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Chiral rings from BINOL dicarboxylic acids and alkane ditin(IV) linkers

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Abstract

The first series of building blocks for metal-organic frameworks (MOFs) utilizing the (*S*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-dicarboxylic acid ligand linked with a number of α,ω-bis(chlorodiorganostannyl) alkane spacers and α,ω-bis(dichloroorganostannyl) alkane spacers has been synthesized and characterized. The new compounds have been shown to form monomeric chiral rings with the potential to generate large coordination networks. The potential formation of chiral supramolecular and polymeric materials from the chiral precursors was explored by investigating the structures that form as a result of the hypervalency available at metal centers. These chiral compounds were built using the concept that stemmed from the construction of MOFs. The 'pre-organized' chiral rings synthesized here can potentially find use in chiral catalysis, enantioselective synthesis and in designing chiral polymers.

Keywords: BINOL ligand; chirality; metal-organic framework; organotin (IV) linkers; tin carboxylates.

Introduction

Metal-organic frameworks (MOFs) are of interest for a number of important chemical processes such as catalysis, separation, sensor technology and optoelectronics (Xiong et al., 2001; Evans and Lin, 2002; Jiang et al., 2003; Jeon et al., 2007; Wu and Lin, 2007; Czaja et al., 2009; Farrusseng et al., 2009; Li et al., 2009; Ma et al., 2009). The addition of a chiral entity to the intended system makes MOFs particularly useful in enantioselective separation and catalysis (Jiang et al., 2003; Wu et al., 2005; Jeon et al., 2007; Wu and Lin, 2007).

MOFs are assembled from modular organic building blocks linked by coordination bonds, such as covalent and non-covalent interactions. The modular construction of MOFs allows flexible and rational design, as both the architecture and chemical functionality of the cavities can, in principle, be precisely controlled. The choice of ligand requires significant consideration. Of particular interest is the chiral 1,1′-binaphthalene unit due to its versatility and structural features such as C_2 symmetry (Burk et al., 1991; Trotta et al., 2002). Importantly, both enantiomers (*R* and *S* forms) of BINOL are readily available and inexpensive. The incorporation of chiral BINOL into MOFs can prepare systems useful for asymmetric synthesis and chiral catalytic processes (Burk et al., 1991; Kumaraswamy et al., 2001; Pandiaraju et al., 2001; Trotta et al., 2002; Jayaprakash et al., 2003; Shibasaki and Matsunaga, 2006).

Typically, organotin compounds exist in two oxidation states, tin(II) and tin(IV). An immense variety of structural types stem from these oxidation states, where a coordination number ranging from 2 to 7 is possible. In the solid state, the geometry of tin(IV) includes bent, trigonal planar, tetrahedral, trigonal bipyramidal, octahedral and pentagonal bipyramidal shapes (Liška, 1990). Consequently, each coordination number has a specific angle at the tin center, leading to the idea of 'fine-tuning' for the final desired structure. The introduction of electronegative groups to the tin(II) and tin(IV) compounds increases the effective nuclear charge at the tin and hence the ability for tin to increase its coordination number (Liška, 1990; Krishnamurti et al., 1991). One or more chiral groups may be attached directly to the tin atom, which can also be connected by a rigid linker to form part of the cavity structure preceding the formation of the porous material. Incorporation of Lewis acidic organotin compounds offers a method for the fine-tuning of the adsorption characteristics. This occurs through the moderation of hypervalency of the tin element.

Additionally, the supramolecular associations between metal centers have proved to be useful for crystal engineering (Buntine et al., 2003). These new molecular building block combinations enable controlled synthesis of porous materials, which contain both chirality and functionality within the framework and the ability to direct the formation of specific crystal structures (Buntine et al., 2003; Kesanli and Lin, 2003). Generally, organotin compounds are easily monitored and characterized using multinuclear nuclear magnetic resonance (NMR) (^{1}H-, ^{13}C- and ^{119}Sn-). ^{119}Sn NMR spectroscopy is particularly useful, in that it provides a very sensitive tool for the elucidation of the relative coordination numbers in an organotin compound.

Main group metals have received much less attention than transition metals and lanthanides in the field of supramolecular chemistry (Garcia-Zarracino and Hopfl, 2005b). This is, to some extent, astonishing, given that they often have better thermodynamic and kinetic stabilities available from main group metals. Organotin compounds are used for many different applications, such as PVC stabilizers, biocides and metal-based drugs (Tiekink, 1991; Fang et al., 2001; Shankar et al., 2003; Mahmood et al., 2004; Yin et al., 2004; Tian et al., 2005; Beghidja et al., 2006; Bowen et al., 2006; Ahmad et al., 2007). Additionally, they are used as catalysts for polyurethane and esterification reactions (Dakternieks et al., 2003; Baul et al., 2005; Bowen et al., 2006). Recently, organotin compounds have also shown potential as anti-tumor agents (Tiekink, 1991; Willem et al., 1997; Gielen et al., 2000; Dakternieks et al., 2003; Mahmood et al., 2004; Yin et al., 2004; Tian et al., 2005; Bowen et al., 2006; Ahmad et al., 2007).

