C_7), 166.7 (C_2), 170.4 (C_8)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HB5**	46.1 [^{1}J(^{119}Sn-^{13}C) = 654 Hz] δ(Sn-CH_2), 110.9, 111.1, 111.8, 117.9, 123.2, 123.8, 124.2, 125.3, 126.1, 126.9, 128.1, 128.3, 129.0, 129.6, 130.6, 135.2, 136.0, 136.4, 137.6, 138.3, 155.2, 160.3 (C_7), 168.1 (C_2), 170.1 (C_8)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HB6**	45.8 [^{1}J(^{119}Sn-^{13}C) = 615 Hz] δ(Sn-CH_2), 108.4, 110.9, 117.4, 117.7, 123.3, 123.5, 126.0, 126.2, 126.8, 127.2, 127.5, 128.0, 128.8, 130.2, 131.1, 133.0, 135.0, 135.2, 136.7, 137.9, 155.2, 160.0 (C_7), 165.8 (C_2), 169.8 (C_8)
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HB7**	45.8 [^{1}J(^{119}Sn-^{13}C) = 653 Hz] δ(Sn-CH_2), 109.2, 110.9, 117.4, 118.2, 120.4, 123.3, 123.6, 126.8, 127.2, 127.6, 128.0, 128.8, 128.9, 130.2, 131.1, 133.3, 135.0, 135.5, 136.8, 137.9, 155.5, 163.6 (C_7), 168.6 (C_2), 169.2 (C_8)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.8c
^{13}C NMR chemical shifts for [*N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

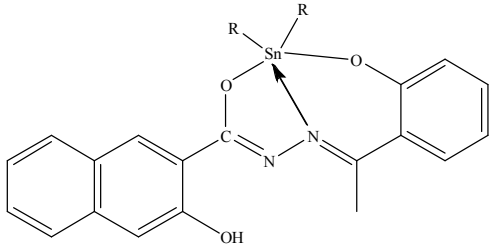
Complex	Assignments [δ(^{13}C)/ppm]
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HC1**	1.9 [^{1}J(^{119}Sn-^{13}C) = 660 Hz] δ(Sn-Me), 108.4, 111.1, 116.9, 117.8, 121.8, 123.4, 124.0, 126.1, 128.1, 128.8, 131.0, 132.4, 135.6, 136.8, 155.3, 160.3 (C_7), 165.1 (C_2), 170.1 (C_8)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HC2**	13.6, 22.8 [^{1}J(^{119}Sn-^{13}C) = 593 Hz], 26.4 [^{3}J(^{119}Sn-^{13}C) = 79 Hz], 26.7 [^{2}J(^{119}Sn-^{13}C) = 33 Hz] δ(Sn-Bu), 108.1, 111.1, 111.8, 118.0, 123.4, 123.8, 126.1, 127.3, 128.0, 130.9, 132.3, 135.5, 136.8, 138.2, 155.4, 160.0 (C_7), 165.7 (C_2), 170.3 (C_8)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HC3**	108.4, 111.4, 116.5, 117.0, 122.2, 123.5, 123.7, 126.2, 127.4, 128.5 [^{3}J(^{119}Sn-^{13}C) = 90 Hz], 128.9, 129.2, 130.9, 131.2, 132.7, 135.7, 136.1, 136.5 [^{2}J(^{119}Sn-^{13}C) = 24 Hz], 136.9, 138.0 [^{1}J(^{119}Sn-^{13}C) = 582 Hz], 155.4, 160.3 (C_7), 165.8 (C_2), 170.1 (C_8)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HC4**	26.5, 28.8 [^{3}J(^{119}Sn-^{13}C) = 80 Hz], 29.9 [^{2}J(^{119}Sn-^{13}C) = 21 Hz], 43.8 [^{1}J(^{119}Sn-^{13}C) = 708 Hz] δ(Sn-Cyh), 108.9, 111.1, 116.3, 117.9, 121.3, 123.5, 124.9, 126.2, 128.3, 129.0, 131.2, 132.5, 135.6, 136.9, 155.6, 163.6 (C_7), 168.4 (C_2), 169.0 (C_8)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HC5**	8.6 [^{1}J(^{119}Sn-^{13}C) = 776 Hz] δ(Sn-CH_2), 108.8, 111.7, 112.5, 118.1, 118.3, 119.7, 120.7, 123.9, 124.2, 126.3, 127.1, 128.7, 128.8, 129.3, 129.9, 130.1, 132.5, 134.2, 136.5, 138.1, 155.0, 163.6 (C_7), 168.4 (C_2), 169.0 (C_8)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HC6**	9.5 [^{1}J(^{119}Sn-^{13}C) = 746 Hz] δ(Sn-CH_2), 103.2, 104.8, 116.5, 118.1, 118.3, 119.7, 120.7, 124.2, 125.0, 126.2, 128.6, 129.1, 129.5, 130.7, 131.7, 133.2, 134.8, 136.6, 138.0, 141.5, 152.6, 163.6 (C_7), 167.0 (C_2), 172.2 (C_8)
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HC7**	8.9 [^{1}J(^{119}Sn-^{13}C) = 697 Hz] δ(Sn-CH_2), 111.1, 118.5, 120.5, 124.1, 124.3, 126.4, 127.0, 127.3, 128.0, 128.4, 128.7, 129.0, 129.5, 130.8, 131.3, 133.1, 134.2, 136.5, 138.1, 141.7, 155.4, 164.5 (C_7), 167.2 (C_2), 171.0 (C_8)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.8d
^{13}C NMR chemical shifts for {*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

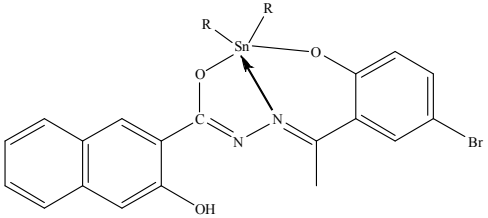
Complex	Assignments [$\delta(^{13}C)$/ppm]
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HD1**	5.4 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 678 Hz], 19.4 (C_{19}), 110.9, 115.2, 118.1, 118.2, 119.7, 122.9, 123.3, 126.1, 126.5, 127.3, 128.0, 128.9, 130.5, 130.9, 134.3, 136.7, 155.6, 168.5 (C_7), 169.7 (C_8)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HD2**	20.0 (C_{19}), 13.6, 24.9 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 520 Hz], 25.9 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 80 Hz], 26.7 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 28 Hz] δ(Sn-Bu), 110.8, 114.3, 120.3, 122.4, 123.9, 125.2, 125.8, 126.0, 126.8, 128.4, 128.9, 129.1, 131.9, 136.0, 137.4, 155.1, 160.5 (C_7), 168.0 (C_8)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HD3**	18.5 (C_{19}), 110.9, 117.7, 118.6, 119.0, 123.8, 126.0, 126.4, 127.1, 128.1, 128.8 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 98 Hz], 129.1, 130.6, 131.5, 132.4, 133.5, 133.9, 134.8, 135.2 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 40 Hz], 136.1, 136.4[$^{1}J(^{119}Sn\text{-}^{13}C)$ = 634 Hz], 152.9, 155.5, 159.8 (C_7), 169.2 (C_8)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HD4**	20.0 (C_{19}), 26.5, 28.8 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 78 Hz], 29.9 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 24 Hz], 43.8 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 590 Hz] δ(Sn-Cyh), 108.6, 110.9, 118.4, 121.3, 123.3, 124.8, 126.1, 127.4, 128.0, 128.9, 129.4, 130.9, 132.4, 136.5, 136.8, 155.7, 164.7 (C_7), 169.2 (C_8)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HD5**	9.0 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 776 Hz] δ(Sn-CH_2), 19.8 (C_{19}), 111.1, 118.9, 124.3, 126.2, 127.2, 127.8, 128.2, 128.6, 128.9, 129.1, 129.4, 130.4, 131.0, 132.8, 136.2, 154. 8, 167.1(C_7), 169.2 (C_8)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)tin(IV), **HD6**	9.0 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 697 Hz] δ(Sn-CH_2), 18.8 (C_{19}), 110.8, 119. 3, 122.7, 124.3, 126.0, 126.2, 127.5, 128.4, 129.2, 129.8, 130.4, 131.3, 135.8, 138.2, 155.0, 160.6 (C_7), 167.5 (C_8)
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)tin(IV), **HD7**	8.7 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 523 Hz] δ(Sn-CH_2), 20.0 (C_{19}), 110.8, 118.4, 119.9, 122.3, 123.8, 125.4, 125.9, 126.9, 127.9, 128.3, 129.4, 130.2, 131.9, 136.0, 138.3, 155.0, 160.2 (C_7), 167.1 (C_8)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.8e
^{13}C NMR chemical shifts for {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

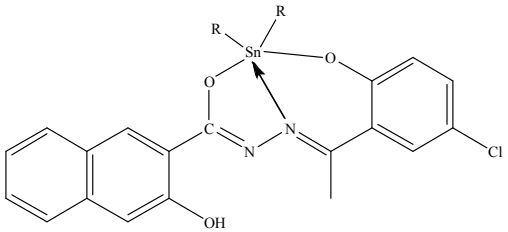
Complex	Assignments [$\delta(^{13}C)$/ppm]
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HE1**	0.2 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 616 Hz] δ(Sn-Me), 20.0 (C_{19}), 111.1, 115.3, 118.1, 121.3,123.5, 124.9, 126.2, 127.4, 128.3, 129.0, 131.2, 132.5, 136.9, 138.0, 155.6, 163.6 (C_7), 168.4 (C_2), 169.0 (C_8)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HE2**	19.9 (C_{19}), 13.7, 21.5 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 590 Hz], 26.2 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 79 Hz], 27.2 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 30 Hz] δ(Sn-Bu), 111.1, 116.2, 118.5, 123.5, 124.4, 126.2, 127.5, 128.2, 129.0, 129.5, 131.1, 133.9, 136.9, 155.7, 163.7 (C_7), 168.1 (C_2), 169.1 (C_8)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HE3**	20.0 (C_{19}), 111.0, 116.0, 118.8, 123.9, 124.3, 126.3, 127.2, 127.4, 128.7 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 99 Hz], 129.0, 129.2, 129.5, 130.8, 131.2, 131.8, 135.2, 135.4 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 20 Hz], 136.2, 136.9, 137.9 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 656 Hz], 155.7, 126.0 (C_7), 167.2 (C_2), 169.8 (C_8)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dicyclohexyltin(IV), **HE4**	19.8 (C_{19}), 26.5, 28.5 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 68 Hz], 30.1 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 24 Hz], 40.2 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 582 Hz] δ(Sn-Cyh), 108.6, 110.9, 118.4, 121.3, 123.3, 124.8, 126.1, 127.4, 128.0, 128.9, 130.9, 132.4, 136.5, 136.8, 155.7, 164.7 (C_7), 167.7 (C_2), 169.2 (C_8)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HE5**	9.0 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 701 Hz] δ(Sn-CH_2), 18.4 (C_{19}), 111.0, 124.3, 124.4, 125.6, 126.2, 127.0, 127.3, 127.6, 127.8, 128.2, 128.6, 128.7, 129.0, 129.2, 129.4, 129.8, 130.9, 136.2, 136.3, 149.4, 154.3, 164.5 (C_7), 167.2 (C_2), 169.8 (C_8)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **HE6**	8.8 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 701 Hz] δ(Sn-CH_2), 18.3 (C_{19}), 110.6, 123.9, 124.9, 125.8, 126.2, 126.3, 126.8, 127.2, 127.8, 128.3, 128.6, 128.9, 129.2, 130.9, 132.3, 132.8, 135.5, 136.4, 136.6, 138.2, 155.4, 164.1 (C_7), 167.7 (C_2), 169.8 (C_8)
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **HE7**	8.9 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 720 Hz] δ(Sn-CH_2), 18.2 (C_{19}), 111.0, 118.9, 124.2, 126.1, 127.1, 128.4, 128.6, 128.7, 129.1, 129.4, 129.8, 130.0, 131.2, 132.5, 135.3, 136.1, 136.4, 139.5, 141.7, 154.9, 156.1, 164.5 (C_7), 167.0 (C_2), 169.0 (C_8)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.8f
^{13}C NMR chemical shifts for {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

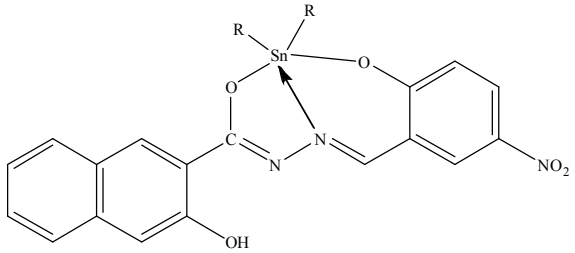
Complex	Assignments [$\delta(^{13}C)$/ppm]
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HF1**	0.2 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 616 Hz] δ(Sn-Me), 19.9 (C_{19}), 111.1, 122.6, 123.5, 124.4, 126.2, 127.4, 128.0, 128.3, 129.0, 129.6, 130.2, 131.2, 134.1, 136.9, 155.6, 163.1 (C_7), 168.5 (C_2), 169.0 (C_8)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HF2**	19.8(C_{19}), 13.6, 21.4 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 610 Hz], 26.5 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 79 Hz], 27.0 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 35 Hz] δ(Sn-Bu), 111.0, 122.1, 123.4, 124.3, 126.1, 127.0, 127.4, 128.1, 128.5, 128.9, 129.4, 131.0, 133.8, 136.8, 155.6, 163.7 (C_7), 168.0 (C_2), 169.0 (C_8)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HF3**	19.9 (C_{19}), 111.2, 117.9, 121.1, 122.6, 123.0, 123.6, 124.8, 126.2, 127.1, 127.5, 128.3, 129.0 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 93 Hz], 129.1, 129.8, 130.9, 131.2, 134.4, 136.3 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 20 Hz], 136.9, 137.7[$^{1}J(^{119}Sn\text{-}^{13}C)$ = 751 Hz], 155.6, 162.1 (C_7), 168.5 (C_2), 169.8 (C_8)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dicyclohexyltin(IV), **HF4**	19.8 (C_{19}), 21.5, 26.6 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 70 Hz], 27.2 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 31 Hz], 45.9 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 708 Hz] δ(Sn-Cyh), 109.0, 111.0, 118.3, 121.4, 123.4, 124.8, 126.1, 127.3, 128.2, 128.9, 131.0, 132.5, 136.7 136.9, 155.6, 164.1 (C_7), 167.9 (C_2), 169.0 (C_8)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HF5**	8.7 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 535 Hz] δ(Sn-CH_2), 19.4 (C_{19}), 110.8, 114.2, 117.8, 118.1, 122.2, 122.6, 123.4, , 124.9, 125.6, 126.3, 127.3, 128.4, 128.6, 129.0, 129.4, 131.1, 132.7, 133.7, 136.8, 137.1, 155.4, 159.7, 163.9 (C_7), 168.6 (C_2), 169.5 (C_8)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **HF6**	8.5 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 580 Hz] δ(Sn-CH_2), 19.4 (C_{19}), 110.7, 112.3, 114.7, 117.8, 122.4, 123.3, 124.0, 125.0, 126.2, 126.8, 128.0, 128.3, 129.1, 130.4, 132.5, 133.6, 135.8, 136.7, 137.1, 155.9, 159.5, 163.5 (C_7), 164.4 (C_2), 168.6 (C_8)
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **HF7**	8.2 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 580 Hz] δ(Sn-CH_2), 18.8 (C_{19}), 110.3, 114.4, 118.8, 120.3, 121.6, 123.4, 123.9, 125.9, 126.8, 127.3, 128.1, 128.6, 128.9, 129.6, 129.9, 130.2, 132.4, 136.2, 138.6, 145.9, 155.6, 163.7 (C_7), 164.7 (C_2), 167.5 (C_8)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.8g
^{13}C NMR chemical shifts for [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

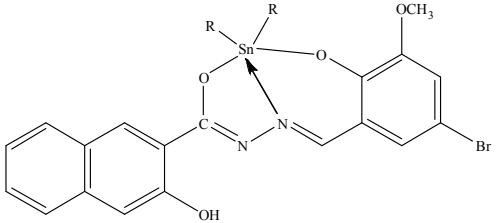
Complex	Assignments [$\delta(^{13}C)$/ppm]
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HG1**	2.4 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 622 Hz] δ(Sn-Me), 111.3, 115.3, 117.4, 122.5, 123.6, 125.3, 126.1, 127.2, 128.3, 128.8, 130.1, 131.0, 136.9, 138.2, 155.3, 160.0 (C_7), 170.5 (C_2), 171.3 (C_8)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HG2**	13.5, 23.3 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 646 Hz], 26.4 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 78 Hz], 26.8 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 35 Hz] δ(Sn-Bu), 111.3, 115.4, 117.5, 122.5, 123.5, 126.2, 127.3, 128.3, 128.9, 130.1, 131.1, 131.2, 136.9, 138.2, 155.4, 159.9 (C_7), 170.9 (C_2), 172.0 (C_8)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HG3**	111.6, 114.3, 115.6, 117.3, 123.0, 123.7, 126.3, 127.4, 128.5, 128.8, 129.0 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 99 Hz], 129.4, 130.4, 131.2, 131.4, 136.0 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 18 Hz], 137.1, 137.2 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 688 Hz], 138.8, 151.0, 155.4, 160.0 (C_7), 170.5 (C_2), 171.8 (C_8)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HG4**	26.2, 28.7 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 85 Hz], 29.9 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 39 Hz], 41.7 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 734 Hz] δ(Sn-Cyh), 111.3, 115.5, 117.7, 122.5, 123.5, 126.2, 127.3, 128.2, 128.9, 129.5, 130.0, 131.1, 136.9, 138.0, 155.4, 159.6 (C_7),171.0 (C_2), 172.6 (C_8)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HG5**	8.7 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 709 Hz] δ(Sn-CH_2), 103.9, 110.3, 117.3, 119.0, 119.7, 120.5, 121.3, 123.3, 123.8, 124.3, 125.9, 126.8, 127.4, 127.9, 128.8, 130.0, 131.1, 135.7, 136.0, 138.8, 154.5, 164.5 (C_7), 169.0 (C_2), 173.0 (C_8)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HG6**	9.4 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 630 Hz] δ(Sn-CH_2), 110.7, 111.1, 117.3, 119.2, 121.9, 122.1, 123.9, 124.5, 124.9, 126.3, 126.6, 128.5, 128.9, 129.1, 129.2, 130.7, 131.6, 132.6, 136.5, 137.2, 155.6, 159.1 (C_7), 169.2 (C_2), 172.8 (C_8)
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HG7**	8.9 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 580 Hz] δ(Sn-CH_2), 111.2, 118.2, 120.2, 122.2, 123.0, 123.4, 124.7, 125.2, 126.4, 127.0, 127.4, 128.3, 129.2, 129.4, 129.7, 131.2, 131.6, 135.0, 140.1, 154.4, 156.0, 160.5 (C_7), 164.8 (C_2), 171.2 (C_8)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

