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Synthesis of chiral organotin reagents: synthesis and X-ray crystal structures of bicyclo[2.2.1]heptan-2-yl(diphenyl)tin chlorides with *cis*-disposed nitrogen containing substituents

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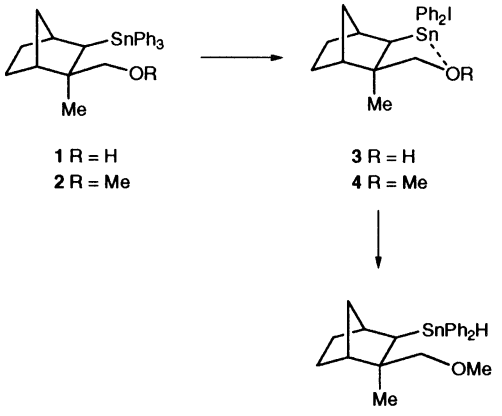
Abstract—Diels Alder reactions between cyclopentadiene and methyl (*E*)-3-triphenylstannylpropenoate **8** and (*E*)-3-triphenylstannylpropenal **14** gave predominantly the adducts **18** and **19** in which the triphenyltin substituents were in the *exo*-positions. Alkylation of the ester **18** took place from the *endo*-face with excellent stereoselectivity to give the *exo*-ester **20** the structure of which was confirmed by X-ray crystallography. Reduction and oxidation of this ester gave the *exo*-aldehyde **22** the structure of which was again confirmed by crystallography. Treatment of the aldehyde **22** with hydroxylamine and *O*-methylhydroxylamine gave the oxime **23** and *O*-methyl oxime **25**, in which one of the phenyl groups had been lost from the tin together, in the latter case, with the expected triphenylstannyl substituted *O*-methyl oxime **24**. The structures of oximes **23** and **25** were confirmed by X-ray crystallography which showed clear evidence for co-ordination of the tin by the nitrogen. The aldehyde **22** was also converted into the hydrazone **26**, loss of a phenyl substituent from the tin not being observed in this case although the double-bond had been reduced in situ. The loss of the phenyl groups observed during the reactions between the aldehyde **22** and hydroxylamine and *O*-methylhydroxylamine may be due to steric congestion in these systems.

1. Introduction

Organotin halides and hydrides are widely used as reagents in organic synthesis.[1] Recently the introduction of enantiomerically enriched organotin halides and hydrides has been of some interest in the context of developing procedures for asymmetric synthesis. Reagents which are chiral solely at the tin tend to undergo ready racemisation, and so most of the chiral tin halides and hydrides which have been evaluated to date for asymmetric synthesis have made use of chiral ligands on the tin.[2–10] Since isopinocampheylboranes have found widespread use in organic synthesis, we decided to develop the chemistry of bicyclo[2.2.1]heptan-2-yl tin hydrides.[11] Of particular interest were such tin hydrides in which the tin was co-ordinated to a suitably positioned, heteroatom containing, functional group since this should help to determine the trajectory of donation of the hydrogen from the tin hydride.[5–7]

With this goal in mind we prepared the *exo*-3-hydroxymethyl- and 3-methoxymethyl-3-methyl-2-triphenylstannylbicyclo[2.2.1]heptanes **1** and **2**.[12–14] Treatment with 1 equiv. of iodine led to cleavage of one of the phenyl groups from the tin to give the tin iodides **3** and **4** with NMR data suggesting that the tin in these tin iodides was partly co-ordinated to the oxygen of the hydroxyl or methoxy groups.[14] However, attempts to convert the tin iodide **3** into a tin hydride were unsuccessful and although the methoxy substituted tin hydride **5** could be prepared and there was some spectroscopic evidence in support of a small degree of co-ordination of the tin by the methoxy substituent, only racemic products were obtained when this tin hydride was used to reduce acetophenone and methyl 2-bromo-2-phenylpropanoate. Since amines are known to co-ordinate to tin halides and hydrides more effectively than ethers,[5–7] it was of interest to extend this work to



1 R = H
2 R = Me

3 R = H
4 R = Me

5

Keywords: chiral organotin reagents; Diels Alder reactions; adducts.