Research into organotin(IV) carboxylates continues to be plentiful, as the different coordination numbers and geometries about the tin provide a number of structural possibilities (Tiekink, 1994; Garcia-Zarracino and Hoepfl, 2005a; Deak and Tarkanyi, 2006). To date, there are no known difuctional tin-carboxylate BINOL precursors synthesized using organotin(IV) carboxylates. The ability for carboxylate anions to change from one coordination mode to another, and the variety of coordination modes, possibly make them an appealing ligand for main group coordination complexes.

Additionally, organotin(IV) chlorides provide an interesting avenue for further functionalizating the precursors and have also been explored in this study.

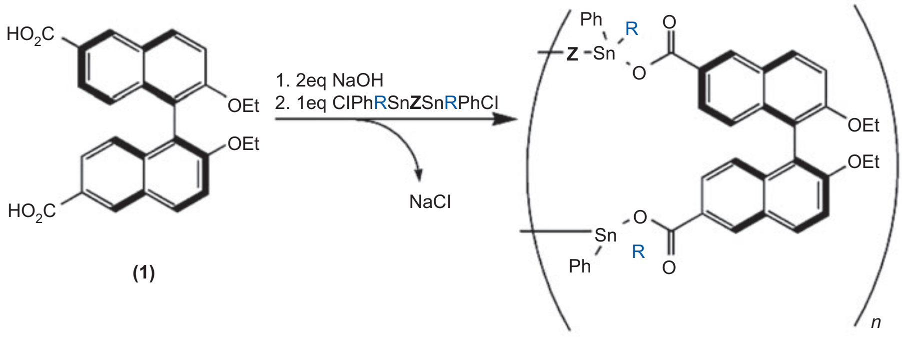
The organotin(IV) linkers used in this work include α,ω-bis(chlorodiorganostannyl)alkanes and α,ω-bis(dichloroorganostannyl)alkanes where the alkane chain length varies from n=1–6, including aryl bridged with the formula: *m*-$(CH_2)_2C_6H_4(CH_2)_2$, and *p*-$(CH_2)_2C_6H_4(CH_2)_2$; linkers with this formula have been used as precursors for a number of reactions, such as for the formation of double and triple ladders and a number of hybrid materials (Gielen and Jurkschat, 1984; Jurkschat et al., 1990; Dakternieks et al., 1995, 2003; Mehring et al., 1997, 1999; Zobel et al., 2001a,b; Beckmann et al., 2002a,b, 2004; Jousseaume et al., 2002; Elhamzaoui et al., 2004, 2007, 2008).

This work focuses on determining the ideal pathway to synthetize chiral building blocks capable of MOF assembly. The construction of (*S*)-1,1′-binaphthalene derivatives incorporating carboxylate linkers forming a series of useful ligands will be investigated. Furthermore, the outcome of coordination reactions with various tin(IV) compounds and the chiral linkers will be assessed. The intention will be to form unique building blocks capable of creating organized MOF networks. The unique chiral building blocks can potentially be applied to catalysis and separation.

Results and discussion

The design strategy involved the coordination of the carboxylate functionality of the BINOL ligand with α,ω-bis(chlorodiorganostannyl)alkane and α,ω-bis(dichloroorganostannyl)alkane linkers to generate suitable building blocks for the formation of precursor chiral MOFs. The results of these coordination reactions have been studied and discussed below.

In Scheme 1, the general synthesis of a series of (*S*)-6,6′-dicarboxyl-(bis(diorganostannyl)alkanes)-2,2′-diethoxy-1,1′-binaphthylene compounds is shown. The initial step required the preparation of the sodium salt of (*S*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-dicarboxylic acid (**1**), where sodium hydroxide was added to the dicarboxylic acid in a 3:1 ethanol:water mix. Once prepared, the disodium (*S*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-dicarboxylate was slowly added drop wise to a solution of each



(1)

R=Ph, **Z**=CH_2 **(2)**
=$(CH_2)_3$ **(3)**
=$(CH_2)_4$ **(4)**
=$(CH_2)_5$ **(5)**
=$(CH_2)_6$ **(6)**
=*m*-$(CH_2)_2C_6H_4(CH_2)_2$ **(7)**
=*p*-$(CH_2)_2C_6H_4(CH_2)_2$ **(8)**
R=CH_2SiMe_3, **Z**=CH_2 **(9)**
=$(CH_2)_4$ **(10)**

Scheme 1 Reactions of α,ω-bis(chlorodiorganostannyl)alkane spacers with (*S*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis(carboxylic acid) precursor.

α,ω-bis(trimethylsilylmethylchlorophenylstannyl)alkanes or α,ω-bis(trimethylsilylmethylchlorophenylstannyl)alkanes in ethanol. The reaction mixture was stirred overnight, followed by the collection of the resulting precipitate.

For characterization, the ^{119}Sn NMR and ^{13}C NMR spectrum of samples **2–10** was collected. In addition, electrospray mass spectrometry experiments were carried out to determine the $[M+H]^+$ mass cluster for each of the compounds formed from the reaction. IR analysis was used to determine the presence of the C(O)(O-Sn) functionality.