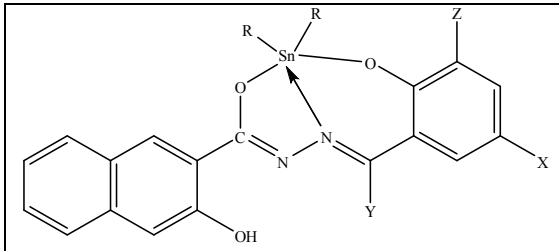
Table 4.3.8h
^{13}C NMR chemical shifts for [*N'*-(5-bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	Assignments [$\delta(^{13}C)$/ppm]
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HH1**	2.6 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 579 Hz] δ(Sn-Me), 56.5 (-O<u>C</u>H$_3$), 107.6, 111.2, 117.0, 119.1, 123.4, 126.1, 126.9, 127.4, 128.1, 128.2, 128.8, 131.0, 136.9, 152.3, 155.5, 156.5 (C_7), 160.4 (C_2), 170.1 (C_8)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HH2**	13.8, 25.2 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 708 Hz], 26.9 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 79 Hz], 27.9 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 35 Hz] δ(Sn-Bu), 56.1 (-O<u>C</u>H$_3$), 105.8, 110.7, 118.0, 118.8, 123.8, 126.1, 127.1, 128.4, 129.0, 129.3, 129.8, 130.3, 136.4, 152.3, 155.5, 157.9 (C_7), 160.0 (C_2), 169.6 (C_8)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diphenyltin(IV), **HH3**	56.7 (-O<u>C</u>H$_3$), 108.1, 111.4, 117.2, 117.8, 119.7, 123.5, 126.2, 126.9, 127.5, 128.2, 129.0, 129.1, 129.2 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 104 Hz], 130.9, 131.1, 136.2[$^{2}J(^{119}Sn\text{-}^{13}C)$ = 19 Hz], 136.3, 137.0, 138.0 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 758 Hz], 152.8, 155.5, 157.8 (C_7), 160.5 (C_2), 170.2 (C_8)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HH4**	20.3, 28.5 [$^{3}J(^{119}Sn\text{-}^{13}C)$ = 67 Hz], 29.9 [$^{2}J(^{119}Sn\text{-}^{13}C)$ = 30 Hz], 42.0 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 688 Hz] δ(Sn-Cyh), 56.3 (-O<u>C</u>H$_3$), 109.1, 110.4, 115.9, 120.2, 120.8, 122.0, 123.5, 125.8, 126.6, 128.0, 128.7, 130.3, 134.9, 136.0, 155.1, 159.2 (C_7), 165.6 (C_2), 170.4 (C_8)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibenzyltin(IV), **HH5**	8.6 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 709 Hz] δ(Sn-CH$_2$), 56.3 (-O<u>C</u>H$_3$), 110.8, 117.1, 119.1, 124.1, 126.0, 126.6, 127.0, 127.4, 127.8, 128.7, 129.6, 130.6, 131.2, 132.3, 133.0, 134.6, 136.3, 138.6, 139.4, 152.5, 155.7, 159.8 (C_7), 167.0 (C_2), 169.0 (C_8)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*o*-chlorobenzyl)tin(IV), **HH6**	8.7 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 709 Hz] δ(Sn-CH$_2$), 56.1 (-O<u>C</u>H$_3$), 110.0, 117.6, 118.9, 123.2, 126.0, 126.7, 127.8, 128.2, 128.7, 129.3, 130.1, 130.9, 131.7, 132.1, 133.1, 134.3, 135.9, 137.0, 138.2, 152.0, 156.1, 158.8 (C_7), 168.5 (C_2), 169.6 (C_8)
[*N'*-(5-Bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*p*-chlorobenzyl)tin(IV), **HH7**	9.1 [$^{1}J(^{119}Sn\text{-}^{13}C)$ = 645 Hz] δ(Sn-CH$_2$), 56.9 (-O<u>C</u>H$_3$), 111.1, 116.7, 120.2, 122.3, 124.6, 126.4, 127.4, 128.7, 128.9, 129.3, 130.2, 131.1, 131.6, 132.0, 133.3, 134.5, 136.4, 138.3, 146.9, 149.7, 153.2, 154.2 (C_7), 164.4 (C_2), 168.2 (C_8)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.9
^{119}Sn NMR chemical shifts of diorganotin complexes, **HA1-HH7**

	^{119}Sn NMR chemical shifts [δ(^{119}Sn)/ppm]						
	R = Me	R = Bu	R = Ph	R = Cy	R = Bz	R = *o*-ClBz	R = *p*-ClBz
HA : X = H, Y = H, Z = H	159.7	-197.5	-338.9	-276.5	-322.0	-226.6	-529.3
HB : X = Br, Y = H, Z = H	-157.5	-196.4	-340.5	-262.7	-217.6	-278.9	-500.9
HC : X = Cl, Y = H, Z = H	-157.4	-196.5	-340.4	-245.9	-404.0	-163.1	-500.7
HD : X = H, Y = CH_3, Z = H	-177.7	-261.5	-445.4	-268.9	-262.3	-334.6	-513.4
HE : X = Br, Y = CH_3, Z = H	-176.2	-216.7	-344.1	-283.9	-405.6	-394.1	-514.3
HF : X = Cl, Y = CH_3, Z = H	-176.1	-216.5	-355.3	-283.1	-275.6	-283.8	-413.5
HG : X = NO_2, Y = H, Z = H	-156.1	-195.6	-514.3	-263.4	-252.6	-426.7	-454.7
HH : X = Br, Y = H, Z = OCH_3	-285.4	-297.5	-462.8	-463.5	-317.9	-301.8	-337.2

4.3.4 Electronic Spectra

The electronic spectral data of the Schiff base ligands and diorganotin complexes in acetonitrile (CH_3CN) were recorded in the 190-600 nm regions. As some of the complexes had poor solubility in CH_3CN and most solvents, some of the complexes showed weak intensity in the energy band. The selected spectra data for the free tridentate Schiff base ligands **HA**, **HB**, **HC**, **HD**, **HE**, **HF**, **HG** and **HH** and the diorganotin complexes are given in tables 4.3.10 and 4.3.11, respectively.

In general, the absorption bands of the Schiff base ligands could be classified into two absorption regions of 300-329 nm and 330-440 nm regions. Molecular orbital calculations indicated that the band in the 385-420 nm region was $n \longrightarrow \pi^*$ electronic transition type involving promotion of an electron of the free electron pair on the nitrogen to an antibonding π-orbital of the azomethine group. Therefore, an intense band in the 330-340 nm could be attributed to the $n \longrightarrow \pi^*$ electronic transitions which were associated with azomethine chromophore [Bella *et al.*, 1997]. However, in the diorganotin complexes, this band showed a small bathochromic shift, probably because only one of the azomethine nitrogen atoms was coordinated to the metal centre in the complexes. Bathochromic shift is related to the donation of the lone pair of electrons to the metal centre due to the coordination of the azomethine group to the tin centre.

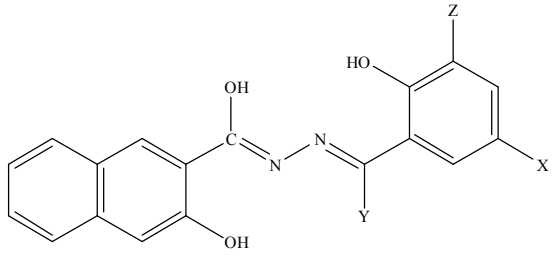
The ligand band between 300-310 nm was assigned as $\pi \longrightarrow \pi^*$ electronic transition which occurred in all the free tridentate Schiff bases ligands and the organotin complexes. This $\pi \longrightarrow \pi^*$ electronic transition involved the molecular orbitals of the C=N chromophore, the phenyl and naphthalene rings.

For the **HD**, **HE** and **HF** complexes, the $\pi \longrightarrow \pi^*$ electronic transition showed a strong bathochromic shift between 5-30 nm. This could be attributed to the presence of the electron-donating methyl group on the carbonyl carbon, which increased the number of electrons in the phenyl ring upon complexation.

For the **HG** series, a hypsochromic shift in the $n \longrightarrow \pi^*$ electronic transition could not be explained extensively due the presence of the electron-withdrawing 5-nitro group in the phenyl rings. This could be attributed to the delocalization of the number of electrons in the phenyl ring.

Table 4.3.10
Electronic spectral data for the NAP ligands

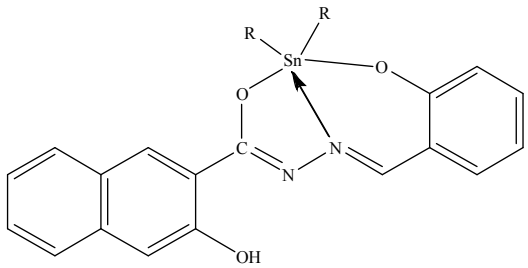
Ligands	Intraligand transfer transition	
	π-π*	n-π*
N'-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA**	305	331
N'-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB**	307	335
N'-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC**	307	333
N'-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HD**	307	332
N'-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HE**	305	340
N'-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HF**	304	339
N'-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG**	304	340
N'-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphthohydrazide, **HH**	307	340



HA: X = H, Y= H, Z = H ; **HB**: X = Br, Y = H, Z = H;
HC: X = Cl, Y = H, Z = H; **HD**: X = H, Y = CH_3, Z = H;
HE: X= Br, Y = CH_3, Z = H; **HF**: X = Cl, Y = CH_3, Z = H;
HG: X = NO_2, Y = H , Z = H; **HH**: X = Br, Y = H, Z = OCH_3

Table 4.3.11a
Electronic spectral data for [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

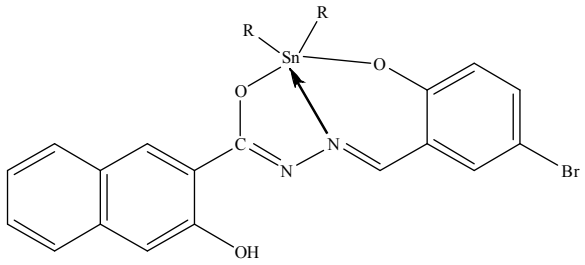
Complex	Intraligand transfer transition	
	π-π^*	n-π^*
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dimethyltin(IV), **HA1**	308	335, 409
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibutyltin(IV), **HA2**	309	335, 413
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]diphenyltin(IV), **HA3**	308	343, 427
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dicyclohexyltin(IV), **HA4**	308	335, 416
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibenzyltin(IV), **HA5**	308	337, 408
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*o*-chlorobenzyl)tin(IV), **HA6**	309	337, 415
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*p*-chlorobenzyl)tin(IV), **HA7**	308	335, 409



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.11b
Electronic spectral data for [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

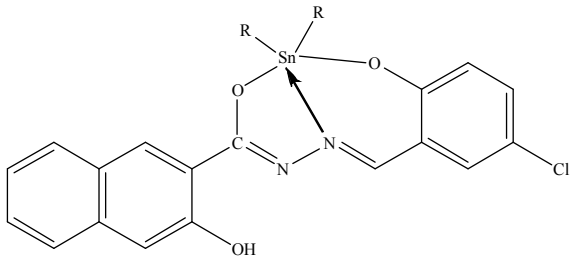
Complex	Intraligand transfer transition	
	π-π^*	n-π^*
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HB1**	310	338,420
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HB2**	310	339, 424
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HB3**	310	340, 420
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HB4**	310	339, 427
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HB5**	308	339, 425
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HB6**	310	336, 422
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HB7**	309	334, 411



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.11c
Electronic spectral data for [*N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

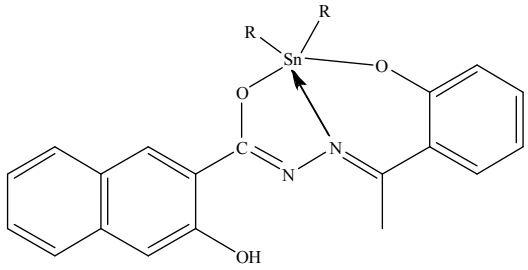
Complex	Intraligand transfer transition	
	π-π^*	n-π^*
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HC1**	310	338, 421
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HC2**	309	338, 423
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HC3**	310	338, 425
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HC4**	310	339, 426
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HC5**	310	341, 425
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HC6**	310	338, 418
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HC7**	309	333, 415



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.11d
Electronic spectral data for {*N'*- [1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

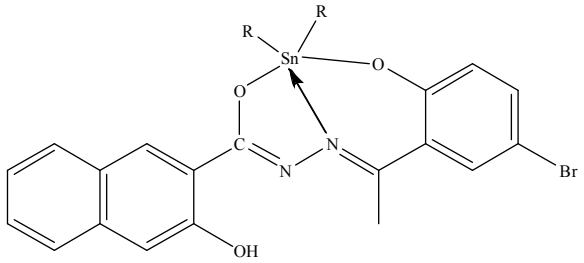
Complex	Intraligand transfer transition	
	π-π^*	n-π^*
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HD1**	312	334, 398
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HD2**	307	333, 396
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HD3**	311	334, 402
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HD4**	312	333, 401
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HD5**	310	333, 400
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*o*-chlorobenzyl)-tin(IV), **HD6**	311	337, 399
{*N'*-[1-(2-Oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(*p*-chlorobenzyl)-tin(IV), **HD7**	309	337, 400



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.11e
Electronic spectral data for {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

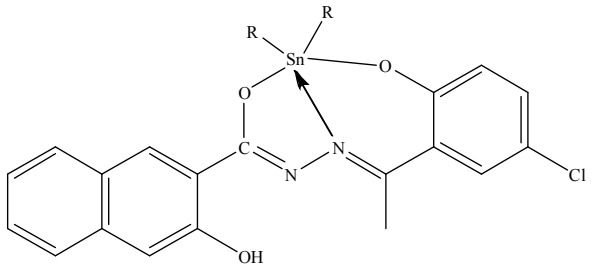
Complex	Intraligand transfer transition	
	π-π^*	n-π^*
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HE1**	320	331, 399
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HE2**	322	332, 404
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HE3**	328	345, 410
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dicyclohexyltin(IV), **HE4**	323	346, 406
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HE5**	327	341, 405
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **HE6**	326	340, 410
{*N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **HE7**	326	338, 409



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 4.3.11f
Electronic spectral data for {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphtho-hydrazidato}diorganotin complexes

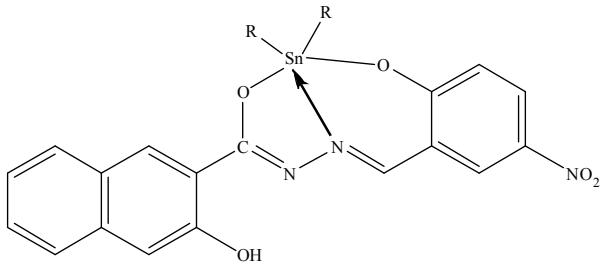
Complex	Intraligand transfer transition	
	π-π^*	n-π^*
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HF1**	320	331, 401
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HF2**	321	332, 404
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), **HF3**	320	333, 399
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dicyclohexyltin(IV), **HF4**	322	335, 407
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), **HF5**	327	338, 399
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **HF6**	322	336, 404
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **HF7**	326	338, 409



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

Table 4.3.11g
Electronic spectral data for [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]diorganotin complexes

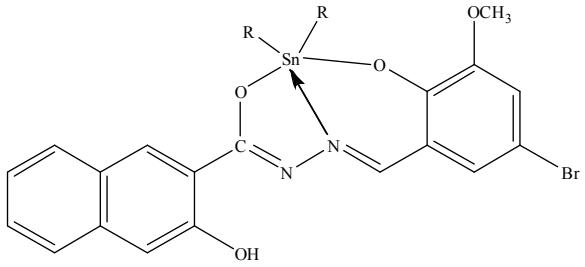
Complex	Intraligand transfer transition	
	π-π^*	n-π^*
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HG1**	301	321, 396
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HG2**	300	322, 399
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HG3**	309	328, 394
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HG4**	312	324, 402
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HG5**	308	328, 400
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HG6**	301	321, 401
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)tin(IV), **HG7**	300	322, 401



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p* -ClBz)

Table 4.3.11h
Electronic spectral data for [*N'*-(5-bromo-3-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Complex	Intraligand transfer transition	
	π-π^*	n-π^*
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]dimethyltin(IV), **HH1**	312	340, 429
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibutyltin(IV), **HH2**	312	341, 434
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]diphenyltin(IV), **HH3**	312	343, 427
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]dicyclohexyltin(IV), **HH4**	310	342, 430
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibenzyltin(IV), **HH5**	311	342, 426
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*o*-chlorobenzyl)tin(IV), **HH6**	312	345, 423
[*N'*-(5-Bromo-3-methoxy-2-oxido-benzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*p*-chlorobenzyl)tin(IV), **HH7**	311	345, 414

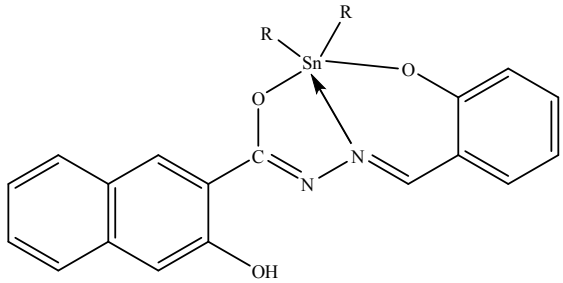


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p* -chlorobenzyl (*p*-ClBz)

4.3.5 X-Ray Structures

[*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin(IV), R = Bu (HA2), R = Cy (HA4) and R = *o*-ClBz (HA6)

The complexes [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HA2**, [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HA4** and [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HA6** were obtained from the reaction between *N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide with the respective diorganotins. **HA2** crystallizes in monoclinic, $P2_1/c$ space group, **HA4** crystallizes in monoclinic, $P2_1/n$ space group while **HA6** crystallizes in triclinic, $P\bar{1}$ space group. Details of the crystallographic parameters are given in table 4.3.12 and the selected bond lengths and angles of **HA2**, **HA4** and **HA6** are tabulated in table 4.3.13. The molecular structures of complexes **HA2**, **HA4** and **HA6** are shown in figure 4.3.2a, 4.3.2b and 4.3.2c respectively.



R = Bu (**HA2**), Cy (**HA4**), *o*-ClBz (**HA6**)

As shown in figure 4.3.2b, there are two unique molecules in the asymmetric units of complex **HA4** whereas for complexes **HA2** and **HA6**, only one discrete molecule was found in each of the crystal structure. In each case, the tin atom was five-coordinated and adopted a distorted *cis*-C_2NO_2Sn trigonal-bipyramidal geometry. The equatorial plane was made up from the imine nitrogen and two alkyls/aryls from the

molecules in the asymmetric total angle subtended at tin for the first and second molecules in **HA4** were 359.59^{o} and 360.54^{o} respectively. For complex **HA6,** the total angle around the tin atom was 360.02^{o}.

In **HA2**, the O(2)-Sn(1)-N(1)-N(2)-C(8) plane and O(1)-Sn(1)-N(1)-C(7)-C(1)-C(2) plane made an angle of 1.7^{o}. As **HA4** had two discrete molecules, the dihedral angle between the planes varied slightly for the two molecules. In the first molecule, the dihedral angle was 6.9^{o} whereas the dihedral angle for the second molecule was smaller, at 5.7^{o}. For **HA6**, the dihedral angle was 6.4^{o}. This indicated that the equatorial planes for each of the complexes were rather planar, as the deviation value was nearly zero.

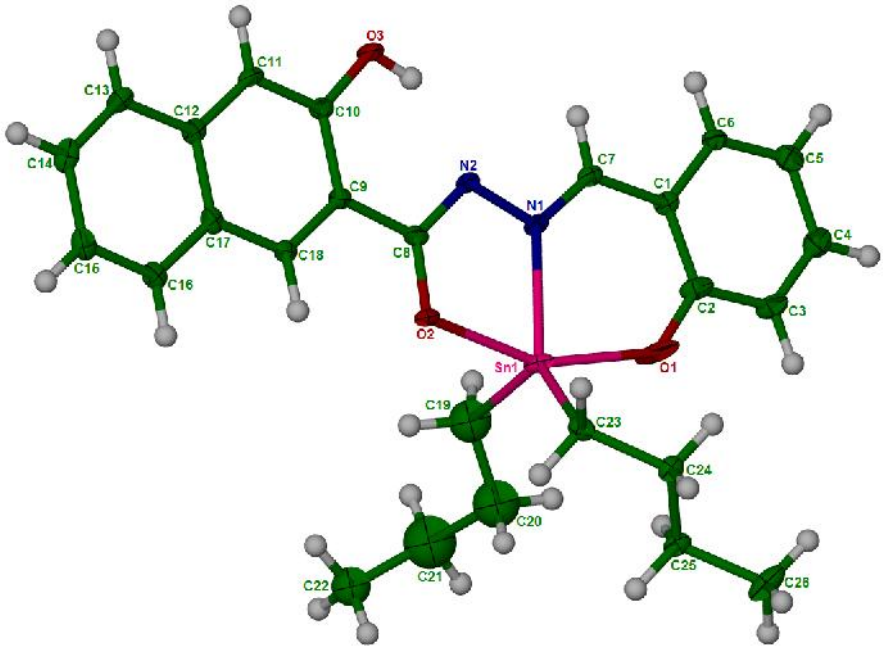
For complex **HA4**, the apical angle, O(1)-Sn(1)-O(2) was 152.11(11)^{o} and O(4)-Sn(2)-O(5) was 154.33(10)^{o}. As can be observed, both the molecules were quite similar as the difference in the apical angle was about 2^{o}. For complexes **HA2** and **HA6**, the apical angles were 155.76(16)^{o} and 153.0(2)^{o} respectively. The C_i-Sn(1)-C_i*'* angle for the **HA4** was 132.59(17)^{o} and 122.03(14)^{o}, and 125.6(3)^{o} in **HA6**.