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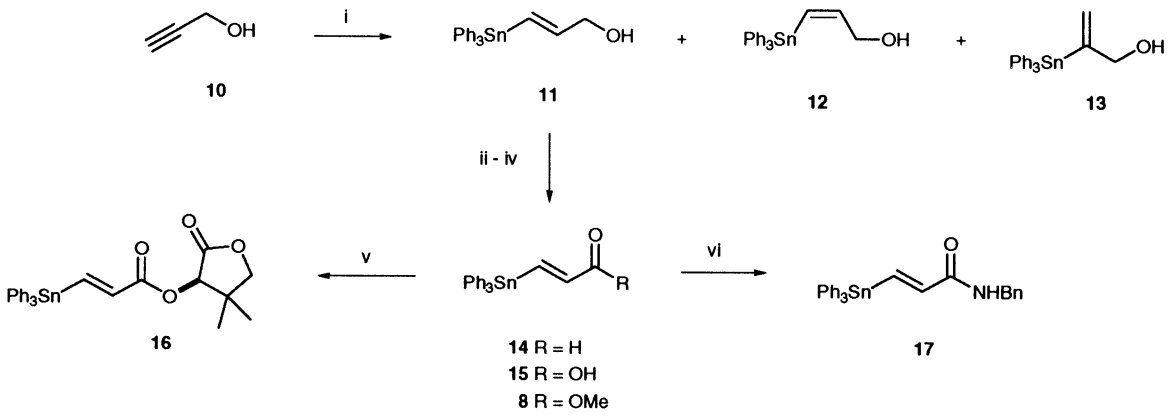
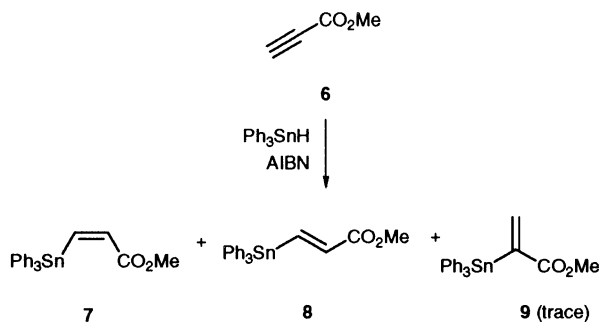


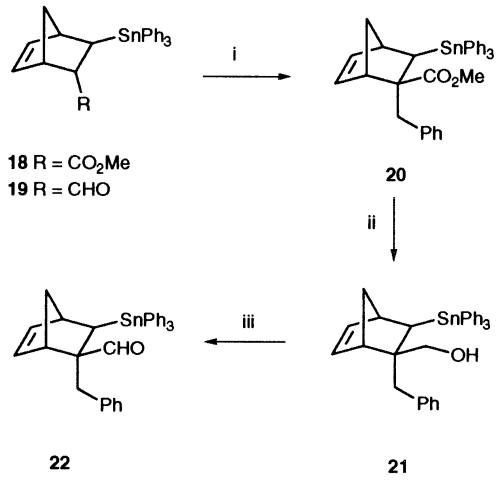
Scheme 1. *Reagents and conditions*: (i) Bu_3SnH, AIBN, toluene, 110°C, 25 h (**11**, 58%; **13**, 10%); (ii) MnO_2, dichloromethane, rt, 24 h (89%); (iii) $NaClO_2$, $NaH_2PO_4{\cdot}2H_2O$, water, *t*-butanol, 2-methyl-2-but-2-ene (88%); (iv) Me_3SiCHN_2, hexane, methanol (91%); (v) (*R*)-pantolactone, DMAP, DCC (85%);

include the synthesis of nitrogen containing tin compounds. We now report, en route to amino-functionalised tin hydrides, the preparation of bicyclo[2.2.1]heptyltin halides in which the electron deficient tin is co-ordinated with a suitably disposed nitrogen containing functional group. The structures of these compounds, including the *N*-Sn co-ordination, were confirmed by X-ray crystallography. This work will support future studies of amino-functionalised, chiral tin hydrides.

2. Results and discussion

Following the approach of our earlier work, bicyclo[2.2.1]-heptan-2-yl(triphenyl)stannanes were to be prepared using a Diels Alder reaction between cyclopentadiene and methyl (*E*)-3-triphenylstannylprop-2-enoate **8** followed by enolate anion alkylation and functional group modification. Triphenylstannanes were to be used since mild procedures are known for the stepwise removal of phenyl groups off the tin using halogens, specifically iodine.[12] Previously, methyl (*E*)-triphenylstannylprop-2-enoate **8** had been prepared by free-radical addition of triphenyltin hydride to methyl propiolate.[12] However, this procedure gave mixtures of the (*E*)- and (*Z*)-adducts **7** and **8** in which the unwanted (*Z*)-isomer **7** predominated, together with smaller amounts of the regioisomeric adduct **9**. Although sufficient (*E*)-isomer had been prepared for the earlier work by this route and by the conjugate addition of a triphenylstannyl copper reagent to methyl propiolate,[12] it was decided to investigate alternative syntheses of this compound.