Table 1 shows the ^{119}Sn NMR chemical shifts obtained for the series of novel compounds **2–10**, the $[M+H]^+$ mass clusters found from the electrospray mass spectrometry experiments, and the IR frequencies corresponding to ν[C(O)(O-Sn)]. The ^{1}H and ^{13}C NMR spectrum was collected for compounds **2–10;** refer to the experimental section for chemical shifts. The ^{1}H NMR shifts are reported only for compound **4;** all compounds presented similar spectra where the proton integration correlated well with the monomeric compounds.

As can be seen in Table 1, the ^{119}Sn NMR chemical shift for (*S*)-6,6′-dicarboxyl-(bis(diphenylstannyl)methane)-2,2′-diethoxy-1,1′-binaphthylene (**2**) is significantly different from the other compounds in the series synthesized under the same conditions (Scheme 1). It was postulated that compound **1** was five coordinate and the other compounds, **3-10,** contain tin species that are four coordinate. This conclusion was drawn due to the high frequency of the ^{119}Sn NMR chemical shift (Wrackmeyer, 1985).

The spectra collected from electrospray mass spectrometry for the series of **2–10** correlate with the calculated $[M+H]^+$ mass clusters for the monomeric compound, including correct isotopic patterns. In addition, the isotopic pattern observed from the spectra of each compound from the series of **2–10,** mimics the simulated isotopic patterns calculated for the monomeric species (Figures 1A and 1B, respectively, for compound **2**). However, it must also be mentioned that a dimeric species of the series of **1–9**, where the molecular ion is $[2M+H]^+$ and $[M_2+2H]^{2+}$, were observed (where n=2, Scheme 1). Nevertheless, the clusters assigned to the dimeric species were observed at significantly lower intensities compared to the monomeric species.

Further investigation into the concentration of the solutions and the effect on the yields of oligomer formation were performed. The relative intensities in the mass spectrum were also compared. The results from each revealed that it was difficult to determine whether the concentration of the solutions were a contributing factor to the formation of varying sized oligomers. The mass spectrometry results obtained did not confirm the proposed theory; this, however, does not rule out the possibility that the peaks seen are not dimeric doubly charged species and that the dimeric species may be formed during the electrospray process.

Table 1 Characterization details found for compounds **2–10**.

Compound	^{119}Sn NMR Chemical Shift ppm (δ)	ESMS $[M+H]^+$ (m/z)	IR (cm^{-1}) ν[C(O)(O-Sn)]
2	-198.7	989.0982	1620.2
3	-47.3	1017.2011	1623.0
4	-46.2	1031.1405	1623.0
5	-45.4	1045.1912	1632.1
6	-36.9	1059.1734	1632.5
7	-48.8	1107.1749	1623.0
8	-48.8	1107.2097	1623.2
9	-58.9	1009.1802	1623.3
10	-47.2	1051.1864	1623.2

The ring sizes were estimated using van der Waals radii values and ranged between 5 and 10 Å for the series of new compounds.

The added functionality provided by a halogen group on the organotin(IV) spacer creates a reactive site for easy access to prepare larger networks.

The reaction of α,ω-bis(dichloroorganostannyl)alkanes with the (*S*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-dicarboxylic acid building unit was explored. These substitution reactions were achieved in a similar manner to that described above. However, an alternate method for preparing the sodium salt of the carboxylic acid was employed, where sodium carbonate was used. The reaction proceeded by the slow addition of the ditin spacer, where the solvent used was 70% dichloromethane in methanol. The reaction is shown in Scheme 2.

A number of characterization techniques were carried out to identify the structure of compounds **12–18**; these include ^{119}Sn NMR, ^{13}C NMR, electrospray mass spectrometry and IR spectroscopy. The ^{1}H NMR spectra are not included in this series of compounds. Similar results were seen as for compounds **2–10;** no additional structural information was sought. Again, with compounds **12–18,** crystallization techniques were attempted using a number of solvent combinations, however, powders were always produced. Table 2 below provides a summary of the results obtained.

The position of the chemical shift in the ^{119}Sn NMR spectra indicates a four coordinate geometry about the tin atom in all cases (Wrackmeyer, 1985). The ^{119}Sn NMR spectra for each compound vary in the chemical shift position, especially for compounds **12** and **13**; this observation can be justified by the nature of the spacer as the compounds in the series differ.

IR analysis indicates that a [C(O)(O-Sn)] functionality still exists in the new compounds, where the IR band appears with a frequency of ~1620 cm^{-1} for the series of compounds as shown in Table 2; this correlates with analysis found in the literature (Ronconi et al., 2002).

Electrospray mass spectrometry analysis was conducted on the series of compounds **10–16**. The $[M+H]^+$ mass was found and identified with the correct isotopic pattern for the monomeric species. The experimental spectrum was in agreement with that simulated. Additionally, as mentioned previously for compounds **2–10**, close inspection of the experimental mass spectrum revealed small (5% intensity) peaks observed between the main peaks of the monomeric species, which may be the result of doubly charged dimers.