In **HA2**, **HA4** and **HA6**, the complexes were on the whole stabilized by a strong intramolecular hydrogen bonding between N(2) and O(3)-H(3). The N(2)-O(3) bond distances were almost the same for all three complexes [**HA2** : 2.601(6) Å, **HA4**: 2.596(4) and 2.578(4) Å and **HA6**: 2.596(7) Å]

For **HA4**, a good R_1 value of 0.0399 was obtained after the final refinement of the structure. The presence of a high Q peak near the Sn(1) could not be improved after numerous attempts to constrain or restrain the structure. Similarly for **HA6**, the *R*-

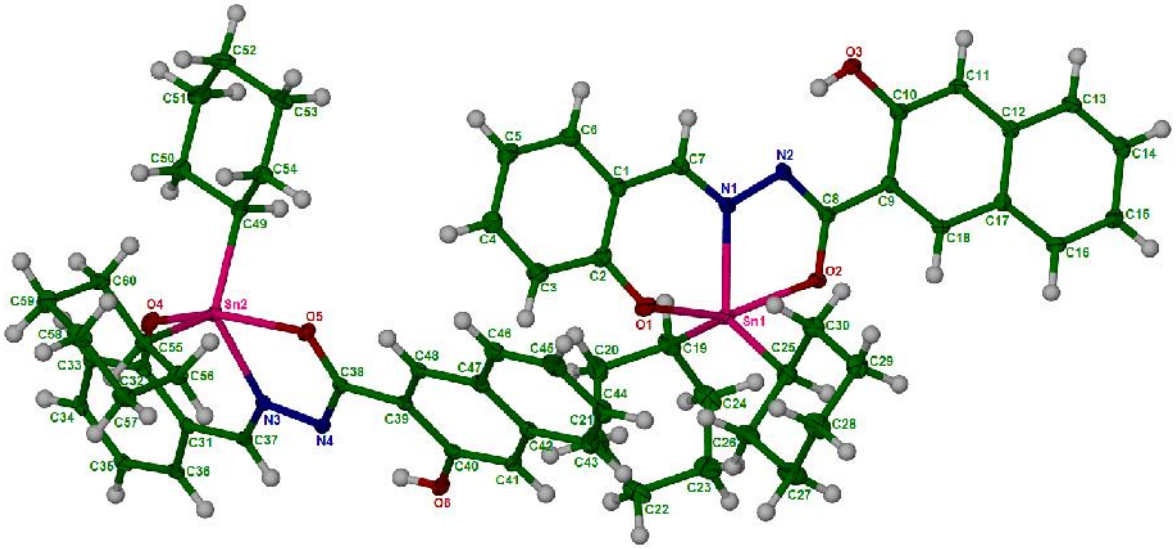
factor value was at 0.062 after the final refinement and the model obtained for the molecular structure was satisfactory. However, due to the presence of four high Q peaks near the tin atom, a better model could not be obtained.

Figure 4.3.2a
Molecular plot of [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HA2**



(note: C19, C20, C21, and C22 were rendered isotropic due to disorder in the butyl chain)

Figure 4.3.2b
Molecular plot of [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HA4**



(note: C26, C27, C28, C29, C30 were rendered isotropic due to disorder in the cyclohexyl ring)

Figure 4.3.2c
Molecular plot of [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*o*-chlorobenzyl)tin(IV), **HA6**

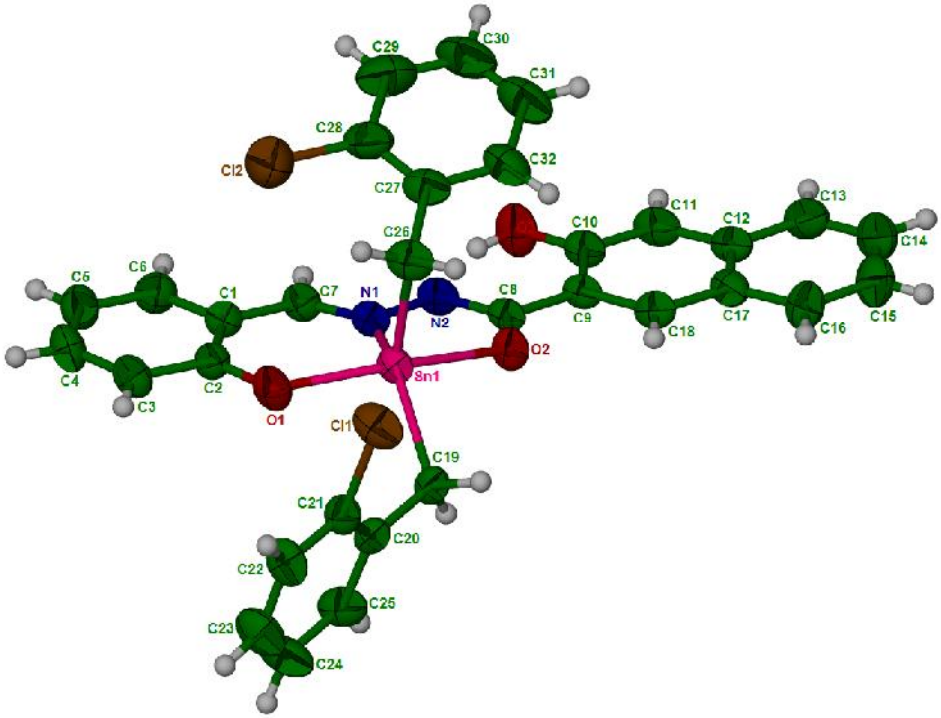


Table 4.3.12
Crystallographic parameters for complexes **HA2**, **HA4** and **HA6**

	HA2	**HA4**	**HA6**
Empirical formula	$C_{26}H_{30}N_2O_3Sn$	$C_{30}H_{34}N_2O_3Sn$	$C_{32}H_{24}Cl_2N_2O_3Sn$
Formula weight	537.21	589.28	674.12
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	9.8546(14)	22.7150(6)	10.2323(6)
b (Å)	33.692(5)	9.2096(3)	11.2177(7)
c (Å)	7.2727(10)	25.4224(7)	14.2188(10)
α (°)	90	90	85.030(4)
β (°)	108.760(2)	101.315(2)	73.222(4)
γ (°)	90	90	63.541(4)
Volume (Å^3)	2286.4(6)	5214.9(3)	1397.24(15)
Z	4	8	2
Calculated density, D_{calc} (Mgm^{-3})	1.561	1.501	1.602
Absorption coefficient, μ (mm^{-1})	1.148	1.014	1.143
F(000)	1096	2416	676
Crystal size (mm)	0.27 x 0.23 x 0.05	0.40 x 0.15 x 0.15	0.30 x 0.15 x 0.10
Limiting indices	$-11 \le h \le 11$, $-40 \le k \le 40$, $-8 \le l \le 8$	$-27 \le h \le 27$, $-10 \le k \le 10$, $-30 \le l \le 2$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-16 \le l \le 16$

Reflections collected / unique	17719 / 4035 [$R_{(int)}$ = 0.0321]	39797 / 9171 [$R_{(int)}$ = 0.0319]	7898 / 4836 [$R_{(int)}$ = 0.0435]
Max. and min. transmission	0.9448 and 0.7468	0.8627 and 0.6871	0.8943 and 0.7255
Data / restraints / parameters	4035 / 0 / 292	9171 / 0 / 651	4836 / 0 / 362
Goodness-of-fit on F^2	1.254	1.025	1.063
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0545, wR_2 = 0.1118	R_1 = 0.0400, wR_2 = 0.0945	R_1 = 0.0662, wR_2 = 0.1742
R indices (all data)	R_1 = 0.0575, wR_2 = 0.1132	R_1 = 0.0448, wR_2 = 0.0981	R_1 = 0.0774, wR_2 = 0.1915
Largest diff. peak and hole ($eÅ^{-3}$)	2.957 and -1.386	5.451 and -1.594	3.390 and -1.186

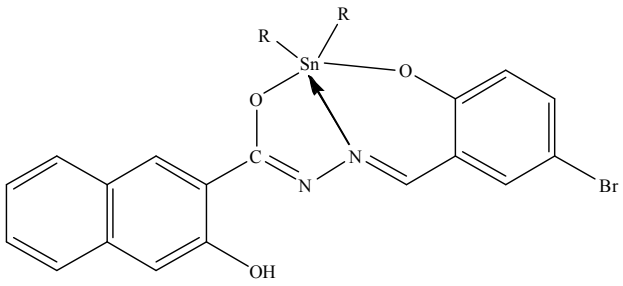
Table 4.3.13
Selected bond lengths (Å) and angles (^{o}) with estimated standard deviation for complexes **HA2**, **HA4** and **HA6**

	HA2	**HA4**	**HA6**
Bond lengths			
Sn(1)-O(1)	2.074(5)	2.076(3), 2.092(3)	2.064(5)
Sn(1)-O(2)	2.155(4)	2.176(3), 2.160(3)	2.155(4)
Sn(1)-N(1)	2.175(5)	2.203(3), 2.186(3)	2.172(5)
Sn(1)-C_i	2.147(7)	2.153(4), 2.152(4)	2.139(6)
Sn(1)-C_i'	2.129(5)	2.131(4), 2.149(5)	2.144(7)
C(2)-O(1)	1.324(7)	1.329(5), 1.323(5)	1.315(7)
C(8)-O(2)	1.289(7)	1.293(5), 1.290(9)	1.289(7)
C(7)-N(1)	1.306(7)	1.297(5), 1.300(5)	1.287(8)
C(8)-N(2)	1.318(7)	1.315(5), 1.318(5)	1.333(8)
N(2)-O(3)	2.601(6)	2.596(4), 2.578(4)	2.596(7)
Bond angles			
O(1)-Sn(1)-O(2)	155.76(16)	152.11(11), 154.33(10)	153.0(2)
C_i-Sn(1)- C_i'	124.8(2)	132.59(17), 122.03(14)	125.6(3)
N(1)-Sn(1)- C_i	109.8(2)	117.10(4), 125.96(13)	127.3(2)
N(1)-Sn(1)- C_i'	124.3(2)	109.85(15), 111.55(13)	104.7(2)

Note:
C_i and C_i'refer to the *ipso*-carbon of the diorganotin moieties attached to the central tin atom

[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diorganotin(IV), R = Me (HB1), R = Bu (HB2), R = Cy (HB4) and R = *o*-ClBz (HB6)

The complexes [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HB1** and [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HB2**; both crystallize in the triclinic, $P\bar{1}$ space group while [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HB4** crystallizes in $P2_1/c$ space group and [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)tin(IV), **HB6** crystallizes in $P2_1/n$ space group. The molecular structures of the complexes are shown in figures 4.3.3a, 4.3.3b, 4.3.3c and 4.3.3d, respectively while the crystallographic data and selected bond lengths and angles are tabulated in tables 4.3.14 and 4.3.15.



R = Me (**HB1**), Bu (**HB2**), Cy (**HB4**), *o*-ClBz (**HB6**)

As observed in their molecular structures, it was found that the tin atom for all the complexes adopted a distorted *cis*-C_2NO_2Sn trigonal-bipyramidal geometry. The trigonal plane consisted of the nitrogen atom, and two alkyl/aryl carbons of the diorganotin moieties. The sum of angles subtended at tin for **HB1** was 359.59°, **HB2** was 360.02°, **HB4** was 359.86° and for **HB6**, it was 359.57°.

The dihedral angle between the O(2)-Sn(1)-N(1)-N(2)-C(8) plane and O(1)-Sn(1)-N(1)-C(7)-C(1)-C(2) plane in **HB1** was 2.1^{o} whereas for **HB2**, it was 4.0^{o}. For **HB4**, the dihedral angle was rather similar to **HB1**, which was 2.3^{o}. All three complexes had a rather flat plane due to the small dihedral angle values. However, for **HB6**, the dihedral angle was 15.4^{o} indicating that the corresponding ligand planes were not co-planar and this could be due to the steric influence from the presence of the two substituted *ortho*-chloro groups in the benzyl rings.

In **HB2**, the Sn(1)-O(1) was 2.057(17) Å and it was shorter than the value reported in **HB1** [2.084(2) Å], **HB4** [2.094(3) Å] and **HB6** [2.076(3) Å]. The angle, C_i-Sn(1)-C_i*'* was 127.84(14)^{o} in **HB1**, 126.0(2)^{o} in **HB2**, 125.81(15)^{o} in **HB4** and 134.30(18)^{o} in **HB6**. The large C_i-Sn(1)-C_i*'* angle in **HB6** could be attributed to the repulsion of the chlorine atoms in the *ortho*-position in the ring on both the aryl rings of the diorganotin moieties.

The axial position for the complexes was occupied by the two deprotonated hydroxyl oxygen atoms. For complex **HB1**, the apical angle, O(1)-Sn(1)-O(2), was 155.27(9)^{o}, **HB2** was 153.96(7)^{o}, **HB4** was 155.97(9)^{o} while for **HB6**, it was 153.25(11)^{o}. These values showed that the apical angle decreased in the order, **HB4**, **HB1**, **HB2** and **HB6**. **HB6** which consisted of the di(*o*-chlorobenzyl)tin moieties showed the smallest apical angle value due to the influence of the electronegativity contribution from the chloro-substituents in the benzyl rings. Lastly, there was a strong intramolecular hydrogen bonding between N(2) and O(3)-H(3) which helped to stabilize the overall molecular structures of **HB1**, **HB2**, **HB4** and **HB6**.

Figure 4.3.3a
Molecular plot of [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dimethyltin(IV), **HB1**

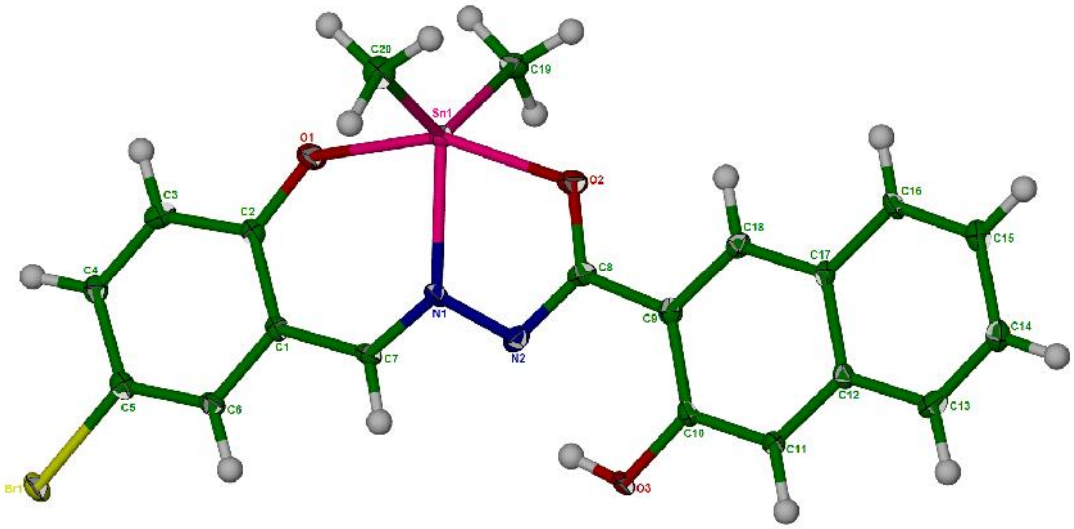


Figure 4.3.3b
Molecular plot of [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dibutyltin (IV), **HB2**

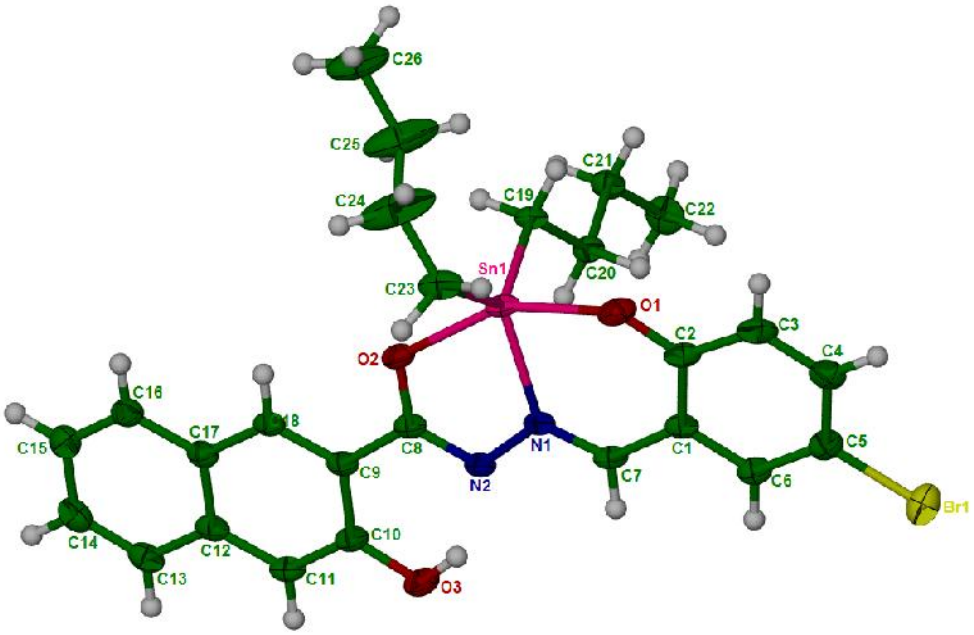


Figure 4.3.3c
Molecular plot of [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]dicyclohexyltin(IV), **HB4**

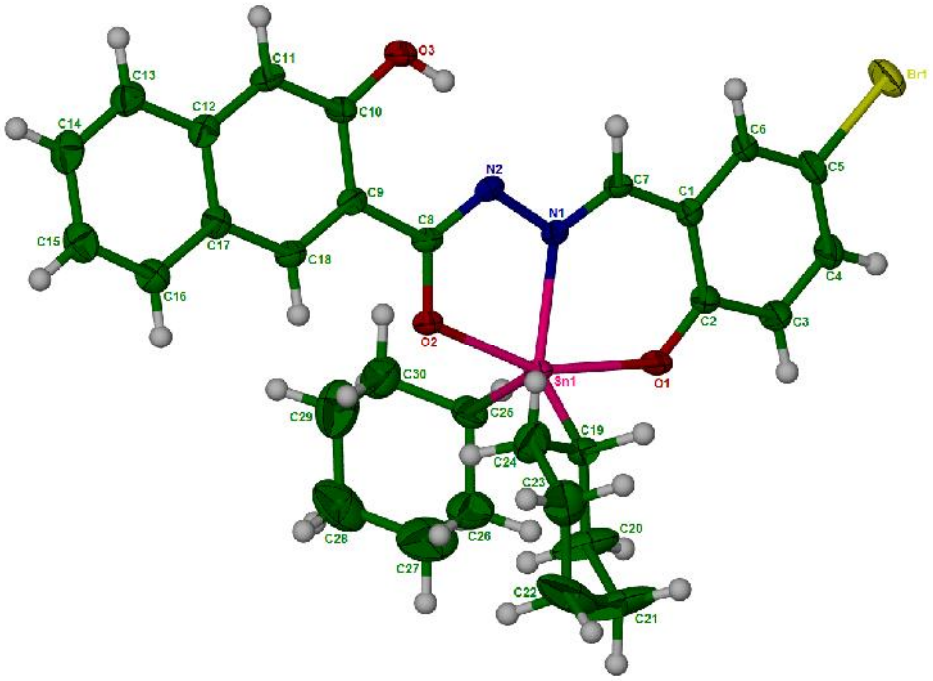


Figure 4.3.3d
Molecular plot of [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphtho-hydrazidato]di(*o*-chlorobenzyl)tin(IV), **HB6**

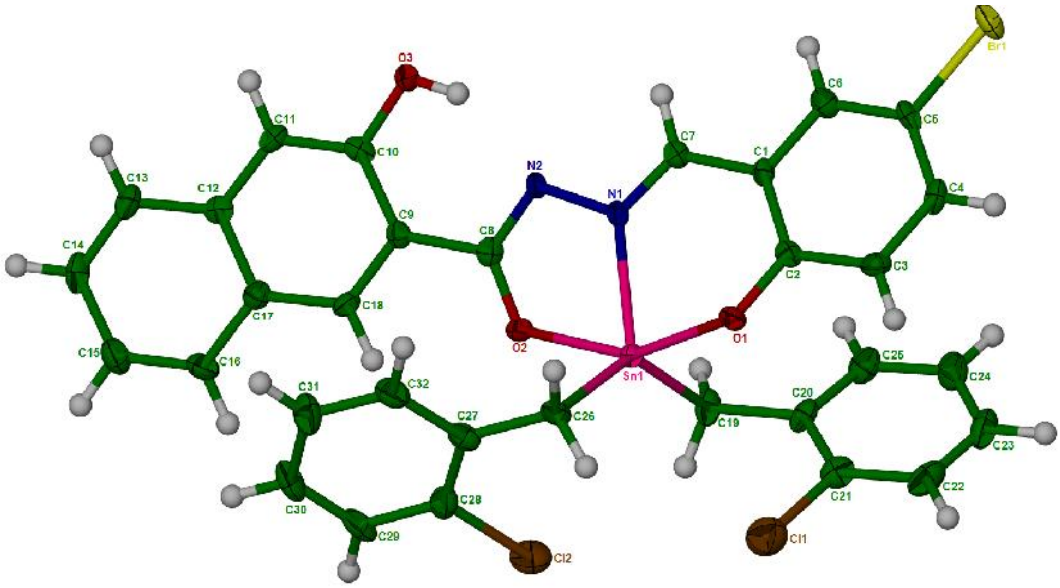


Table 4.3.14
Crystallographic parameter for complexes **HB1**, **HB2**, **HB4** and **HB6**