Scheme 2. *Reagents and conditions*: (i) **18**, LDA, −78°C, BnBr (74%); (ii) DIBAL-H, dichloromethane, rt 2.5 h (86%); (iii) DMSO, $(COCl)_2$, dichloromethane, then Et_3N (93%).

In the present work, the (*E*)-ester **8** was prepared by free-radical addition of triphenyltin hydride to prop-2-ynol **10** followed by oxidation and esterification, see Scheme 1. The addition of the tin hydride to the alkyne gave the required (*E*)-isomer as the major product (55–60%) together with minor quantities (10–15%) of the isomeric adducts **12** (from reactions in benzene) and **13** (from reactions in toluene). Although an acceptable synthesis of the (*E*)-adduct **11**, it should be noted that in our hands this addition of triphenyltin hydride to the alkynol **10** was less stereo- and regioselective than the corresponding addition of tributyltin hydride.[15] Oxidation of the alcohol **11** using manganese dioxide gave the aldehyde **14** which was further oxidised to the acid **15** using sodium chlorite.[16] Despite the presence of a carboxylic acid functionality and the vinylstannane in the same molecule, this acid was a useful synthetic intermediate. Esterification using trimethylsilyl diazomethane gave the methyl ester **8**. The acid was also converted into the chiral ester **16** and the amide **17** using dicyclohexylcarbodi-imide as the coupling reagent so confirming the use of this acid for the preparation of triphenyltin substituted carboxylic acid derivatives.

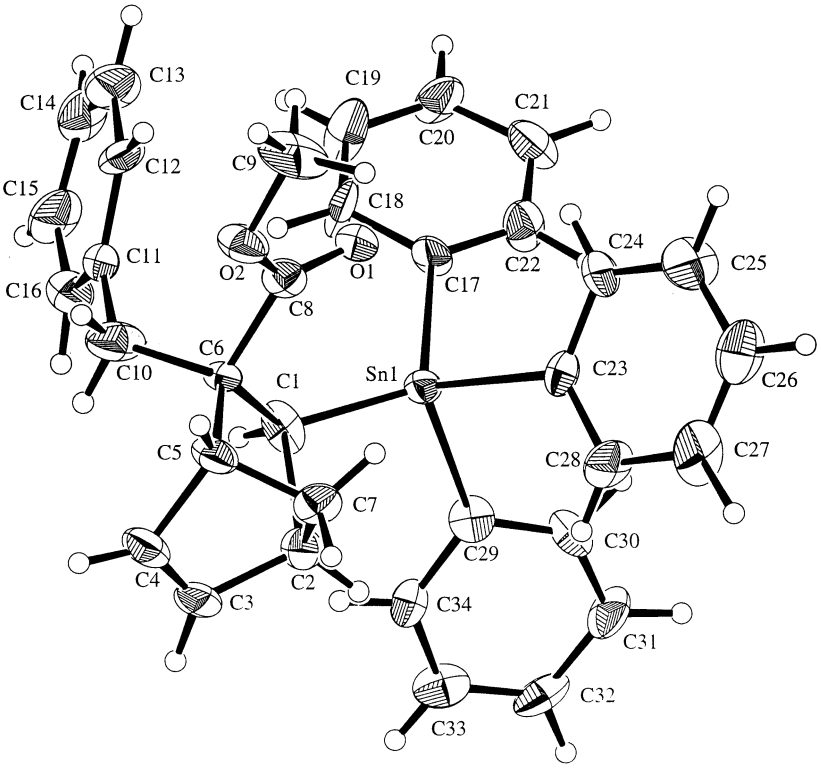


Figure 1. A projection of the structure of the *endo*-alkylated ester **20** as established by the X-ray crystal structure determination.

The Diels Alder reaction of the ester **8** with cyclopentadiene proceeded as reported previously to give the adduct **18**, in which the methoxycarbonyl group is in the *endo* position, as the predominant product, although small amount (ca. 10%) of an isomeric adduct was detected but not isolated. The aldehyde **14** was also found to undergo a usefully stereoselective Diels Alder reaction with cyclopentadiene to give the *endo*-adduct **19** as the major product (Scheme 2).