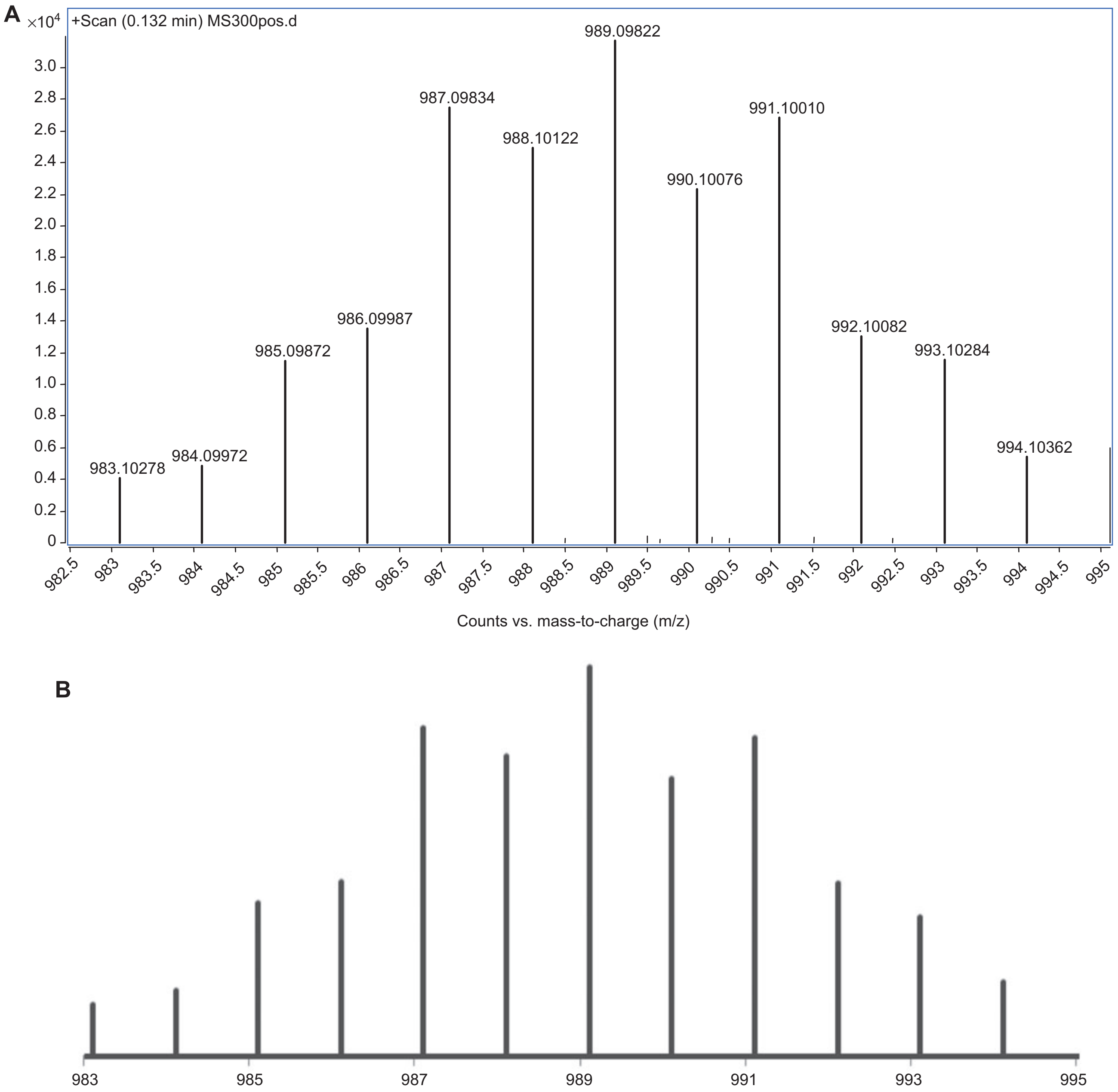


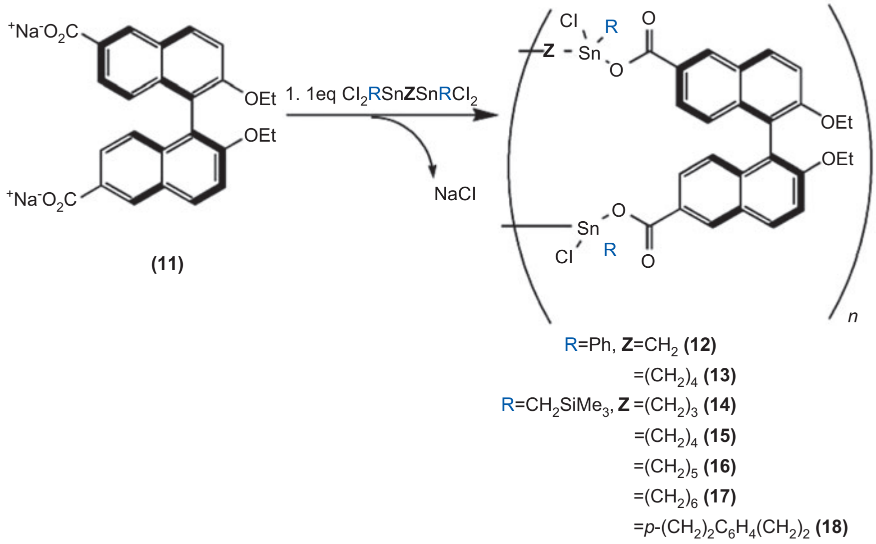
Figure 1 Experimental spectrum (A) of the mass cluster centered about m/z 989.09 found for compound (*S*)-6,6′-dicarboxyl-(bis(diphenylstannyl)-methane)-2,2′-diethoxy-1,1′-binaphthalene, **2**, $[C_{51}H_{43}O_6Sn_2]^+$ and the simulated spectrum (B).