	HB1	**HB2**	**HB4**	**HB6**
Empirical formula	$C_{20}H_{17}BrN_2O_3Sn$	$C_{26}H_{29}BrN_2O_3Sn$	$C_{30}H_{33}BrN_2O_3Sn$	$C_{32}H_{23}BrCl_2N_2O_3Sn$
Formula weight	531.96	616.11	668.18	753.02
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	6.8662(5)	10.1626(1)	9.2442(2)	17.6531(12)
b (Å)	11.7998(9)	12.2534(1)	9.9949(2)	6.7016(5)
c (Å)	11.9365(9)	12.5583(1)	29.6493(5)	24.2085(16)
α (°)	87.464(1)	62.309(1)	90	90
β (°)	76.128(1)	83.809(1)	94.874(1)	96.069(1)
γ (°)	81.213(1)	65.802(1)	90	90
Volume (Å^3)	927.84(12)	1256.431(19)	2729.54(9)	2847.9(3)
Z	2	2	4	4
Calculated density, D_{calc} (Mgm^{-3})	1.904	1.629	1.626	1.756
Absorption coefficient, μ (mm^{-1})	3.554	2.637	2.434	2.526
F(000)	520	616	1344	1488
Crystal size (mm)	0.39 x 0.37 x 0.09	0.29 x 0.26 x 0.20	0.33 x 0.30 x 0.14	0.20 x 0.05 x 0.05
Limiting indices	$-8 \le h \le 8, -10 \le k \le 15, -15 \le l \le 5$	$-13 \le h \le 3, -15 \le k \le 15, -16 \le l \le 16$	$-10 \le h \le 10, -11 \le k \le 11, -35 \le l \le 35$	$-22 \le h \le 22, -8 \le k \le 8, -31 \le l \le 31$
Reflections collected / unique	5350 / 4028 [$R_{(int)}$ = 0.0164]	12053 / 5740 [$R_{(int)}$ = 0.0195]	20482 / 4787 [$R_{(int)}$ = 0.0265]	26730 / 6546 [$R_{(int)}$ = 0.0712]
Max. and min. transmission	0.7404 and 0.3378	0.6206 and 0.5152	0.7268 and 0.5005	0.8841 and 0.6320

Data / restraints / parameters	4028 / 1 / 245	5740 / 0 / 301	4787 / 1 / 335	6546 / 0 / 371
Goodness-of-fit on F^2	1.141	1.036	1.091	1.050
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0239$, $wR_2 = 0.0653$	$R_1 = 0.0281$, $wR_2 = 0.0612$	$R_1 = 0.0347$, $wR_2 = 0.0759$	$R_1 = 0.0373$, $wR_2 = 0.0788$
R indices (all data)	$R_1 = 0.0276$, $wR_2 = 0.0785$	$R_1 = 0.0371$, $wR_2 = 0.0649$	$R_1 = 0.0439$, $wR_2 = 0.0793$	$R_1 = 0.0694$, $wR_2 = 0.1006$
Largest diff. peak and hole ($eÅ^{-3}$)	0.633 and -0.755	0.702 and -0.711	1.595 and -0.492	0.638 and -0.913

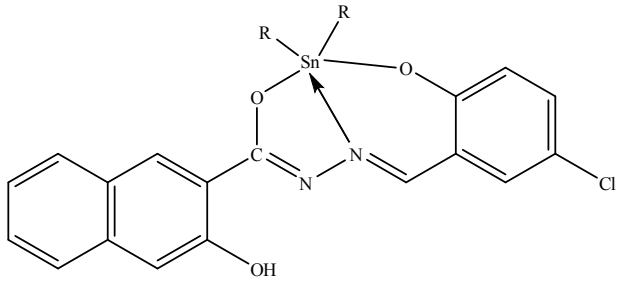
Table 4.3.15
Selected bond lengths (Å) and angles (°) with estimated standard deviation for complexes **HB1, HB2**, **HB4** and **HB6**

	HB1	**HB2**	**HB4**	**HB6**
Bond lengths				
Sn(1)-O(1)	2.084(2)	2.057(17)	2.094(3)	2.076(3)
Sn(1)-O(2)	2.143(2)	2.153(2)	2.153(3)	2.142(3)
Sn(1)-N(1)	2.194(3)	2.193(2)	2.178(3)	2.196(3)
Sn(1)-C_i	2.116(3)	2.089(15)	2.145(4)	2.142(2)
Sn(1)-C_i'	2.120(3)	2.126(2)	2.145(4)	2.142(2)
C(2)-O(1)	1.320(4)	1.319(3)	1.319(5)	1.326(5)
C(8)-O(2)	1.290(4)	1.295(3)	1.294(4)	1.291(5)
C(7)-N(1)	1.300(4)	1.296(3)	1.296(5)	1.294(5)
C(8)-N(2)	1.324(5)	1.316(3)	1.313(5)	1.330(5)
N(2)-O(3)	2.611(4)	2.606(2)	2.600(4)	2.604(4)
Bond angles				
O(1)-Sn(1)-O(2)	155.76(16)	153.96(7)	155.97(9)	153.25(11)
C_i-Sn(1)- C_i'	124.8(2)	127.02(10)	125.81(15)	134.30(18)
N(1)-Sn(1)- C_i	110.12(12)	126.95(9)	116.02(14)	110.68(16)
N(1)-Sn(1)- C_i'	121.63(12)	105.83(9)	118.03(13)	114.59(15)

Note:
C_i and C_i'refer to the *ipso*-carbon of the diorganotin moieties attached to the central tin atom

[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diorganotin(IV), R = Me (HC1), R = Bu (HC2) and R = Ph (HC3)

The molecular structures of complexes **HC1**, **HC2** and **HC3** are shown in figures 4.3.4a, 4.3.4b and 4.3.4c respectively. The crystallographic data and selected bond lengths and angles of **HC1**, **HC2** and **HC3** are tabulated in tables 4.3.16 and 4.3.17.



R = Me (**HC1**), Bu (**HC2**) and Ph (**HC3**)

Each of the structures in the **HC** series was five-coordinated with the central tin atom in a distorted *cis*-C_2NO_2Sn trigonal-bipyramidal geometry. The trigonal equatorial plane consisted of the imine nitrogen and two alkyls/aryls from the diorganotin moieties. For comparison, the sum of angles subtended at tin in **HC1** was 359.69°; **HC2**, 359.78° while for **HC3**, the value was 359.08°. The smaller sum of angle for **HC3** showed that it was more distorted as compared to **HC1** and **HC2**. For **HC1**, the C_i-Sn(1)-C_i*'* angle was 127.2(1)°, **HC2** was 126.77(9)° and in **HC3**, the value was 125.7(2)°. It could be concluded that the C_i-Sn(1)-C_i*'* angle decreased as the size of the alkyl/aryl of the organotin moieties became larger.

The apical angle, O(1)-Sn-O(2), for **HC1** was 155.31(7)°, **HC2** was 154.1(2)° and **HC3** was 157.65(14)°. Here, the value for the dibutyltin derivative was found to be smaller compared to those reported for the dimethyltin and diphenyltin analogues. The

small apical angle for **HC2** indicated that it had a larger distortion from the ideal trigonal bipyramidal geometry and this was probably due to the significant steric effect from the two butyl groups. As a result, the O(2)-Sn(1)-N(1)-N(2)-C(8) plane and O(1)-Sn(1)-N(1)-C(7)-C(1)-C(2) plane made a dihedral angle of 4.3^{o} which was larger than those for the dimethyltin, diphenyltin and dicyclohexyltin derivatives. The O(2)-Sn(1)-N(1)-N(2)-C(8) and O(1)-Sn(1)-N(1)-C(7)-C(1)-C(2) planes were near planar, with the rms deviation from planarity of 0.006 Å and 0.07 Å respectively.

There was strong intramolecular hydrogen bonding between N(2) and O(3)-H(3) [O-H….N 2.590(2) Å] which helped to stabilize the overall structures of **HC1**, **HC2** and **HC3**.

Figure 4.3.4a
Molecular plot of [5-chloro-2-oxidobenzylidene-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HC1**

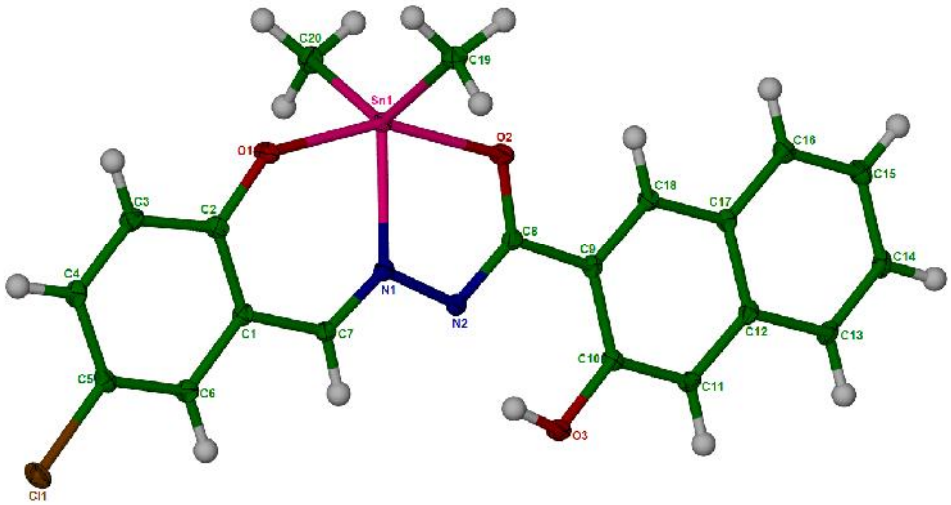


Figure 4.3.4b
Molecular plot of [5-chloro-2-oxidobenzylidene-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HC2**

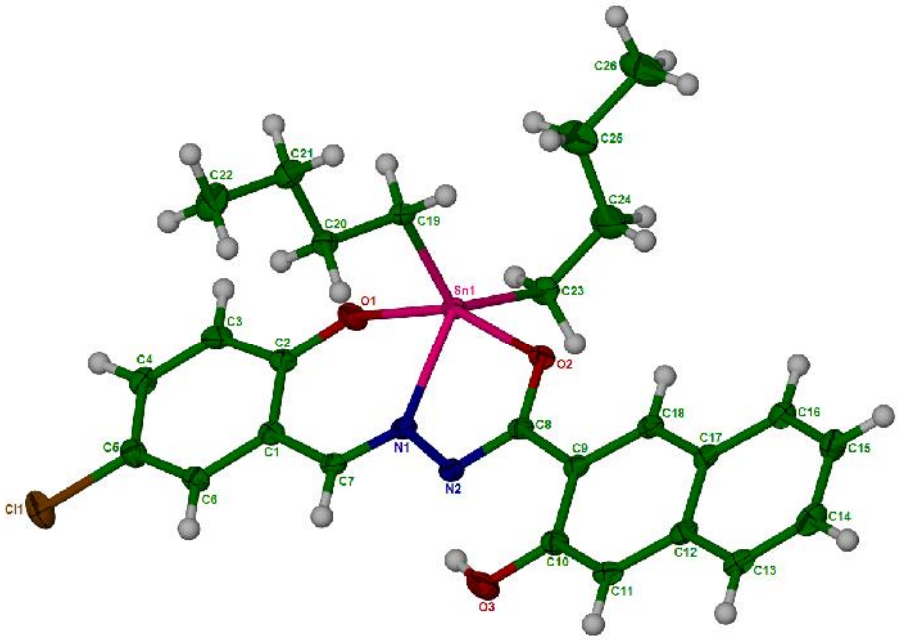


Figure 4.3.4c
Molecular plot of [5-chloro-2-oxidobenzylidene-3-hydroxy-2-naphthohydrazidato]-diphenyltin(IV), **HC3**

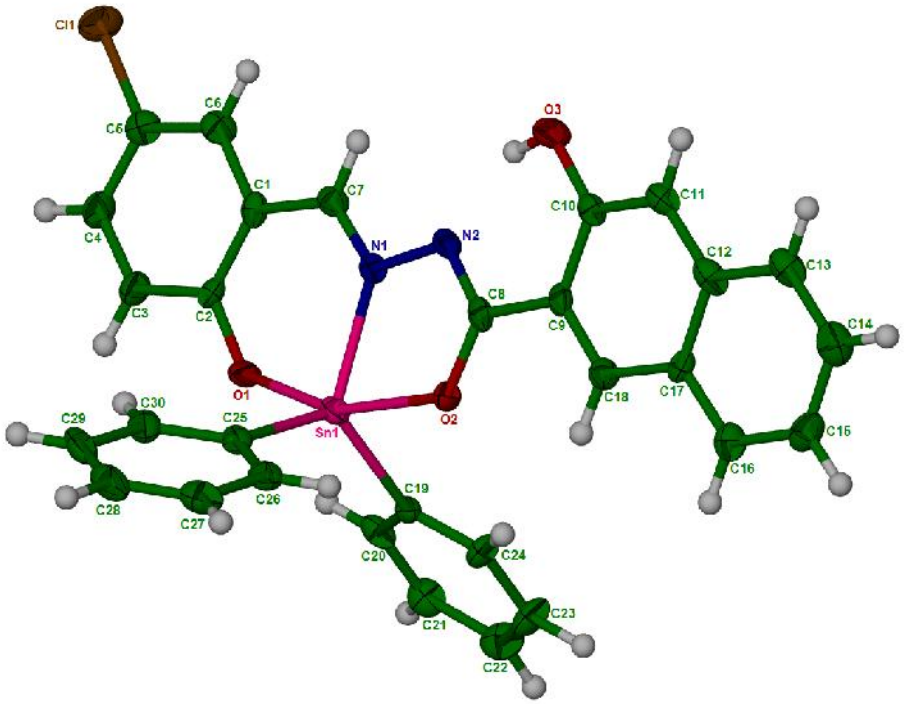


Table 4.3.16
Crystallographic parameters for complexes **HC1**, **HC2** and **HC3**

	HC1	**HC2**	**HC3**
Empirical formula	$C_{20}H_{17}ClN_2O_3Sn$	$C_{26}H_{29}ClN_2O_3Sn$	$C_{30}H_{21}ClN_2O_3Sn$
Formula weight	487.50	571.65	611.63
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.8368(2)	10.0704(1)	10.5690(4)
b (Å)	11.6210(3)	11.9259(1)	10.9788(4)
c (Å)	12.0159(3)	12.7460(2)	11.8319(4)
α (^{o})	86.876(1)	62.957(1)	68.381(2)
β (^{o})	75.928(1)	84.504(1)	82.450(2)
γ (^{o})	80.632(1)	66.574(1)	82.672(2)
Volume (Å^3)	913.56(4)	1244.25(3)	1260.60(8)
Z	2	2	2
Calculated density, D_{calc} (Mgm^{-3})	1.772	1.526	1.611
Absorption coefficient, μ (mm^{-1})	1.569	1.164	1.155
F(000)	484	580	612
Crystal size (mm)	0.30 x 0.18 x 0.09	0.34 x 0.27 x 0.07	0.30 × 0.25 × 0.20
Limiting indices	$-8 \le h \le 7$, $-13 \le k \le 15$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-15 \le l \le 15$	$-9 \le h \le 12$, $-12 \le k \le 13$, $-14 \le l \le 14$

Reflections collected / unique	5373 / 3948 [$R_{(int)}$ = 0.0140]	9781 / 4376 [$R_{(int)}$ = 0.0183]	6086 / 4287 [$R_{(int)}$ = 0.0288]
Max. and min. transmission	0.8717 and 0.6504	0.9261 and 0.6930	0.798 and 1.000
Data / restraints / parameters	948 / 0 / 245	4376 / 1 / 301	4287 / 1 / 338
Goodness-of-fit on F^2	1.102	1.078	1.068
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0226, wR_2 = 0.0584	R_1 = 0.0222, wR_2 = 0.0551	R_1 = 0.0426, wR_2 = 0.1157
R indices (all data)	R_1 = 0.0253, wR_2 = 0.0621	R_1 = 0.0251, wR_2 = 0.0567	R_1 = 0.0554, wR_2 = 0.1272
Largest diff. peak and hole ($eÅ^{-3}$)	0.689 and -0.775	0.837 and -0.365	1.390 and -0.671

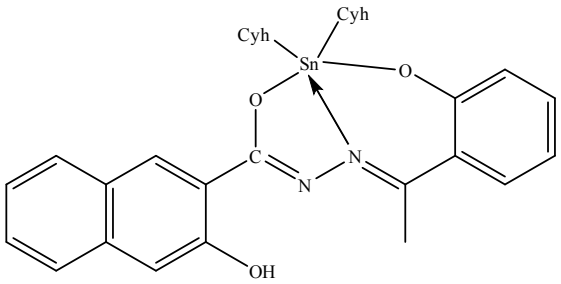
Table 4.3.17
Selected bond lengths (Å) and angles (^{o}) with estimated standard deviation for complexes **HC1**, **HC2** and **HC3**

	HC1	**HC2**	**HC3**
Bond lengths			
Sn(1)-O(1)	2.092(2)	2.090(16)	2.057(4)
Sn(1)-O(2)	2.145(2)	2.158(2)	2.150(3)
Sn(1)-N(1)	2.189(2)	2.187(2)	2.165(4)
Sn(1)-C_i	2.105(3)	2.128(2)	2.131(5)
Sn(1)-C_i'	2.110(3)	2.129(2)	2.124(2)
C(2)-O(1)	1.325(2)	1.319(3)	1.337(6)
C(8)-O(2)	1.291(3)	1.290(3)	1.306(6)
C(7)-N(1)	1.298(3)	1.295(3)	1.302(7)
C(8)-N(1)	1.318(3)	1.316(3)	1.324(7)
N(2)-O(3)	2.604(2)	2.590(2)	2.623(6)
Bond angles			
O(1)-Sn(1)-O(2)	155.31(7)	154.09(6)	157.65(14)
C_i-Sn(1)- C_i'	127.22(11)	126.77(9)	125.72(19)
N(1)-Sn(1)- C_i	122.35(9)	126.40(9)	121.41(17)
N(1)-Sn(1)- C_i'	110.12(10)	106.61(8)	111.95(17)

Note:
C_i and C_i'refer to the *ipso*-carbon of the diorganotin moieties attached to the central tin atom

{*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dicyclohexyltin(IV), (HD4)

The molecular structure of the complex {*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HD4** is shown in figure 4.3.5. The crystallographic data and selected bond lengths and angles of **HD4** are tabulated in tables 4.3.18 and 4.3.19.



HD4 was five-coordinated with the tin atom adopting a distorted trigonal-bipyramidal geometry. The structure of **HD4** consisted of a deprotonated *ONO* dibasic tridentate ligand bonded to the dicyclohexyltin moieties *via* the two oxygen atoms and a nitrogen atom, to form a $-O_2NC_2$ core around the Sn atom. Like the other complexes, the equatorial plane consisted of the imine nitrogen and two cyclohexyl groups, whereby the sum of angles subtended at tin was 359.53°. The C_i-Sn(1)-C_i' angle was 127.6(2)° while the O(2)-Sn(1)-N(1)-N(2)-C(8) and O(1)-Sn(1)-N(1)-C(7)-C(1)-C(2) planes made a dihedral angle of 13.1°, indicating that the ligand plane was not planar. This was probably due to the steric requirements of the six and five-membered chelate rings.

The Sn-N(1) bond distance was 2.187 Å, which was quite close to the sum of covalent radii of Sn and N (2.15 Å), and significantly less than the sum of van der Waals radii (3.75 Å).

There was a strong intramolecular hydrogen bonding between N(2) and O(3)-H(3) [O-H….N 2.571(4) Å] which helped to stabilize the overall structure of **HD4**.

Figure 4.3.5
Molecular plot of {*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphtho-hydrazidato}dicyclohexyltin(IV), **HD4**

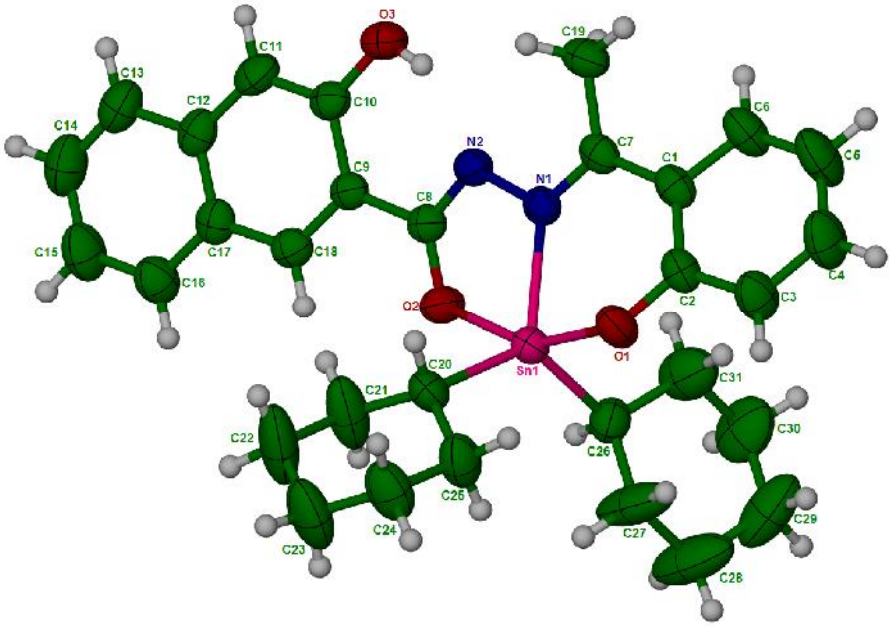


Table 4.3.18
Crystal data and structure refinement for {*N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HD4**

Empirical formula	$C_{31}H_{36}N_2O_3Sn$
Formula weight	603.31
Crystal system	Monoclinic
Space group	*C*2/*c*
	a (Å) = 30.236(6) *b* (Å) = 7.7030(15) *c* (Å) = 25.853(5) α (°) = 90 β (°) = 111.25(3) γ (°) = 90
Volume (Å^3)	5611.9(19)
Z	8
Calculated density, D_{calc} (Mgm^{-3})	1.428
Absorption coefficient, μ (mm^{-1})	0.945
F(000)	2480
Crystal size (mm)	0.30 x 0.10 x 0.10
Limiting indices	$-40 \leq h \leq 40$, $-10 \leq k \leq 10$, $-34 \leq l \leq 34$
Reflections collected / unique	27737 / 6981 [$R_{(int)}$ = 0.0501]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6981 / 1 / 336
Goodness-of-fit on F^2	1.002
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0440, wR_2 = 0.0906
R indices (all data)	R_1 = 0.0930, wR_2 = 0.1092
Largest diff. peak and hole (eÅ^{-3})	0.524 and -0.446

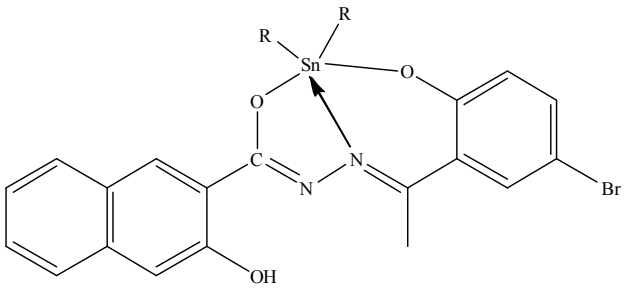
Table 4.3.19
Bond lengths (Å) and angles (°) with estimated standard deviation for *N'*-[1-(2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HD4**

Sn(1)-O(1)	2.062(3)	N(1)-C(7)-C(1)	121.3(3)
Sn(1)-O(2)	2.163(2)	N(1)-C(7)-C(19)	118.5(4)
Sn(1)-N(1)	2.187(3)	N(2)-N(1)-Sn(1)	113.7(2)
Sn(1)-C(20)	2.146(4)	N(2)-C(8)-C(9)	117.1(3)
Sn(1)-C(26)	2.136(4)	O(1)-Sn(1)-O(2)	154.80(10)
N(1)-N(2)	1.398(4)	O(1)-Sn(1)-N(1)	82.39(11)
N(1)-C(7)	1.310(4)	O(1)-Sn(1)-C(20)	94.21(14)
N(2)-C(8)	1.307(4)	O(1)-Sn(1)-C(26)	98.87(14)
O(1)-C(2)	1.322(4)	O(1)-C(2)-C(1)	123.6(4)
O(2)-C(8)	1.287(4)	O(1)-C(2)-C(3)	117.0(4)
O(3)-C(10)	1.351(4)	O(2)-Sn(1)-N(1)	72.61(10)
C(1)-C(2)	1.405(5)	O(2)-C(8)-N(2)	124.5(3)
C(1)-C(6)	1.398(5)	O(2)-C(8)-C(9)	118.3(3)
C(1)-C(7)	1.461(5)	O(3)-C(10)-C(9)	121.5(3)
C(2)-C(3)	1.398(5)	O(3)-C(10)-C(11)	119.1(4)
C(3)-C(4)	1.378(6)	C(1)-C(7)-C(19)	120.2(3)
C(4)-C(5)	1.367(7)	C(2)-O(1)-Sn(1)	126.9(2)
C(5)-C(6)	1.358(6)	C(2)-C(1)-C(7)	123.9(3)
C(7)-C(19)	1.501(5)	C(3)-C(2)-C(1)	119.3(4)
C(8)-C(9)	1.479(5)	C(4)-C(3)-C(2)	120.6(4)
C(9)-C(10)	1.435(5)	C(5)-C(4)-C(3)	120.2(5)
C(9)-C(18)	1.364(5)	C(5)-C(6)-C(1)	122.3(5)
C(10)-C(11)	1.357(5)	C(6)-C(1)-C(2)	117.6(4)
C(11)-C(12)	1.398(6)	C(6)-C(1)-C(7)	118.5(4)
C(12)-C(13)	1.414(6)	C(6)-C(5)-C(4)	119.9(5)
C(12)-C(17)	1.410(6)	C(7)-N(1)-Sn(1)	129.5(3)
C(13)-C(14)	1.354(7)	C(7)-N(1)-N(2)	116.5(3)
C(14)-C(15)	1.378(7)	C(8)-N(2)-N(1)	112.2(3)
C(15)-C(16)	1.357(6)	C(8)-O(2)-Sn(1)	112.6(2)
C(16)-C(17)	1.404(6)	C(9)-C(18)-C(17)	122.9(4)
C(17)-C(18)	1.412(5)	C(10)-C(9)-C(8)	121.9(3)
C(20)-C(21)	1.454(6)	C(10)-C(11)-C(12)	122.6(4)
C(20)-C(25)	1.503(5)	C(11)-C(10)-C(9)	119.4(4)
C(21)-C(22)	1.516(7)	C(11)-C(12)-C(13)	123.3(4)
C(22)-C(23)	1.485(7)	C(11)-C(12)-C(17)	118.8(4)
C(23)-C(24)	1.445(7)	C(12)-C(17)-C(18)	118.0(4)
C(24)-C(25)	1.514(6)	C(13)-C(14)-C(15)	121.0(5)
C(26)-C(27)	1.490(6)	C(14)-C(13)-C(12)	120.9(5)
C(26)-C(31)	1.485(6)	C(15)-C(16)-C(17)	121.1(5)
C(27)-C(28)	1.529(7)	C(16)-C(15)-C(14)	120.0(5)
C(28)-C(29)	1.466(10)	C(16)-C(17)-C(12)	119.0(4)
C(29)-C(30)	1.460(8)	C(16)-C(17)-C(18)	123.0(4)
C(30)-C(31)	1.525(7)	C(17)-C(12)-C(13)	117.9(4)
		C(18)-C(9)-C(8)	119.8(3)
		C(18)-C(9)-C(10)	118.2(3)
		C(20)-Sn(1)-N(1)	115.93(14)
		C(20)-Sn(1)-O(2)	93.95(13)
		C(20)-C(21)-C(22)	112.9(4)
		C(20)-C(25)-C(24)	112.0(4)
		C(21)-C(20)-Sn(1)	115.6(3)
		C(21)-C(20)-C(25)	113.3(4)
		C(23)-C(22)-C(21)	113.0(5)

C(23)-C(24)-C(25)	113.2(4)
C(24)-C(23)-C(22)	112.6(5)
C(25)-C(20)-Sn(1)	111.7(3)
C(26)-Sn(1)-C(20)	127.60(16)
C(26)-Sn(1)-N(1)	116.00(14)
C(26)-Sn(1)-O(2)	94.89(14)
C(26)-C(27)-C(28)	112.7(5)
C(26)-C(31)-C(30)	112.6(5)
C(27)-C(26)-Sn(1)	111.4(3)
C(29)-C(28)-C(27)	111.7(6)
C(29)-C(30)-C(31)	111.6(5)
C(30)-C(29)-C(28)	111.9(6)
C(31)-C(26)-Sn(1)	113.8(3)
C(31)-C(26)-C(27)	110.1(4)

{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-diorganotin(IV), R = Me (HE1) and R = Bu (HE2)

The complexes {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HE1** and {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HE2** crystallize in the triclinic, $P\bar{1}$ space group and monoclinic, $P2_1/c$ space group respectively.. The molecular structures of **HE1** and **HE2** are shown in figures 4.3.6a and 4.3.6b, respectively. The crystallographic data and selected bond lengths and angles of **HE1** and **HE2** are tabulated in tables 4.3.20 and 4.3.21.



R = Me (**HE1**) and Bu (**HE2**)

From the molecular structures, it was found that the tin atom adopted a distorted *cis*-C_2NO_2Sn trigonal-bipyramidal geometry whereby the trigonal plane consisted of the imine nitrogen atom and two alkyls/aryls from the diorganotin moieties. The sum of angles subtended at tin for **HE1** was 359.68^o and **HE2** was 359.74^o, which was nearly 360^o.

The dihedral angle between the O(2)-Sn(1)-N(1)-N(2)-C(8) plane and O(1)-Sn(1)-N(1)-C(7)-C(1)-C(2) plane in **HE1** was 4.7^o whereas for **HE2**, it was 19.3^o. The

large dihedral angle value for **HE2** could be due to the steric effect from the two bulky butyl rings. Therefore, the ligand plane for **HE2** was not planar but slightly twisted.

In **HE1**, the C_i-Sn(1)-C_i' angle was 128.67(8)^o while in **HE2**, the value was 135.7(3)^o. Again, the large value C_i-Sn(1)-C_i'angle in **HE2** could be attributed to the strong repulsion from the long butyl chains. The distorted geometry in the **HE** complexes could be seen from the deviation of the apical angle from 180^o. The O(1)-Sn(1)-O(2) in **HE1** was 154.86(6)^o while in **HE2** it was 152.96(5)^o. The smaller apical angle value in **HE2** further supported its large distortion from the ideal trigonal-bipyramidal geometry.

In **HE2**, the two butyl chains were disordered over two positions. One of the butyl chains was disordered in all four carbon atoms whereas in the other butyl chain, it was disordered, only in the β, γ and δ carbon positions. The occupancy of the disordered carbons in the butyl chains were refined to nearly 50:50 whereby the C-C distance was tightly restrained to 1.500±0.005 Å and the alternate C···C distance to 2.35±0.01 Å [*eg*. C_α to C_γ, C_β to C_δ]. Also, the naphthalene ring was disordered over two positions. The occupancy was also set as 50:50.

There was a strong intramolecular hydrogen bonding between N(2) and O(3)-H(3) [O-H….N 2.586(2) Å in **HE1** and 2.696(1) Å in **HE2**] in each of the structure which helped to stabilize the overall structure.

Figure 4.3.6a
Molecular plot of {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HE1**

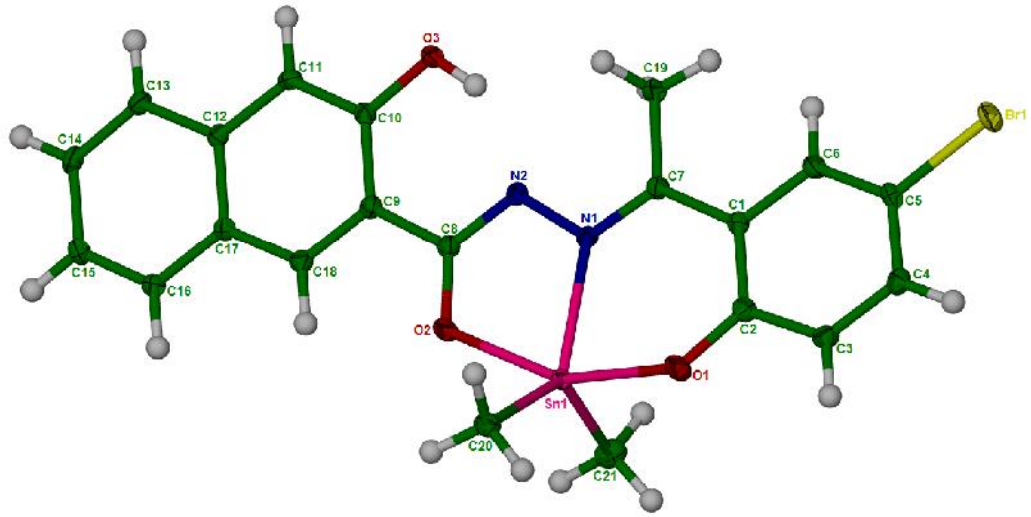


Figure 4.3.6b
Molecular plot of {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HE2**

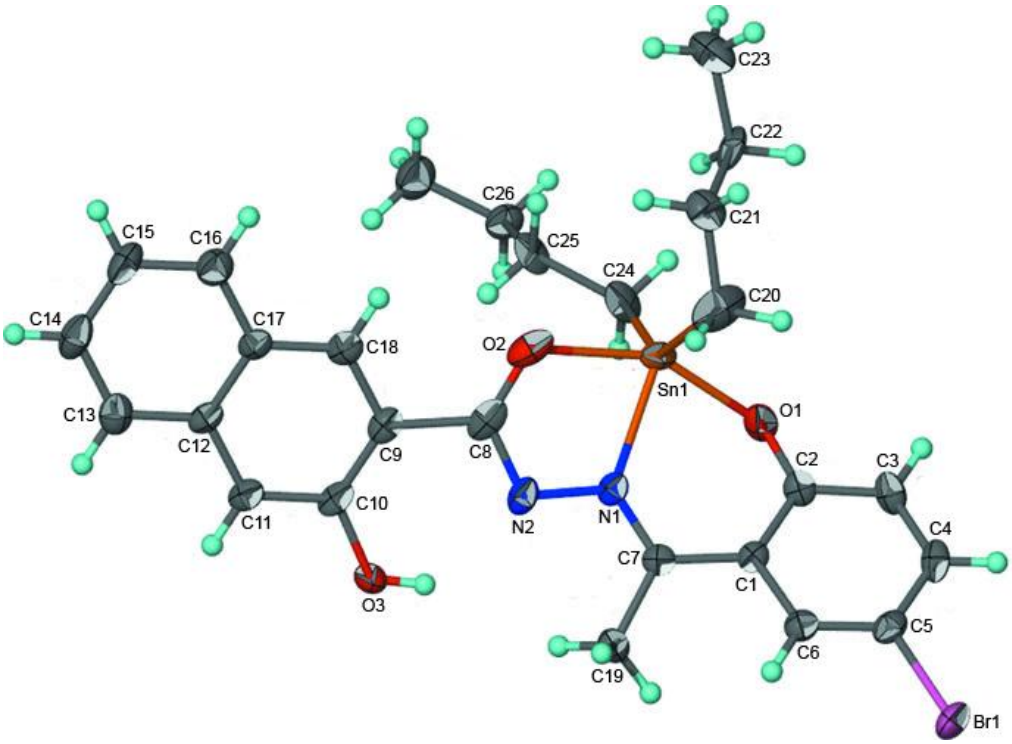


Table 4.3.20
Crystallographic parameters for complexes **HE1** and **HE2**

	HE1	**HE2**
Empirical formula	$C_{21}H_{19}BrN_2O_3Sn$	$C_{27}H_{31}BrN_2O_3Sn$
Formula weight	545.98	630.14
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.6760(1)	14.2649(3)
b (Å)	10.8469(1)	7.22490(10)
c (Å)	12.0039(1)	24.9527(5)
α (^{o})	85.419(1)	90
β (^{o})	78.538(1)	95.4830(10)
γ (^{o})	79.196(1)	90
Volume (Å^3)	961.216(17)	2559.92(8)
Z	2	4
Calculated density, D_{calc} (Mgm^{-3})	1.886	1.635
Absorption coefficient, μ (mm^{-1})	3.433	2.590
F(000)	536	1264
Crystal size (mm)	0.25 x 0.20 x 0.07	0.40 x 0.30 x 0.20

Limiting indices	$-9 \leq h \leq 9, -14 \leq k \leq 14, -15 \leq l \leq 15$	$-20 \leq h \leq 20, -10 \leq k \leq 10, -35 \leq l \leq 35$
Reflections collected / unique	184 / 4388 [$R_{(int)} = 0.0150$]	27443 / 7435 [$R_{(int)} = 0.0330$]
Max. and min. transmission	0.7951 and 0.4807	0.6254 and 0.4239
Data / restraints / parameters	4388 / 1 / 255	7435 / 0 / 314
Goodness-of-fit on F^2	1.057	1.26
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0184$, $wR_2 = 0.0472$	$R_1 = 0.0642$, $wR_2 = 0.1953$
R indices (all data)	$R_1 = 0.0202$, $wR_2 = 0.0479$	$R_1 = 0.0766$, $wR_2 = 0.2043$
Largest diff. peak and hole ($eÅ^{-3}$)	0.523 and -0.419	1.36 and -1.07

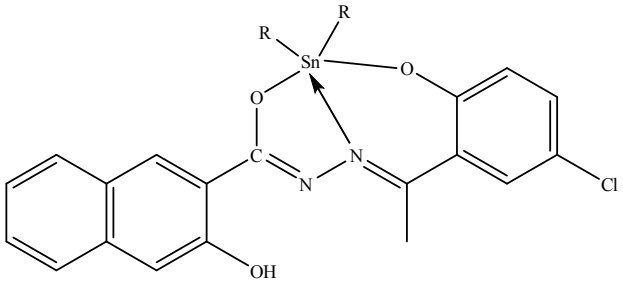
Table 4.3.21
Selected bond lengths (Å) and angles (°) with estimated standard deviation for complexes **HE1** and **HE2**

	HE1	**HE2**
Bond lengths		
Sn(1)-O(1)	2.054(1)	2.068(3)
Sn(1)-O(2)	2.132(1)	2.150(3)
Sn(1)-N(1)	2.204(2)	2.192(3)
Sn(1)-C_i	2.111(2)	2.150(2)
Sn(1)-C_i'	2.111(2)	2.143(4)
C(2)-O(1)	1.322(2)	1.329(5)
C(8)-O(2)	1.291(2)	1.292(6)
C(7)-N(1)	1.311(2)	1.306(5)
C(8)-N(2)	1.320(2)	1.315(3)
N(2)-O(3)	2.586(2)	2.696(1)
Bond angles		
O(1)-Sn(1)-O(2)	154.86(6)	152.85(12)
C_i-Sn(1)- C_i'	128.67(8)	129.00(3)
N(1)-Sn(1)- C_i	122.94(7)	115.70(3)
N(1)-Sn(1)- C_i'	108.07(7)	115.29(16)

Note:
C_i and C_i'refer to the *ipso*-carbon of the diorganotin moieties attached to the central tin atom

{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-diorganotin(IV), R = Me (HF1), R = Bu (HF2) and R = Cy (HF4)

The molecular structure of complexes **HF1**, **HF2** and **HF4** are shown in figures 4.3.7a, 4.3.7b and 4.3.7c respectively. The crystallographic data and selected bond lengths and angles of **HF1**, **HF2** and **HF4** are tabulated in tables 4.3.22 and 4.3.23.



R = Me (**HF1**), Bu (**HF2**) and Cy (**HF4**)

{*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dimethyltin(IV), **HF1** crystallizes in triclinic, $P\bar{1}$ space group, while {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HF2** and {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dicyclohexyltin(IV) **HF4** crystallize in monoclinic, $P2_1/n$ space group. **HF2** has two unique mmolecules in the asymmetric unit.

From the molecular structures, the tin atom was rendered five-coordinated by coordination with the nitrogen atom from the Schiff base ligand. Also, the tin atom was surrounded axially by the two hydroxyl oxygens from the Schiff base ligands and equatorially by one nitrogen and two carbon atoms of the diorganotin moieties. For comparison, the sum of angle subtended at tin for **HF1** was 359.66^{o}. For **HF2**, the trigonal plane was nearly ideal for both the molecules whereby the total sum of angles

was 359.75° and 359.95° while for **HF4**, the sum of angle subtended at tin was 359.12°. The C_i-Sn(1)-C_i*'* angle decreased as the size of the alkyl/aryl of the diorganotin moieties increased. For **HF1**, the C_i-Sn(1)-C_i*'* was 127.66(19)°, **HF2** was 134.95(19)° and 135.8(2)° respectively, while for **HF4**, it was 137.94(7)°.

Like **HE** complexes, the distorted geometry in the **HF** complexes could be seen in the deviation from 180° of its apical angle. The apical angle, O(1)-Sn(1)-O(2) for **HF1** was 154.29(13)°, **HF2** was 153.02(13)° and 152.42(13)°, and **HF4** was 153.64(5)°. The value for the dibutyltin derivative was found to be smaller compared to those reported for the dimethyltin and dicyclohexyltin analogues. This indicated that it had a larger distortion from the ideal trigonal-bipyramidal geometry and again, this was probably due to the steric effect from the two bulky butyl groups.

Each of the structures in complexes **HF1**, **HF2** and **HF4** was stabilized by a strong intramolecular hydrogen bond between N(2) and O(3)-H(3) [**HF1**: O-H….N 2.560(7) Å, **HF2**: O-H….N 2.602(5) and 2.617(5) Å and **HF4**: O-H….N 2.563(2) Å].