Conclusions

The synthesis of compounds **2–10** and **12–18** using ditin precursors with varying chain lengths (alkyl- and aryl-bridged functionalities) led to a series of interesting monomeric compounds with different sized rings. The ring sizes were estimated using van der Waals radii values and range between 5 and 10 Å for the series of new compounds.

The monomeric species were confirmed from the electrospray mass spectrometry analysis, where the mass clusters observed were in agreement with those simulated. In addition, the presence of small peaks in between the main set of signals in the mass spectrometry, was observed for the entire series. This has been attributed to the presence of dimeric species which are doubly charged, being the $[M_2+2H]^{2+}$ molecular mass ion. This was further investigated by varying the concentration of the starting materials. However, no significant change in the monomer to dimer ratio was observed in the ES-MS spectra.

The characterization techniques used throughout were consistent with monomeric species synthesized in high abundance; however, the described reaction procedure could produce oligomers and rings containing varying numbers of repeating building units.



Scheme 2 Reactions of α,ω-bis(dichloroorganostannyl)alkane spacers with (*S*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis(carboxylic acid) precursor.

The novel compounds synthesized here provide intermediates which are suitable for further manipulation, which could potentially form a number of larger structural networks containing channels and cavities, which may accommodate a variety of guest molecules. These host-guest interactions may then be applied to enantioselective synthesis and chiral separation techniques.

Experimental section

General

All solvents and reagents used were of analytical reagent (AR) grade. Reactions were carried out under an atmosphere of dry nitrogen unless stated otherwise. All reagents were purchased from Sigma Aldrich (Castle Hill, NSW, Australia).

NMR spectra were recorded on a Jeol JNM-EX270 spectrometer (JEOL Australiasia, NSW, Australia) at 270.17 MHz (^{13}C), 100.75 MHz (^{119}Sn), 254.19. Also, spectra were recorded on a Jeol JNM-ECP Eclipse plus 400 spectrometer at 399.78 MHz (^{13}C), 161.84 MHz and 149.05 MHz (^{119}Sn). A Varian 300 MHz Unity Plus NMR spectrometer was also used to record spectral data at 299.98 MHz (^{13}C), 121.43 and 111.85 MHz (^{119}Sn). Both ^{13}C and ^{1}H are referenced against internal tetramethylsilane (TMS). Proton spectra are reported as: chemical shift δ (ppm) (integral). ^{119}Sn NMR is referenced against external tetramethyltin (Me_4Sn). Microanalyses were performed at the Australian National University (Canberra, Australia) or at CMAS (Geelong, Australia).

Table 2 Characterization details found for compounds **12–18**.

Compound	^{119}Sn NMR Chemical Shift ppm (δ)	ESMS $[M+H]^+$ (m/z)	IR (cm^{-1}) ν[C(O)(O-Sn)]
12	-55.4	905.9638	1619.8
13	-109.7	948.1155	1620.3
14	-18.9	954.1010	1620.2
15	-22.7	968.0551	1620.2
16	-21.0	982.0707	1619.7
17	-20.2	996.0838	1619.6
18	-27.2	1044.0610	1623.1

Column chromatography was performed with silica gel 60 (70–230 mesh). All solvents used for chromatography were AR grade.

Infrared spectroscopy was performed on a BioRad Excalibur Series FTIR spectrometer with KBr discs. Electrospray mass spectrometry (ESMS) was obtained with an Agilent Technologies (Vic, Australia) LC/MSD TOF with acetonitrile as the mobile phase with a flow rate of 25 μl min^{-1}. The diluted analyte solutions (<1 mg l^{-1} ml in dichloromethane) were injected into the spectrometer, with nitrogen gas used for nebulization. Data was collected using Agilent MassHunter Workstation Data Acquisition software and analyzed using Agilent MassHunter Qualitative Analysis software.

Simulated mass spectra were calculated using Analyst QC and plotted in Microsoft Excel. Optical rotation measurements were performed in dichloromethane using JASCO DIP-1000 Digital Polarimeter, using a Na-lamp (λ=589 nm) and a cell of 100 mm length.