Figure 4.3.7a
Molecular plot of {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **HF1**

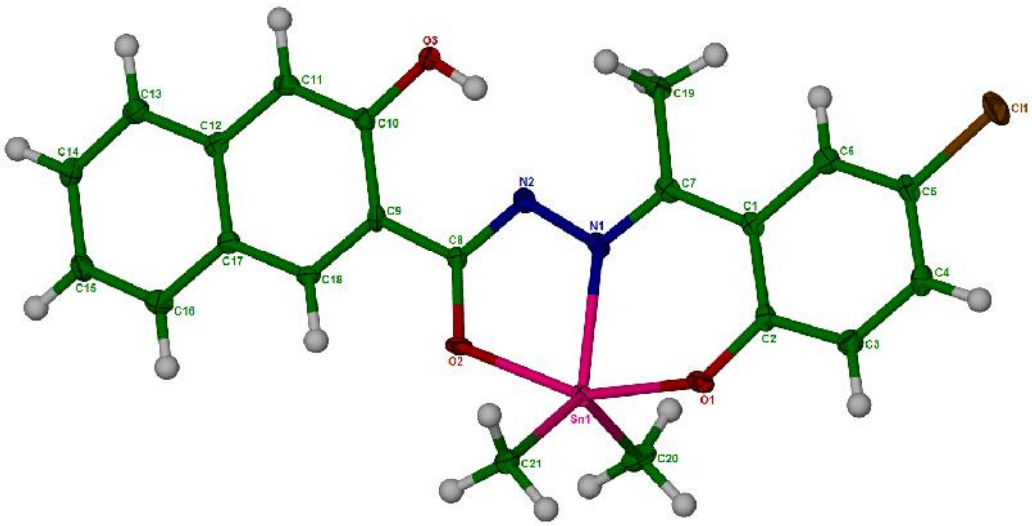


Figure 4.3.7b
Molecular plot of {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **HF2**

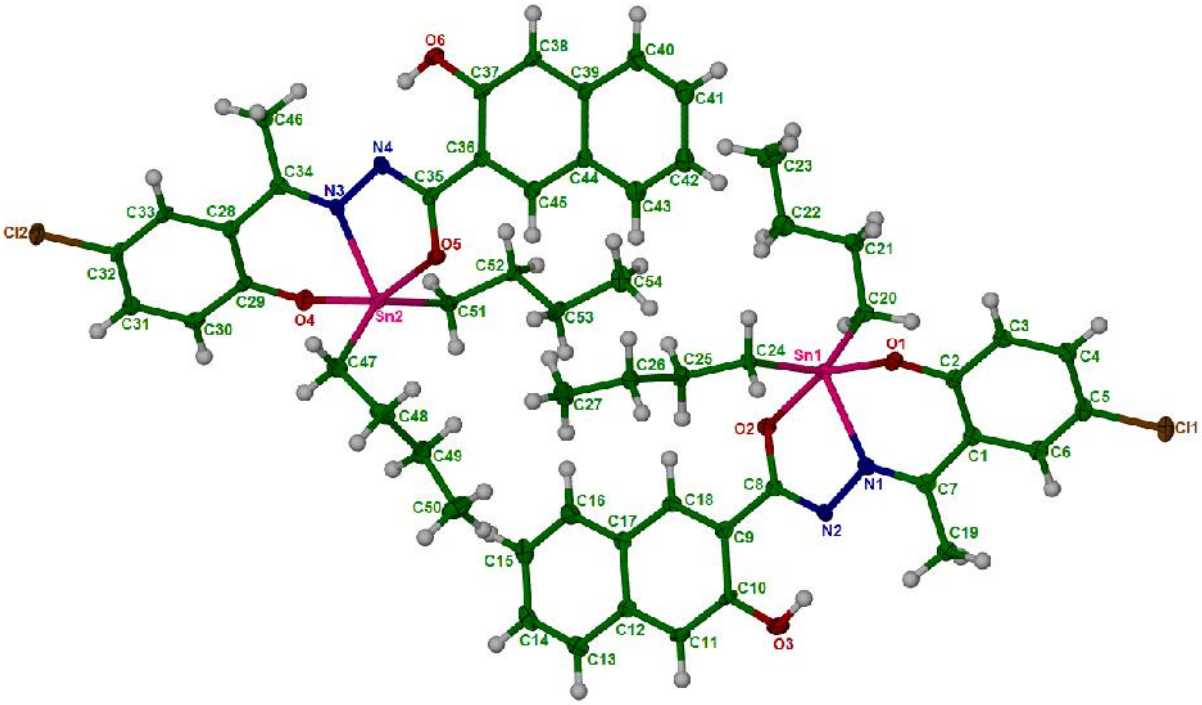


Figure 4.3.7c
Molecular plot of {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **HF4**

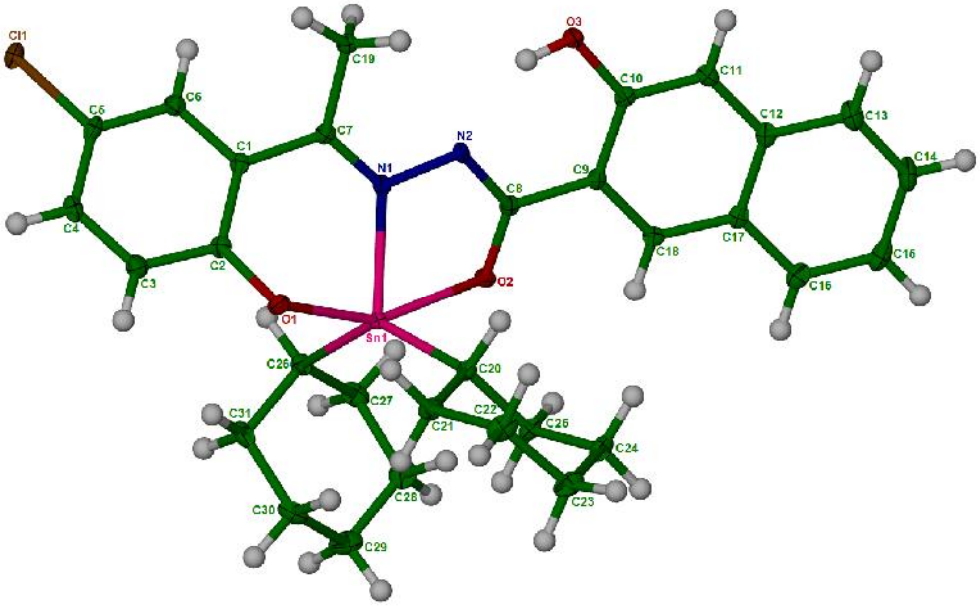


Table 4.3.22
Crystallographic parameters for complexes **HF1**, **HF2** and **HF4**

	HF1	**HF2**	**HF4**
Empirical formula	$C_{21}H_{19}ClN_2O_3Sn$	$C_{27}H_{31}ClN_2O_3Sn$	$C_{31}H_{35}ClN_2O_3Sn$
Formula weight	501.52	585.68	637.75
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	7.6829(8)	24.8256(13)	8.0138(1)
b (Å)	10.7398(10)	7.1994(4)	11.6732(1)
(Å)	12.0209(10)	28.3649(15)	29.5049(3)
α(°)	85.211(6)	90	90
β(°)	78.828(6)	96.376(1)	91.393(1)
γ (°)	78.960(6)	90	90
Volume (Å^3)	953.97(16)	5038.3(5)	2759.27(5)
Z	2	8	4
Calculated density, D_{calc} (Mgm^{-3})	1.746	1.544	1.535
Absorption coefficient, μ (mm^{-1})	1.505	1.152	1.059
F(000)	500	2384	1304
Crystal size (mm)	0.35 x 0.27 x 0.06	0.25 x 0.25 x 0.15	0.26 x 0.08 x 0.05
Limiting indices	$-8 \le h \le 9$, $-12 \le k \le 12$, $-14 \le l \le 14$	$-29 \le h \le 29$, $-8 \le k \le 8$, $-33 \le l \le 33$	$-10 \le h \le 10$, $-14 \le k \le 15$, $-38 \le l \le 38$

Reflections collected / unique	4581 / 3218 [$R_{(int)}$ = 0.0329]	37459 / 8881 [$R_{(int)}$ = 0.0322]	26129 / 6348 [$R_{(int)}$ = 0.0327]
Max. and min. transmission	0.9218 and 0.6209	0.8462 and 0.7616	0.9490 and 0.7704
Data / restraints / parameters	3218 / 169 / 255	8881 / 0 / 621	6348 / 1 / 345
Goodness-of-fit on F^2	1.027	1.315	1.032
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0360, wR_2 = 0.0991	R_1 = 0.0498, wR_2 = 0.0994	R_1 = 0.0242, wR_2 = 0.0519
R indices (all data)	R_1 = 0.0421, wR_2 = 0.1040	R_1 = 0.0532, wR_2 = 0.1008	R_1 = 0.0301, wR_2 = 0.0541
Largest diff. peak and hole ($eÅ^{-3}$)	1.249 and -1.132	0.822 and -1.496	0.434 and -0.325

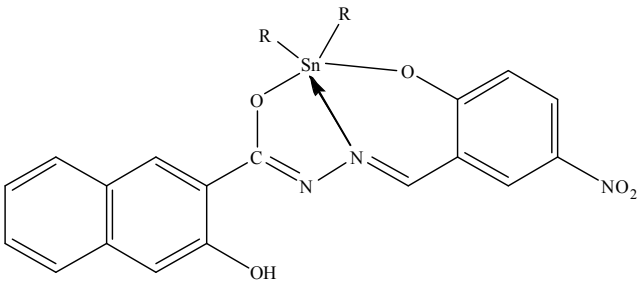
Table 4.3.23
Selected bond lengths (Å) and angles (°) with estimated standard deviation for complexes **HF1, HF2** and **HF4**

	HF1	**HF2**	**HF4**
Bond lengths			
Sn(1)-O(1)	2.059(3)	2.067(3), 2.073(3)	2.0875(13)
Sn(1)-O(2)	2.138(3)	2.150(3), 2.155(3)	2.1996(13)
Sn(1)-N(1)	2.201(4)	2.186(4), 2.198(4)	2.1832(15)
Sn(1)-C_i	2.122(4)	2.126(5), 2.123(5)	2.1443(19)
Sn(1)-C_i'	2.114(4)	2.132(4), 2.135(5)	2.1556(19)
C(2)-O(1)	1.320(6)	1.331(6), 1.333(6)	1.331(2)
C(8)-O(2)	1.288(6)	1.294(6), 1.291(6)	1.289(2)
C(7)-N(1)	1.326(6)	1.316(6), 1.304(6)	1.302(2)
C(8)-N(2)	1.338(6)	1.316(6), 1.319(6)	1.326(2)
N(2)-O(3)	2.560(7)	2.602(5), 2.617(5)	2.563(2)
Bond angles			
O(1)-Sn(1)-O(2)	154.29(13)	153.02(13), 152.42(13)	153.64(5)
C_i-Sn(1)- C_i'	127.66(19)	134.95(19), 135.8(2)	137.94(7)
N(1)-Sn(1)- C_i	108.18(17)	109.07(16), 109.41(17)	107.95(6)
N(1)-Sn(1)- C_i'	123.82(16)	115.74(17), 114.78(17)	113.23(7)

Note:
C_i and C_i'refer to the *ipso*-carbon of the diorganotin moieties attached to the central tin atom

[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diorganotin(IV), R = Me (HG1), R = Bu (HG2) and R = Cy (HG4)

[*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HG1** and [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HG4** crystallizes in the monoclinic $P2_1/c$ space group while [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HG2** crystallizes in triclinic, $P\bar{1}$ space group with two unique molecules in its asymmetric unit.. The molecular structure of complexes **HG1**, **HG2** and **HG4** are shown in figures 4.3.8a, 4.3.8b and 4.3.8c while the crystallographic data and selected bond lengths and angles of **HG1**, **HG2** and **HG4** are tabulated in tables 4.3.24 and 4.3.25.



R = Me (**HG1**), Bu (**HG2**) and Cy (**HG4**)

The Schiff base in this series of complexes also behaved as an *ONO* dibasic tridentate ligand which bonded to the diorganotin moieties *via* the two oxygens and a nitrogen atom, forming a O_2NC_2 core around the tin atom. The equatorial plane comprised of the imine nitrogen and two alkyl/aryl chains, whereby the sum of angle subtended at tin for **HG1** was 359.46° and that of **HG4** was 359.97°. In **HG2** the sum of angle for the trigonal plane for one of the molecule was 365.43° which showed a

slight deviation from the ideal 360°. For the other molecule in **HG2**, the sum of angle subtended at tin is 359.93°.

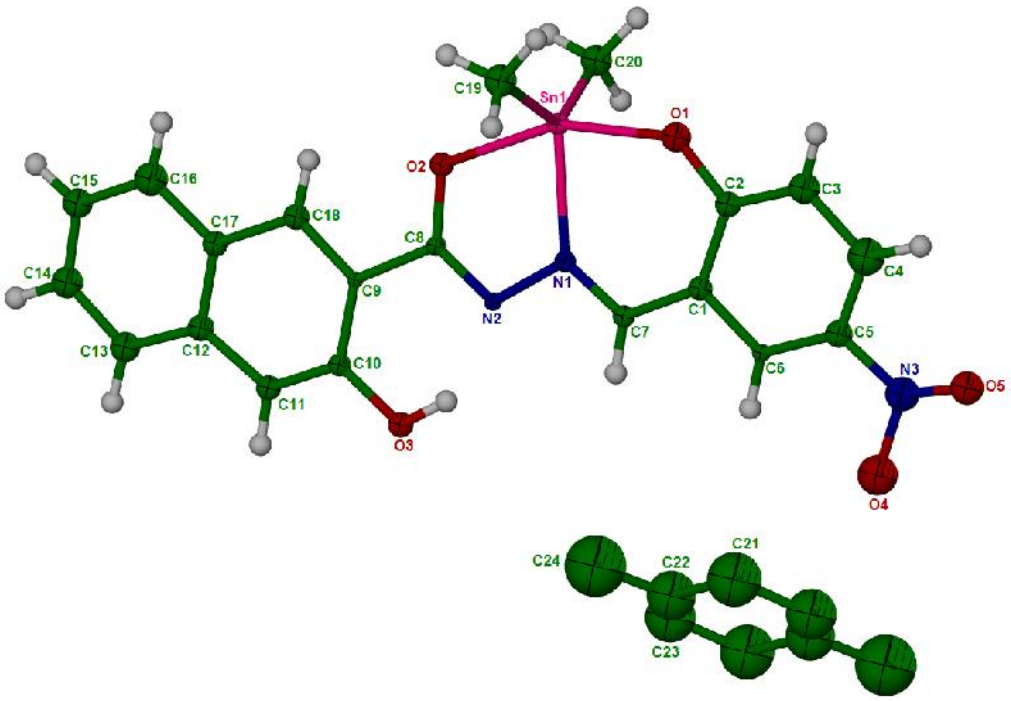
The alkyl/aryl moieties which were bonded to the tin, made an angle [C_i-Sn(1)-C_i] of 131.0(7)° in **HG1**, 129.48(14)° and 131.1(2)° in **HG2** and 125.6(3)° in **HG4**. It could be seen that the angles of C_i-Sn(1)-C_i' decreased when the alkyl chains of the diorganotin moieties increased. The apical angle, O(1)-Sn(1)-O(2) for **HG1** was 156.6(4)°, **HG2** was 156.46(9)° and 156.45(9)° respectively and for **HG4**, 155.9(2)°. There was little variation in the apical angle among the **HG** complexes.

The dihedral angle between the O(2)-Sn(1)-N(1)-N(2)-C(8) plane and O(1)-Sn(1)-N(1)-C(7)-C(1)-C(2) plane in **HG1** was 1.2°. Whereas, the dihedral angle for one of the molecule in **HG2** was 2.7° and the other molecule was smaller at 1.8°. For **HG4**, the dihedral angle was 0.8°. Overall, all three complexes had a planar ligand plane due to the small difference in its dihedral angle values.

The molecular structure of **HG1** was highly disordered in the naphthalene ring and its solvated solvent. So far, a good refinement for the structural model of **HG1** was not obtained although the solvated solvent was deduced to be toluene based on the preparation procedure. The toluene molecule was highly disordered in all the carbon positions including the methyl carbon. Several carbons in the naphthalene ring and phenyl ring; C4, C13 and C16 were disordered. The final R-factor value obtained for **HG1** was 11.7% due to poor data set obtained from the poor crystal quality although it was collected in low temperature, 100K. The highest peak and deepest hole were 3.354 and -1.765 respectively and the several high Q peaks were near the ligand plane.

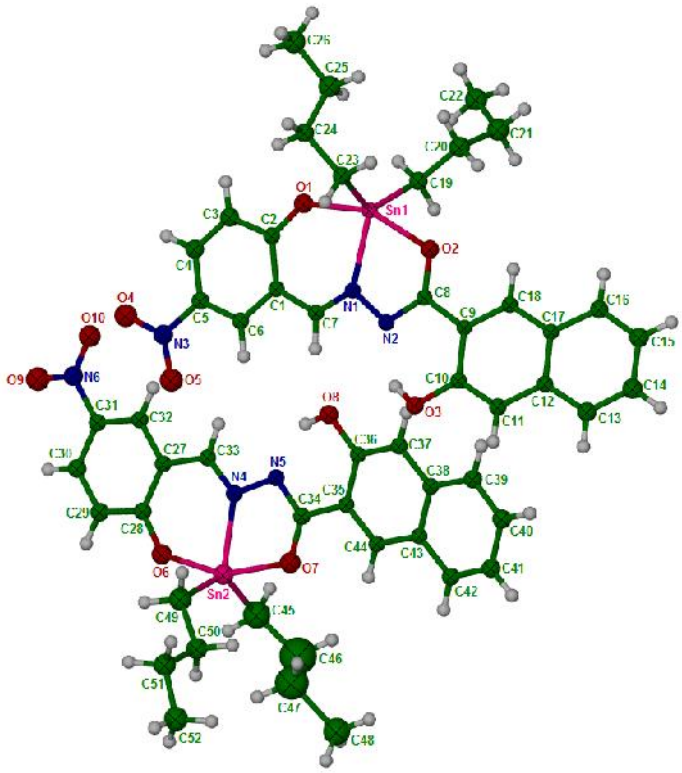
In **HG2**, one of the butyl chains was disordered only in the β carbon position. The occupancy of the disordered carbons in the butyl chains were refined to nearly 50:50 whereby the C-C distance was tightly restrained to 1.500±0.005 Å. For **HG4**, one of the cyclohexyl ring was disordered in 4 positions, carbon C_{β}, C_{γ}, $C_{\beta'}$ and C_{γ}. The highest peak obtained for **HG4** was 2.177 and the molecular structure showed that it had one high Q peak near the cyclohexyl ring. This could be due to the influence of disorder factor in the cyclohexyl ring. However, as both complexes **HG2** and **HG4** had satisfactory refinement factor, which is below 5.0 %, this findings revealed that the atoms in each of the molecular structure were satisfactorily fitted into the predicted structural model.