(*S*)-6,6′-dicarboxyl-2,2′-diethoxy-1,1′-binaphthalene (1) Compound **1** was synthesized according to a procedure reported in the literature (Alcazar et al., 1992). To a cooled -78°C tetrahydrofuran (THF) (250 ml) solution of *n*-butyl lithium (77 ml, 1.3 м, 100 mmol) was added a solution of compound (*S*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene (Cui et al., 2002) (20 g, 40 mmol) in THF (200 ml). The combined reaction mixture was stirred for 1 h. Dry ice (CO_2) was then added slowly with caution. The reaction was allowed to warm slowly to room temperature and stirred overnight. The crude material was dissolved in ethyl acetate and washed several times (×3) with water. The aqueous fractions were collected and acidified by the slow addition of 6 м HCl; the resultant precipitate was collected and dried *in vacuo* (12 g, 70%). ^{13}C NMR (CD_3OD): δ 13.8, 64.4, 115.3, 119.2, 124.8, 125.8, 126.2, 128.1, 130.9, 131.2, 136.2, 156.3, 168.8.

General procedure for the synthesis of (*S*)-6,6′-dicarboxyl-(bis(diphenylstannyl)alkanes)-2,2′-diethoxy-1,1′-binaphthylene (2–10) To a solution of 2,2′-diethoxy-1,1′-

binaphthyl-6,6′-dicarboxylic acid (1.0 g, 2.3 mmol) in a 3:1 ethanol:water mixture (60 ml), sodium hydroxide (0.18 g, 4.6 mmol) was added and stirred until it completely dissolved. The resultant sodium salt was added drop wise to a solution of α,ω-bis(chlorodiorganostannyl)alkanes (1 mol eq.) in a 3:1 ethanol:water mixture (40 ml) and stirred overnight. The precipitate formed was collected on a sintered frit funnel, washed with water and dried *in vacuo* to yield compounds **2**–**10** as a white solid.

(*S*)-6,6′-dicarboxyl-(bis(diphenylstannyl)methane)-2,2′-diethoxy-1,1′-binaphthylene (2) The reaction of the above mentioned sodium salt with bis(chlorodiphenylstannyl)methane (1.5 g, 2.3 mmol) gave compound **2** as a white powder (1.5 g, 66%). $[\alpha]_D^{24}$=+15.8°, ^{13}C NMR ($CDCl_3$): δ -4.1, 15.1, 65.0, 115.5, 120.0, 124.8, 125.4, 126.7, 127.9, 128.8, 130.8, 131.2, 132.1, 136.3, 136.9, 143.0, 155.8, 173.7. ^{119}Sn NMR (CD_2Cl_2): δ -198.7 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1620.2 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=989.0982; calculated [M+H]$^+$ =989.1117.

(*S*)-6,6′-dicarboxyl-(1,3-bis(diphenylstannyl)propane)-2,2′-diethoxy-1,1′-binaphthylene (3) The reaction of the above sodium salt with 1,3-bis(chlorodiphenylstannyl)propane (1.0 g, 2.3 mmol) gave compound **3** as a white powder (1.2 g, 51%). $[\alpha]_D^{24}$=+28.5°, ^{119}Sn NMR (CD_2Cl_2): δ -47.3 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1623.0 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1017.2011; calculated [M+H]$^+$=1017.1430.

(*S*)-6,6′-dicarboxyl-(1,4-bis(diphenylstannyl)butane)-2,2′-diethoxy-1,1′-binaphthylene (4) The reaction of the above sodium salt with 1,4-bis(chlorodiphenylstannyl)butane (1.6 g, 2.3 mmol) gave compound **4** as a white powder (1.4 g, 59%). $[\alpha]_D^{24}$=+30.1°, ^{1}H NMR ($CDCl_3$): δ 1.0 (6H), 1.6–2.0 (8H), 4.0 (4H), 6.9–8.7 (30H). ^{13}C NMR (CD_2Cl_2): δ 15.0, 16.9 [^1J(^{13}C-$^{117/119}$Sn)=950 Hz], 29.8 [^2J(^{13}C-$^{117/119}$Sn)=162 Hz], 65.0, 115.7, 119.9, 125.3, 125.8, 126.8, 128.2, 128.8 [^3J(^{13}C$_m$-$^{117/119}$Sn)=56 Hz], 129.9, 131.0, 132.2, 136.3, 136.7 [^2J(^{13}C$_o$-$^{117/119}$Sn)=48 Hz], 139.9, 156.1, 172.9. ^{119}Sn NMR (CD_2Cl_2): δ -46.2 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1623.0 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1031.1405; calculated [M+H]$^+$=1031.1588.

(*S*)-6,6′-dicarboxyl-(1,5-bis(diphenylstannyl)pentane)-2,2′-diethoxy-1,1′-binaphthylene (5) The reaction of the above sodium salt with 1,5-bis(chlorodiphenylstannyl)pentane (1.6 g, 2.3 mmol) gave compound **5** as a white powder (1.8 g, 75%). $[\alpha]_D^{24}$=+11.6°, ^{13}C NMR (CD_2Cl_2): δ 15.0, 17.1, 25.0, 38.1, 65.0, 115.7, 120.0, 125.2, 125.9, 126.7, 128.2, 128.8 [^3J(^{13}C$_m$-$^{117/119}$Sn)=55 Hz], 130.3, 131.0, 132.2, 135.9, 136.6 [^2J(^{13}C$_o$-$^{117/119}$Sn)=48 Hz], 140.0, 156.1, 172.9. ^{119}Sn NMR (CD_2Cl_2): δ -45.4 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1632.1 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1045.1912; calculated [M+H]$^+$=1045.1744.

(*S*)-6,6′-dicarboxyl-(1,6-bis(diphenylstannyl)hexane)-2,2′-diethoxy-1,1′-binaphthylene (6) The reaction of the above sodium salt with 1,6-bis(chlorodiphenylstannyl)hexane (1.7 g, 2.3 mmol) gave compound **6** as a white powder (1.8 g, 74%). $[\alpha]_D^{24}$=+22.4°, ^{119}Sn NMR (CD_2Cl_2): δ -36.9 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1632.5 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1059.1734; calculated [M+H]$^+$=1059.1901.

(*S*)-6,6′-dicarboxyl-(1,3-bis(2-(diphenylstannyl)ethyl)benzene)-2,2′-diethoxy-1,1′-binaphthylene (7) The reaction of the above sodium salt with 1,3-bis(2-(chlorodiphenylstannyl)ethyl)benzene (1.9 g, 2.3 mmol) gave compound **7** as a white powder (1.6 g, 63%). $[\alpha]_D^{22}$=+36.0°, ^{119}Sn NMR (CD_2Cl_2): δ -48.8 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1623.0 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1107.1749; calculated [M+H]$^+$=1107.1903.

(*S*)-6,6′-dicarboxyl-(1,4-bis(2-(diphenylstannyl)ethyl)benzene)-2,2′-diethoxy-1,1′-binaphthylene (8) The reaction of the above sodium salt with 1,4-bis(2-(chlorodiphenylstannyl)ethyl)benzene (1.9 g, 2.3 mmol) gave compound **8** as a white powder (1.8 g, 71%). $[\alpha]_D^{22}$=+20.5°, ^{119}Sn NMR (CD_2Cl_2): δ -48.8 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1623.2 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1107.2097; calculated [M+H]$^+$=1107.1903.

(*S*)-6,6′-dicarboxyl-(bis[(trimethylsilylmethyl)diphenylstannyl] methane)-2,2′-diethoxy-1,1′-binaphthylene (9) The reaction of the above sodium salt with bis[(trimethylsilylmethyl)chlorodiphenylstannyl]methane (1.5 g, 2.3 mmol) gave compound **9** as a white powder (1.5 g, 65%). ^{119}Sn NMR (CD_2Cl_2): δ -58.9 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1623.3 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1009.1802; calculated [M+H]$^+$=1009.1591.

(*S*)-6,6′-dicarboxyl-(1,4-bis[(trimethylsilylmethyl)-diphenylstannyl]butane)-2,2′-diethoxy-1,1′-binaphthylene (10) The reaction of the above sodium salt with 1,4-bis[(trimethylsilylmethyl)chlorodiphenyl-stannyl]butane (1.6 g, 2.3 mmol) gave compound **10** as a white powder (1.8 g, 75%). ^{119}Sn NMR (CD_2Cl_2): δ -47.2 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1623.2 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1051.1864; calculated [M+H]$^+$=1051.2062.

Sodium (*S*)-6,6′-dicarboxylate-2,2′-diethoxy-1,1′-binaphthalene (11) To a solution of compound **1** (3.0 g, 7.0 mmol) in a 3:1 ethanol:water mix (200 ml) mixture, sodium carbonate (0.75 g, 7.0 mmol) was added and stirred until dissolved. The solvent was removed *in vacuo* to yield compound **11** as a white amorphous powder (3.3 g, 99%). ^{13}C NMR (CD_3OD): δ 13.9, 64.6, 115.2, 119.9, 124.2, 126.2, 128.6, 129.3, 130.2, 132.5, 135.1, 155.2, 174.5. m.p >320°C (decomposed). FTIR (KBr) ν(CO_2Na): 1553.2 cm^{-1}; ν(H_2O): 3386.8 cm^{-1}. Analytically Calculated for $C_{26}H_{20}O_6Na_2\cdot 3H_2O$: C, 59.09; H, 4.95. Found: C, 59.58; H, 5.41.

General procedure for the synthesis of (*S*)-6,6′-dicarboxyl-(α,ω-bis(chlorophenylstannyl)alkanes)-2,2′-diethoxy-1,1′-binaphthylene (12–18) To a solution of the sodium salt of 2,2′-diethoxy-1,1′-binaphthyl-6,6′-dicarboxylic acid (0.15 g, 0.28 mmol) in a 70% dichloromethane methanol mixture (30 ml), was added drop wise to a solution of α,ω-bis(dichloroorganostannyl)alkane (1 mol eq.) in the same solvent mixture (20 ml). The solvent was removed *in vacuo* to yield compound **12–18** as a green/yellow solid.