Figure 4.3.8a
Molecular plot of [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HG1**



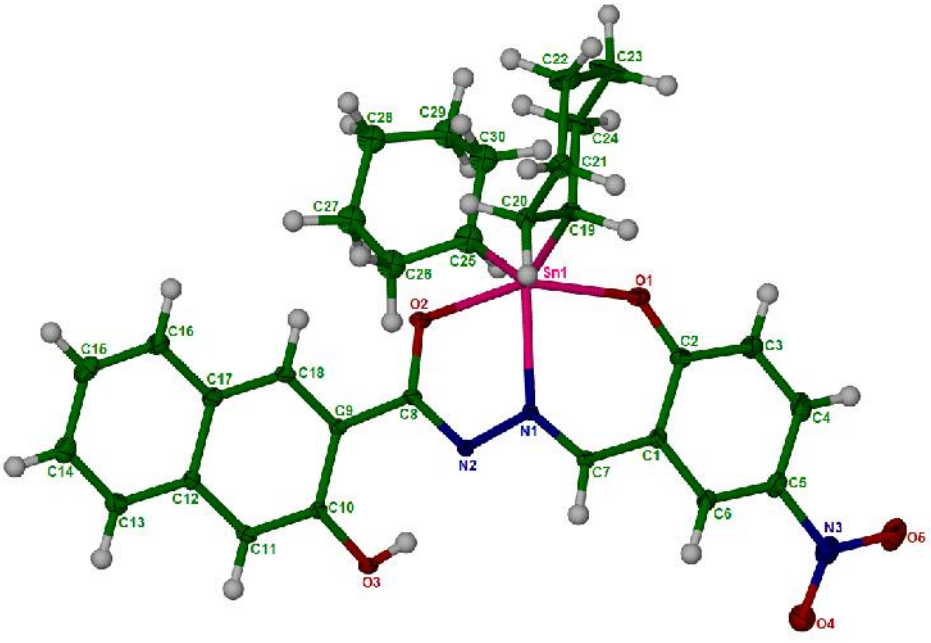
(note: Complex **HG1** was a highly disordered structure. The following atoms were rendered isotropic due to the disordered in the naphthalene ring, phenyl ring and the solvated solvent; C4, C13, C16, C21, C22, C23 and C24. Solvate molecule lain about an inversion centre)

Figure 4.3.8b
Molecular plot of [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HG2**



(note: C45, C46, C47 and C48 were rendered isotropic due to the disordered in the butyl chain)

Figure 4.3.8c
Molecular plot of [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HG4**



(note: C26, C27, C28, C29 and C30 were rendered isotropic due to the disordered in the cyclohexyl ring)

Table 4.3.24
Crystallographic parameters for complexes **HG1**, **HG2** and **HG4**

	HG1	**HG2**	**HG4**
Empirical formula	$C_{20}H_{17}N_3O_5Sn$	$C_{26}H_{29}N_3O_5Sn$	$C_{30}H_{33}N_3O_5Sn$
Formula weight	498.06	582.21	634.28
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.8921(12)	9.3745(2)	9.3242(2)
b (Å)	17.615(2)	9.6680(1)	10.0195(2)
c (Å)	13.4273(16)	29.6491(5)	28.8210(6)
α (^{o})	90	90.611(1)	90
β (^{o})	109.045(8)	96.752(1)	94.194(2)
γ (^{o})	90	109.485(1)	90
Volume (Å^3)	2211.7(5)	2512.13(7)	2685.36(10)
Z	4	4	4
Calculated density, D_{calc} (Mgm^{-3})	1.496	1.539	1.569
Absorption coefficient, μ (mm^{-1})	1.189	1.059	0.998
F(000)	992	1184	1296
Crystal size (mm)	0.31 x 0.27 x 0.12	0.40 x 0.40 x 0.11	0.36 x 0.36 x 0.04
Limiting indices	- 12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -17 ≤ l ≤ 17	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -38 ≤ l ≤ 38	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -34 ≤ l ≤ 34

Reflections collected / unique	14754 / 4347 [$R_{(int)}$ = 0.1011]	24046 / 11534 [$R_{(int)}$ = 0.0196]	20087 / 4724 [$R_{(int)}$ = 0.0398]
Max. and min. transmission	0.8924 and 0.6768	0.8705 and 0.7095	0.9650 and 0.7153
Data / restraints / parameters	4347 / 2 / 307	11534 / 0 / 637	4724 / 1 / 353
Goodness-of-fit on F^2	1.722	1.056	1.026
Final R indices [$I>2\sigma(I)$]	R_1 = 0.1170, wR_2 = 0.2906	R_1 = 0.0404, wR_2 = 0.0861	R_1 = 0.0525, wR_2 = 0.1206
R indices (all data)	R_1 = 0.1627, wR_2 = 0.3092	R_1 = 0.0488, wR_2 = 0.0917	R_1 = 0.0730, wR_2 = 0.1325
Largest diff. peak and hole ($eÅ^{-3}$)	3.354 and -1.765	1.623 and -1.544	2.177 and -1.352

Table 4.3.25
Selected bond lengths (Å) and angles (^{o}) with estimated standard deviation for complexes **HG1, HG2** and **HG4**

	HG1	**HG2**	**HG4**
Bond lengths			
Sn(1)-O(1)	2.082(11)	2.092(2), 2.106(2)	2.12(5)
Sn(1)-O(2)	2.149(11)	2.152(2), 2.128(2)	2.13(5)
Sn(1)-N(1)	2.176(11)	2.170(3), 2.169(3)	2.18(5)
Sn(1)-C_i	2.134(14)	2.117(3), 2.087(6)	2.14(8)
Sn(1)-C_i'	2.116(14)	2.119(3), 2.151(4)	2.15(8)
C(2)-O(1)	1.344(18)	1.304(4), 1.309(4)	1.30(8)
C(8)-O(2)	1.305(15)	1.289(4), 1.286(4)	1.30(7)
C(7)-N(1)	1.315(17)	1.297(4), 1.298(4)	1.29(8)
C(8)-N(2)	1.322(18)	1.317(4), 1.321(4)	1.31(8)
N(2)-O(3)	2.563(13)	2.620(3), 2.597(4)	2.61(6)
Bond angles			
O(1)-Sn(1)-O(2)	156.6(4)	156.46(9), 156.45(9)	155.9(17)
C_i-Sn(1)- C_i'	131.0(7)	129.48(4), 131.1(2)	126(3)
N(1)-Sn(1)- C_i	114.1(6)	116.70(12), 119.10(17)	120(2)
N(1)-Sn(1)- C_i'	114.3(5)	113.25(12), 109.75(15)	113(3)

Note:
C_i and C_i'refer to the *ipso*-carbon of the diorganotin moieties attached to the central tin atom

4.4 CYTOTOXIC ACTIVITY

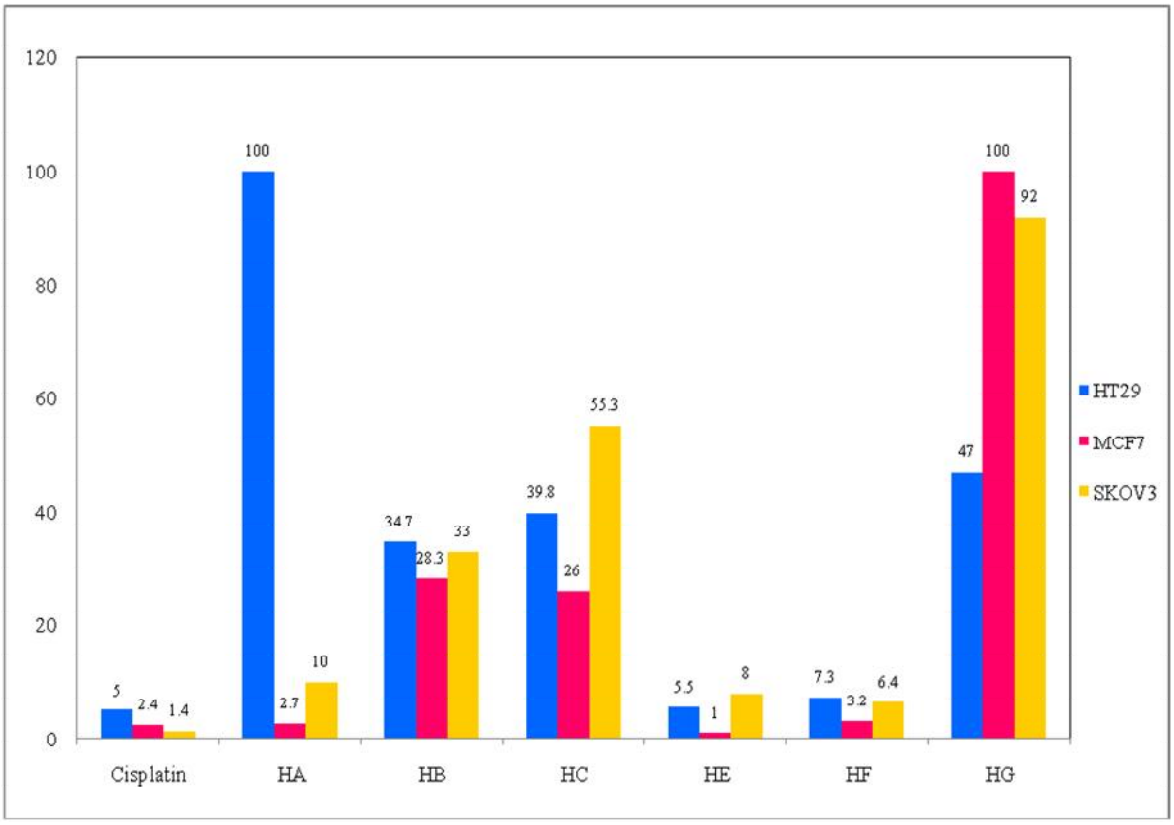
The *in vitro* cytotoxic activity of the Schiff bases and their diorganotin complexes had been evaluated against three human carcinoma cell lines, namely HT-29 (human colon carcinoma cell line), SKOV-3 (human ovarian cancer cell line), MCF-7 (hormone-dependent breast carcinoma cell line) and MRC5 (non-cancer human fibroblast cell line). In the anticancer screening, the Schiff base ligands and their diorganotin complexes were dissolved in DMSO. The amount of DMSO used did not reveal any cytotoxic activity.

Cisplatin was used as positive control and the well containing untreated cells was used as the negative control. The cytotoxicity of each sample was expressed as IC_{50} value which referred to the concentration of test compounds that caused 50 % inhibition or cell death as averaged from the three experiments, and was obtained by plotting the graph of percentage inhibition (%) versus the concentration of test compounds (μg mL^{-1}). Only selected complexes were tested for their anticancer screening whereby the IC_{50} values of the selected Schiff base ligands and the diorganotin complexes are listed in table 4.4.1. However, the IC_{50} values for MRC5 (non-cancer human fibroblast cell line) were only obtained for selected compounds due to the difficulty in growing and maintaining the normal cell lines.

In the present study, *cisplatin* was found to exhibit remarkable growth inhibitory activities with IC_{50} values ranging from 1.4-5.7 μg mL^{-1} on the studied cancer cell lines. The diorganotin complexes generally displayed pronounced cytotoxicity against all the tested human cell lines as compared to the Schiff base ligands.

The overall results as shown in the tabulated data, show that the Schiff base ligands were not as active as most of their diorganotin complexes. In particular, the ligands, **HA**, **HB**, **HC** and **HG** which contained the salicylaldehyde moieties showed poorer cytotoxic activities compared to the substituted 2-hydroxyacetophenone Schiff base ligands, **HE** and **HF**.

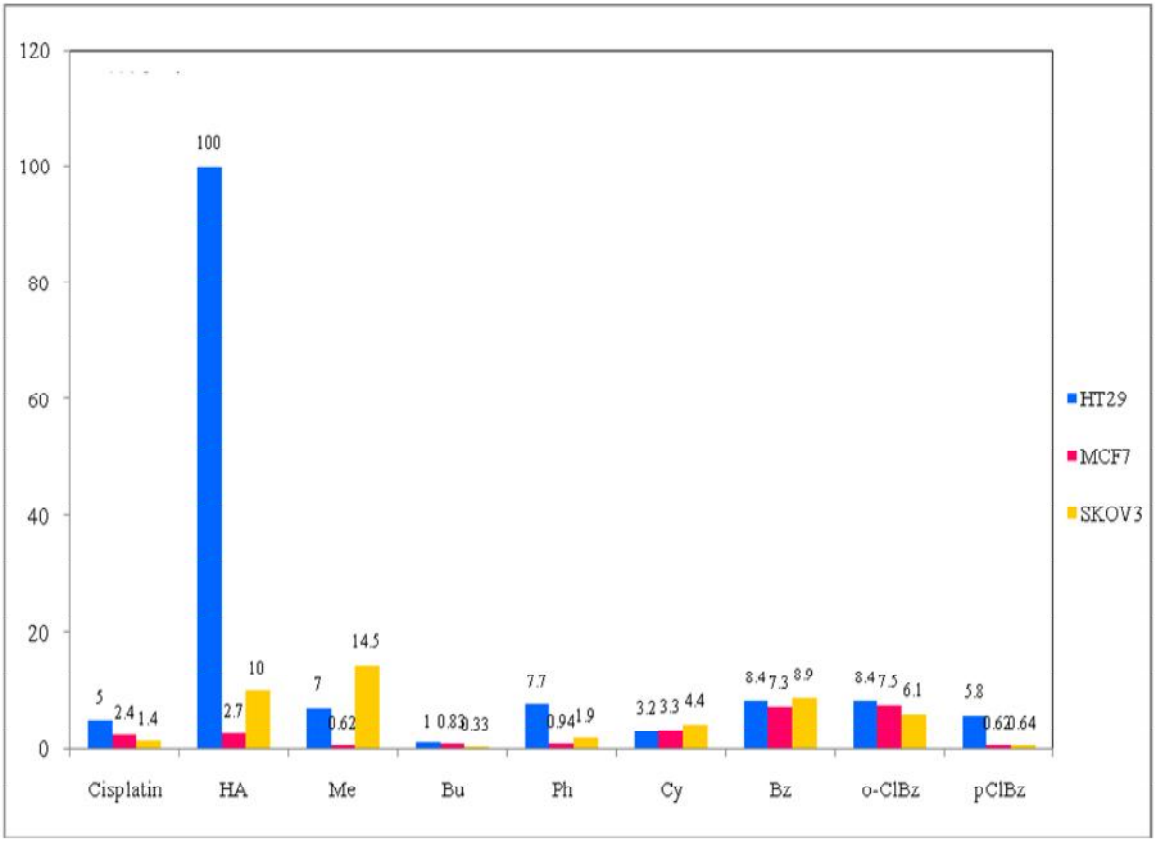
Graph 4.4.1
Bar chart showing the comparison of the IC_{50} value of the 3-hydroxy-2-naphthoic hydrazide Schiff base ligands against *cisplatin*



In **HA** series, the Schiff base ligand was not active against the HT-29 cell lines (IC_{50} > 100 μg ml^{-1}) but it displayed good cytotoxic activity against the MCF-7 and SKOV-3 cell lines (IC_{50} = 2.7 μg ml^{-1} and 10 μg ml^{-1}). The dibutyltin and dicyclohexyltin of this Schiff base ligand showed remarkable anticancer activities as compared to the other tested diorganotins in all the cell lines. The order of activities followed the order: dimethyltin > diphenyltin > dibenzyltin > di(*p*-chlorobenzyl)tin >

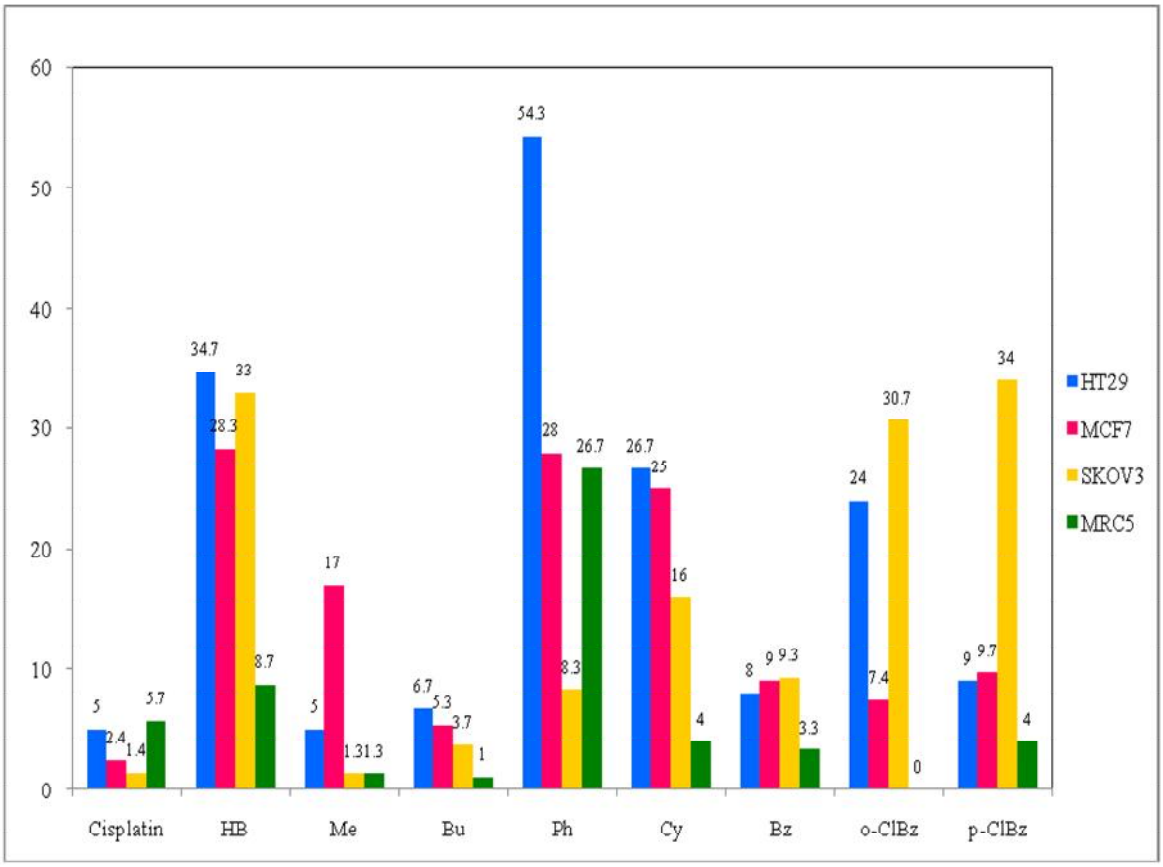
di(*o*-chlorobenzyl)tin derivatives. Overall, the Schiff base ligand and the diorganotin complexes showed prominent activities against the MCF-7 cell line with IC_{50} values of less than 8 μg ml^{-1}.

Graph 4.4.2a
Bar chart showing IC_{50} value of *N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA** and [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes



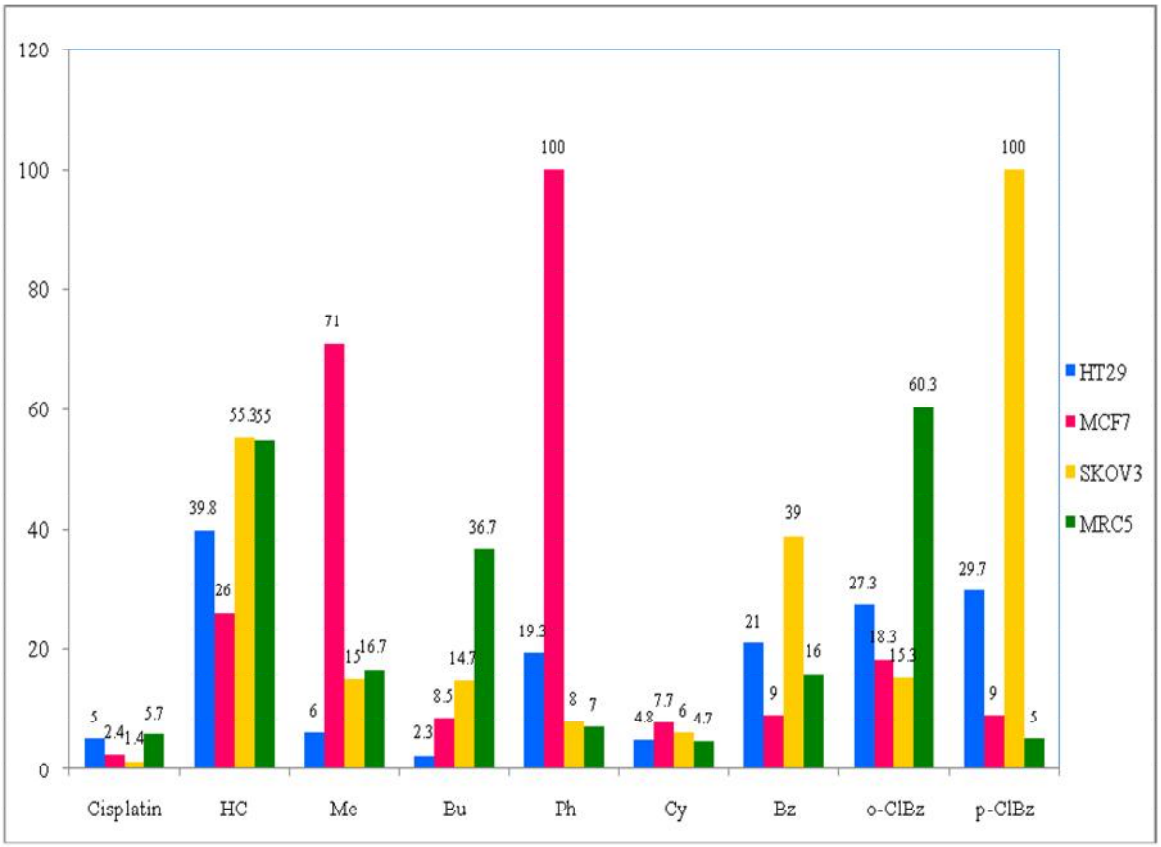
In the case of the **HB** series, the Schiff base ligand was less cytotoxic against the tested human carcinoma cell lines (HT-29, MCF-7 and SKOV-3) in comparison with the MRC5 cell lines with IC_{50} of 8.7 μg ml^{-1}. It was noted that **HB3** which contained the diphenyltin moieties, showed the lowest cytotoxic activity against HT-29 and MCF-7 cell lines compared to the other diorganotin derivatives. The dimethyltin, dibutyltin and dibenzyltin derivatives had comparable IC_{50} values as those for *cisplatin* against all the cell lines, except for **HB1**.

Graph 4.4.2b
Bar chart showing IC_{50} value of *N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB** and [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes



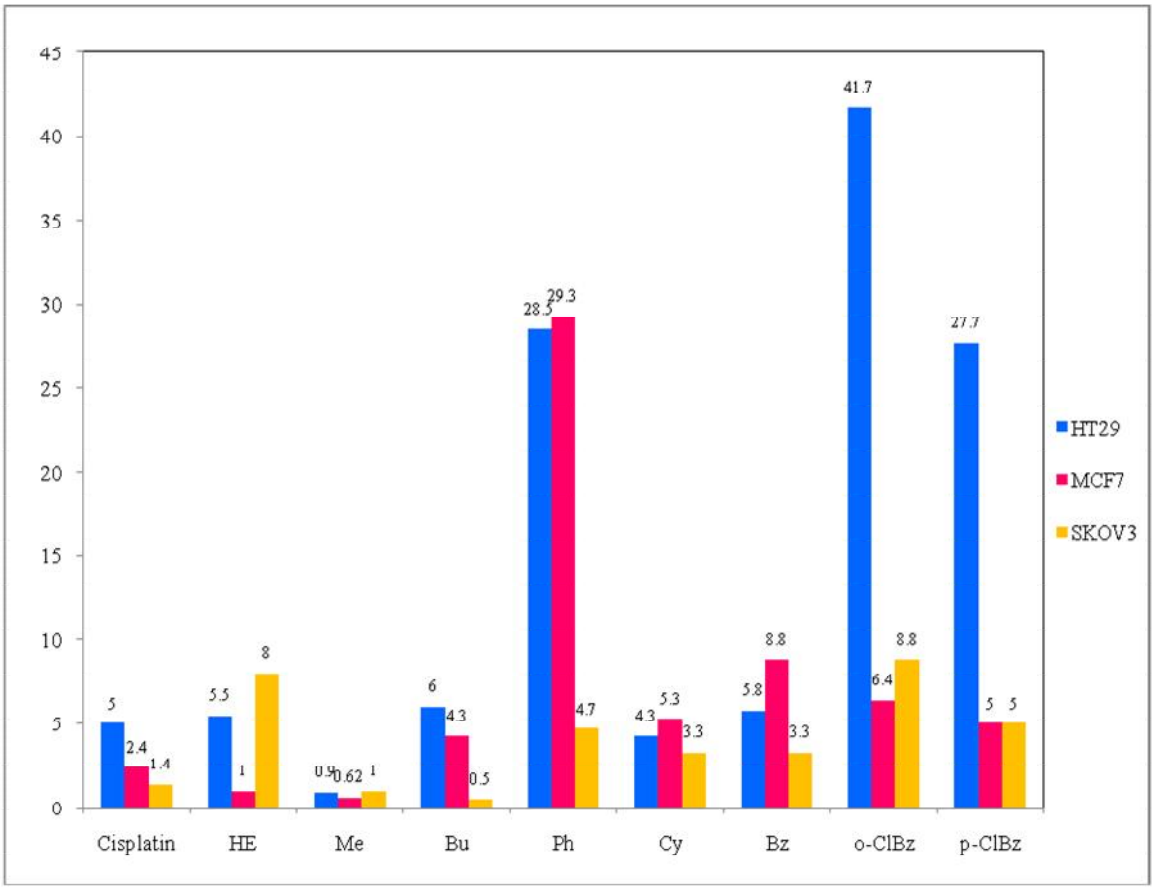
As for the **HC** series, the dimethyltin derivative, **HC1**, was less cytotoxic against MCF-7 and SKOV-3 cell lines. Among the diorganotin complexes in this series, the dicyclohexyltin derivative, **HC4**, showed remarkable cytotoxic activity against all the tested cell lines. Selectivity was observed for dibenzyltin and di(*p*-chlorobenzyl)tin derivatives, **HC5** and **HC7**, which were found to be especially active against MCF-7 cell line. However, the dimethyltin, **HC1** and diphenyltin derivatives, **HC3** were not found to be active against the MCF-7 cell line.

Graph 4.4.2c
Bar chart showing IC_{50} value of *N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC** and [*N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes



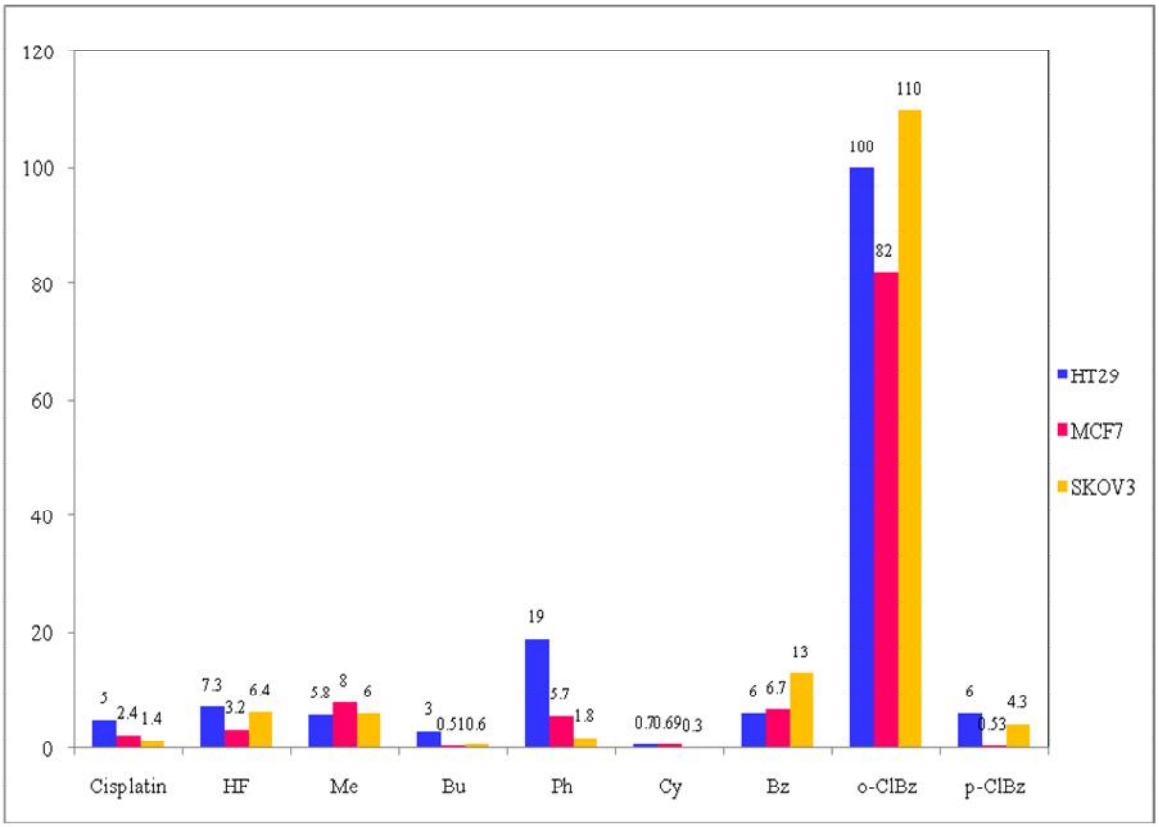
For the **HE** and **HF** series, the Schiff base ligands displayed good cytotoxic activities towards all the cell lines. Both these ligands were especially active against the MCF-7 cell line. For the **HE** series, the dimethyltin derivative displayed the highest activity among the tested diorganotins; followed by dibutyltin, dicyclohexyltin and dibenzyltin. These diorganotins showed comparable cytotoxic activities to the ligand, **HE**. The other diorganotin complexes of **HE**, namely the diphenyltin, di(*o*-chlorobenzyl)tin and di(*p*-chlorobenzyl)tin complexes, displayed moderate activities in all the cell lines especially against HT-29.

Graph 4.4.2d
Bar chart showing IC_{50} value of *N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HE** and {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes



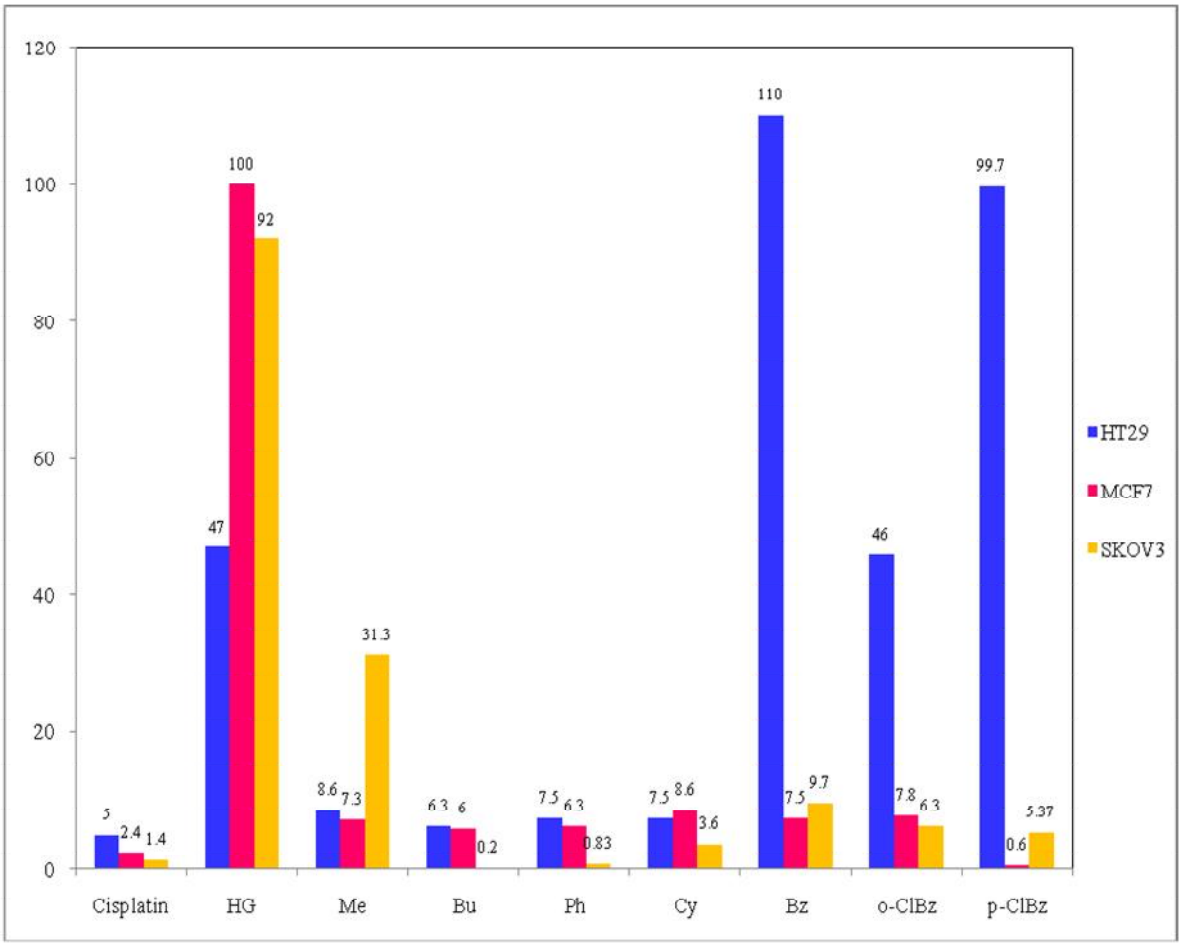
In the case of **HF** series, both the dibutyltin (**HF2**) and dicyclohexyltin (**HF4**) derivatives displayed better cytotoxic activities against all the cell lines as compared to the ligand **HF**. However, the di(*o*-chlorobenzyl)tin derivative, **HF6** hardly killed any of the cell in the tested cell-lines. **HF3** which contained the phenyl moieties only displayed moderate activity against the HT-29 cell line. The dimethyltin, dibenzyltin and di(*p*-chlorobenzyl)tin derivatives displayed equally good cytotoxic activities as the Schiff base ligand.

Graph 4.4.2e
Bar chart showing IC_{50} value of {*N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide}, **HF** and {*N'*-[1-(5-chloro-2-oxidophenyl)-ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes



In the **HG** series, the dibutyltin derivative, **HG2**, again showed the most prominent activity among the diorganotins and the Schiff base ligand. The dicyclohexyltin (**HG4**), dimethyltin (**HG1**) and diphenyltin (**HG3**) derivatives showed much better cytotoxic activities than the ligand. However, the dibenzyltin (**HG5**) and substituted dibenzyltin (**HG6**, **HG7**) derivatives showed poor anticancer activities against the HT-29 cell line but good cytotoxic activities against the MCF-7 and SKOV-3 cell-lines.

Graph 4.4.2f
Bar chart showing IC_{50} value of *N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG** and [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes



In conclusion, the dibutyltin derivatives were found to display good cytotoxic activity against all the tested cell lines, followed by the dicyclohexyltin derivatives. This trend was consistent in most of the cell lines. The diaryltin and substituted diaryltin derivatives showed moderate or poor anticancer activities in all the cell lines. The di(*o*-chlorobenzyl)tin derivatives were the least active among all the diorganotins which were tested for the anticancer screening.

Table 4.4.1a
Cytotoxic activity of *N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA** and [*N'*-(2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Compound	Cell lines (IC_{50} μg ml^{-1})[a]		
	HT-29	**MCF-7**	**SKOV-3**
cisplatin	5± 0	2.4 ± 0.6	1.4 ± 0
N'-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HA**	> 100	2.7 ± 1.5	10 ± 0
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dimethyltin(IV), **HA1**	7.0 ± 0.1	0.62 ± 0.01	14.5 ± 2.3
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibutyltin(IV), **HA2**	1 ± 0	0.83 ± 0.01	0.33 ± 0
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diphenyltin(IV), **HA3**	7.7 ± 0.1	0.94 ± 0.01	1.9 ± 0.2
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dicyclohexyltin(IV), **HA4**	3.2 ± 0.2	3.3 ± 0.3	4.4 ± 0.2
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]dibenzyltin(IV), **HA5**	8.4 ± 0.2	7.3 ± 0.3	8.9 ± 0.4
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*o*-chlorobenzyl)-tin(IV), **HA6**	8.4 ± 0.2	7.5 ± 0.1	6.1 ± 0.2
[*N'*-(2-Oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]di(*p*-chlorobenzyl)-tin(IV), **HA7**	5.8 ± 0.5	0.62 ± 0	0.64 ± 0

[a] IC_{50} values (μg ml^{-1}) = inhibition concentration at 50% *i.e.*, the concentration to reduce growth of cancer cells by 50%

Table 4.4.1b
Cytotoxic activity of *N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB** and [*N'*-(5-bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diorganotin complexes

Compound	Cell lines (IC_{50} μg ml^{-1})[a]			
	HT-29	**MCF-7**	**SKOV-3**	**MRC-5**
cisplatin	5± 0	2.4 ± 0.6	1.4 ± 0	5.7 ± 0.6
N'-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HB**	34.7 ± 1.5	28.3 ± 2.9	33 ± 1.7	8.7 ± 1.5
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HB1**	5± 0	17 ± 3.6	1.3 ± 0.6	1.3 ± 0.6
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HB2**	6.7 ± 0.6	5.3 ± 0.6	3.7± 0.6	1 ± 0
[(*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diphenyltin(IV), **HB3**	54.3 ± 3.1	28 ± 4	8.3 ± 0.6	26.7 ± 9.1
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HB4**	26.7 ± 0.6	25 ± 2	16 ± 1	4 ± 0
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibenzyltin(IV), **HB5**	8 ± 0	9 ± 0	9.3 ± 0.6	3.3 ± 0.6
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*o*-chlorobenzyl)tin(IV), **HB6**	24 ± 0.9	7.4 ± 0	30.7 ± 0.6	-
[*N'*-(5-Bromo-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*p*-chlorobenzyl)tin(IV), **HB7**	9 ± 0	9.7 ± 1.5	34 ± 1.7	4 ± 0

[a] IC_{50} values (μg ml^{-1}) = inhibition concentration at 50% *i.e.*, the concentration to reduce growth of cancer cells by 50%

Table 4.4.1c
Cytotoxic activity of *N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC** and [*N'*-(5-chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diorganotin complexes

Compound	Cell lines (IC_{50} μg ml^{-1})[a]			
	HT-29	**MCF-7**	**SKOV-3**	**MRC-5**
cisplatin	5± 0	2.4 ± 0.6	1.4 ± 0	5.7 ± 0.6
N'-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HC**	39.8 ± 1.0	26 ± 1.7	55.3 ± 0.6	55 ± 8.7
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HC1**	6 ± 0	71 ± 4.6	15 ± 6.2	16.7 ± 3.5
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HC2**	2.3 ± 1.2	8.5 ± 0.5	14.7 ± 4.5	36.7 ± 6.4
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diphenyltin(IV), **HC3**	19.3 ± 1.5	> 100	8 ± 0	7 ± 0
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HC4**	4.8 ± 0.3	7.7 ± 0.6	6 ± 0	4.7 ± 0.6
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibenzyltin(IV), **HC5**	21 ± 0	9 ± 0	39 ± 1	16 ± 0
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*o*-chlorobenzyl)tin(IV), **HC6**	27.3 ± 1.2	18.3 ± 0.6	15.3 ± 1.2	60.3 ± 4.9
[*N'*-(5-Chloro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*p*-chlorobenzyl)tin(IV), **HC7**	29.7 ± 1.2	9 ± 0	> 100	5 ± 0

[a] IC_{50} values (μg ml^{-1}) = inhibition concentration at 50% *i.e.*, the concentration to reduce growth of cancer cells by 50%

Table 4.4.1d
Cytotoxic activity of *N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HE** and {*N'*-[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

Compound	Cell lines (IC_{50} μg ml^{-1})[a]		
	HT-29	**MCF-7**	**SKOV-3**
cisplatin	5± 0	2.4 ± 0.6	1.4 ± 0
N'-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HE**	5.5 ± 0	1 ± 0	8 ± 0.3
{ *N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dimethyltin(IV), **HE1**	0.9 ± 0.1	0.62 ± 0.01	1 ± 0
{ *N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dibutyltin(IV), **HE2**	6 ± 0	4.3 ± 0.3	0.5 ± 0
{ *N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-diphenyltin(IV), **HE3**	28.5 ± 0.5	29.3 ± 1.2	4.7 ± 0.6
{ *N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dicyclohexyltin(IV), **HE4**	4.3 ± 0.3	5.3 ± 0.6	3.3 ± 0.6
{ *N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dibenzyltin(IV), **HE5**	5.8 ± 0.3	8.8 ± 0.3	3.3 ± 0.6
{ *N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **HE6**	41.7 ± 1.5	6.4 ± 0.1	8.8 ± 0.3
{ *N'*-[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **HE7**	27.7 ± 3.1	5± 0	5 ± 0

[a] IC_{50} values (μg ml^{-1}) = inhibition concentration at 50% *i.e.*, the concentration to reduce growth of cancer cells by 50%

Table 4.4.1e
Cytotoxic activity of *N'*-[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HF** and {*N'*-[1-(5-chloro-2-oxidophenyl)-ethylidene]-3-hydroxy-2-naphthohydrazidato}diorganotin complexes

Compound	Cell lines (IC_{50} μg ml^{-1})[a]		
	HT-29	**MCF-7**	**SKOV-3**
cisplatin	5± 0	2.4 ± 0.6	1.4 ± 0
N'-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **HF**	7.3 ± 1.5	3.2 ± 0.1	6.4 ± 1.2
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dimethyltin(IV), **HF1**	5.8 ± 0.3	8 ± 0	6 ± 0
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dibutyltin(IV), **HF2**	3± 0	0.51 ± 0.02	0.6 ± 0.1
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-diphenyltin(IV), **HF3**	19 ± 0	5.7 ± 0.4	1.8 ± 0.3
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dicyclohexyltin(IV), **HF4**	0.7± 0	0.69 ± 0.01	0.3 ± 0
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dibenzyltin(IV), **HF5**	6 ± 0	6.7 ± 0.2	13 ± 0
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **HF6**	100 ± 0	82 ± 1.7	> 100
{*N'*-[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **HF7**	6 ± 0	0.53 ± 0.01	4.3 ± 0.3

[a] IC_{50} values (μg ml^{-1}) = inhibition concentration at 50% *i.e.*, the concentration to reduce growth of cancer cells by 50%

Table 4.4.1f
Cytotoxic activity of *N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG** and [*N'*-(5-nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]diorganotin complexes

Compound	Cell lines (IC_{50} μg ml^{-1})[a]		
	HT-29	**MCF-7**	**SKOV-3**
cisplatin	5± 0	2.4 ± 0.6	1.4 ± 0
N'-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazide, **HG**	47 ± 0	> 100	92 ± 1.0
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dimethyltin(IV), **HG1**	8.6 ± 0.1	7.3 ± 0.6	31.3 ± 0.6
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibutyltin(IV), **HG2**	6.3 ± 1.2	6 ± 0	0.2 ± 0.1
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-diphenyltin(IV), **HG3**	7.5 ± 0.9	6.3 ± 0.6	0.83 ± 0.02
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dicyclohexyltin(IV), **HG4**	7.5 ± 0.3	8.6 ± 0.2	3.6 ± 0.1
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-dibenzyltin(IV), **HG5**	> 100	7.5 ± 0.2	9.7 ± 0.3
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*o*-chlorobenzyl)tin(IV), **HG6**	46 ± 0	7.8 ± 0.2	6.3 ± 0.1
[*N'*-(5-Nitro-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato]-di(*p*-chlorobenzyl)tin(IV), **HG7**	99.7 ± 0.6	0.6 ± 0.01	5.37 ± 0.12

[a] IC_{50} values (μg ml^{-1}) = inhibition concentration at 50% *i.e.*, the concentration to reduce growth of cancer cells by 50%