(*S*)-6,6′-dicarboxyl-(bis(chlorophenylstannyl)methane)-2,2′-diethoxy-1,1′-binaphthylene (12) The reaction of the above sodium salt, compound **11**, with bis(dichlorophenylstannyl)methane (0.15 g, 0.28 mmol) gave compound **12** (0.12 g, 47%) as a green solid. ^{13}C NMR (CD_2Cl_2): δ 14.95, 18.21, 65.25, 115.99, 118.15, 125.60, 126.35, 128.05, 129.61, 131.19, 132.25, 135.17, 136.45, 136.88, 138.64, 151.57, 157.41, 178.5. ^{119}Sn NMR (CD_2Cl_2): δ -55.4 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1619.8 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=905.9638; calculated [M+H]$^+$=905.9707.

(*S*)-6,6′-dicarboxyl-(1,4-bis(chlorophenylstannyl)butane)-2,2′-diethoxy-1,1′-binaphthylene (13) The reaction of the above sodium salt, compound **11**, with 1,4-bis(dichlorophenylstannyl)butane (0.16 g, 0.28 mmol) gave compound **13** (0.14 g, 53%) as a green solid. ^{13}C NMR (CD_2Cl_2): 15.03, 25.31, 28.59, 65.24, 116.0, 119.57, 122.55, 125.74, 126.47, 129.45, 130.45, 131.91, 133.88, 135.25, 137.21, 139.75, 149.98, 157.33, 178.9. ^{119}Sn NMR (CD_2Cl_2):

δ -109.7 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1620.3 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=948.1155; calculated [M+H]$^+$=948.0177.

(*S*)-6,6′-dicarboxyl-(1,3-bis[(trimethylsilylmethyl)chlorostannyl]propane)-2,2′-diethoxy-1,1′-binaphthylene (14) The reaction of the above sodium salt, compound **11**, with 1,3-bis(dichloro(trimethylsilylmethyl)stannyl)propane (0.17 g, 0.28 mmol) gave compound **14** (0.12 g, 45%) as a green solid. ^{13}C NMR (CD$_2$Cl$_2$): δ 0.81, 12.05, 14.69, 20.89, 29.77, 64.90, 115.70, 119.26, 123.07, 125.4, 126.07, 127.96, 131.52, 133.19, 136.79, 156.87, 177.1. ^{119}Sn NMR (CDCl$_3$): δ -18.9 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1620.2 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=954.1010; calculated [M+H]$^+$=954.0493.

(*S*)-6,6′-dicarboxyl-(1,4-bis[(trimethylsilylmethyl)chlorostannyl]butane)-2,2′-diethoxy-1,1′-binaphthylene (15) The reaction of the above sodium salt, compound **11**, with 1,4-bis(dichloro(trimethylsilylmethyl)stannyl)butane (0.17 g, 0.28 mmol) gave compound **15** (0.14 g, 52%) as a green solid. ^{13}C NMR (CD$_2$Cl$_2$): δ 0.52, 11.67, 14.37, 26.10, 27.68, 64.57, 115.38, 118.95, 122.79, 125.07, 125.79, 127.65, 131.19, 132.86, 136.45, 156.54, 176.8. ^{119}Sn NMR (CDCl$_3$): δ -22.7 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1620.2 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=968.0551; calculated [M+H]$^+$=968.0650.

(*S*)-6,6′-dicarboxyl-(1,5-bis[(trimethylsilylmethyl)chloro-stannyl]pentane)-2,2′-diethoxy-1,1′-binaphthylene (16) The reaction of the above sodium salt, compound **11**, with 1,5-bis(dichloro (trimethylsilylmethyl)stannyl)pentane (0.17 g, 0.28 mmol) gave compound **16** (0.18 g, 66%) as a green solid. ^{119}Sn NMR (CDCl$_3$): δ -21.0 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1619.7 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=982.0707; calculated [M+H]$^+$=982.0807.

(*S*)-6,6′-dicarboxyl-(1,6-bis[(trimethylsilylmethyl)chloro-stannyl]hexane)-2,2′-diethoxy-1,1′-binaphthylene (17) The reaction of the above sodium salt, compound **11**, with 1,6-bis(dichloro (trimethylsilylmethyl)stannyl)hexane (0.18 g, 0.28 mmol) gave compound **17** (0.15 g, 54%) as a green solid. ^{119}Sn NMR (CDCl$_3$): δ-20.2 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1619.6 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=996.0838; calculated [M+H]$^+$=996.0964.

(*S*)-6,6′-dicarboxyl-(1,4-bis(2-[(trimethylsilylmethyl)chlorostannyl]ethyl)benzene)-2,2′-diethoxy-1,1′-binaphthylene (18) The reaction of the above sodium salt, compound **11**, with 1,4-bis(2-[(trimethylsilylmethyl)chloro-stannyl]ethyl)benzene (0.19 g, 0.28 mmol) gave compound **18** (0.20 g, 68%) as a green solid. ^{119}Sn NMR (CDCl$_3$): δ -27.2 ppm. FTIR (KBr) ν[C(O)(O-Sn)]: 1623.1 cm^{-1}. ESMS: observed [M+H]$^+$ m/z=1044.0640; calculated [M+H]$^+$=1044.0965.

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