Alkylation of the Diels Alder adduct **18** using lithium diisopropylamide and benzyl bromide gave the *endo*-alkylated product **20** in good yield with none of the *exo*-alkylated isomer being detected.[13] The stereoselectivity of this alkylation has been attributed to co-ordination of the carbonyl oxygen of the intermediate lithium enolate with the tin, and the retention of this co-ordination through the transition state of the alkylation step.

During the present work, the structure of the alkylated product **20** was confirmed by X-ray crystallography.[†] Fig. 1 shows a projection of a molecule of this ester as determined by the crystallographic study which confirms that both the triphenylstannyl group and the methoxycarbonyl group are *cis* to each other in *exo* positions. The carbonyl oxygen lies over the tin atom in the direction consistent with weak co-ordination, but the oxygen–tin distances,[‡] being 2.72 (2.84) Å, are not indicative of significant tin–oxygen bonding. However, the carbonyl group of the ester is shielded, on one side by the relatively large triphenyltin substituent and on the other side by the benzyl substituent and so nucleophilic attack on the carbonyl group is somewhat hindered. It has been observed previously that the combination of a bulky triphenyltin substituent and a quaternary centre α to the carbonyl group made analogous intermediates both inaccessible and difficult to use.[14] In the present case, attempted saponification of the ester **20** with lithium hydroxide in aqueous tetrahydrofuran was unsuccessful with the starting material being recovered.

However, despite the steric hindrance, the ester **20** was reduced to the alcohol **21** using di-isobutylaluminium hydride and oxidation of the alcohol under Swern conditions gave the aldehyde **22**. The structure of the alkylated aldehyde was also examined by X-ray crystallography, see Fig. 2. Again there was little evidence for significant bonding of the carbonyl oxygen to the tin since the carbonyl oxygen–tin bond distances were 2.797 (2.807) Å, although again the oxygen position is suggestive of a weak co-ordination with the tin.

The aldehyde **22** was identified as an intermediate which could be useful for the preparation of 2-triphenylstannylbicyclo[2.2.1]heptanes with nitrogen substituents which could co-ordinate to the tin. Preliminary attempts to effect a reductive amination of the aldehyde using diethylamine and sodium cyanoborohydride were unsuccessful with the aldehyde being recovered unchanged. Of interest, however, were attempts to convert this aldehyde into its oxime. Reaction with hydroxylamine gave the oxime but was accompanied by loss of one of the phenyl substituents from the tin, even under carefully buffered conditions, and

[†] Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

[‡] The asymmetric unit contains two molecules.

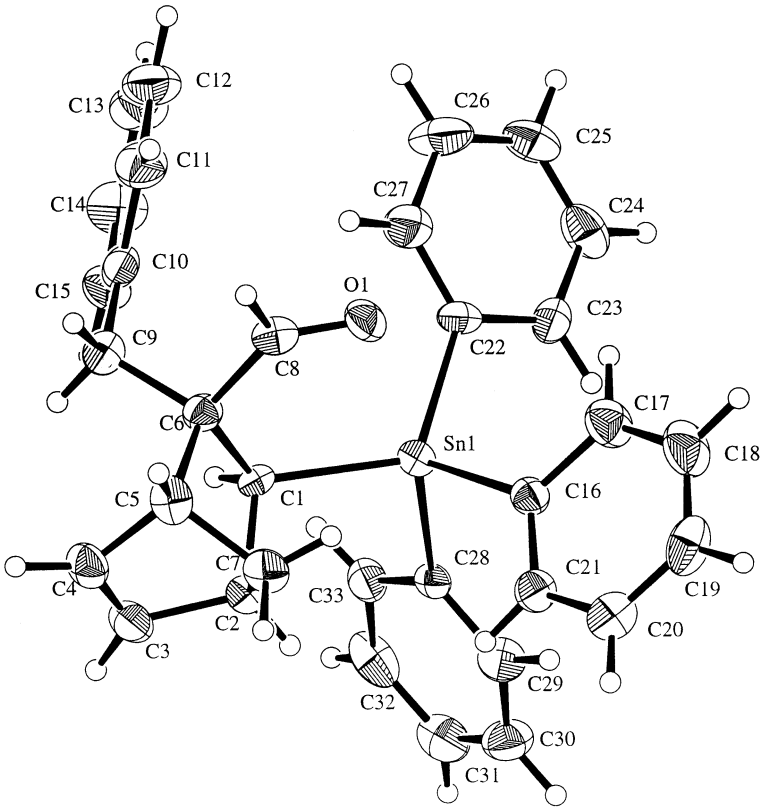


Figure 2. A projection of the structure of the aldehyde **22** as established by the X-ray crystal structure determination.

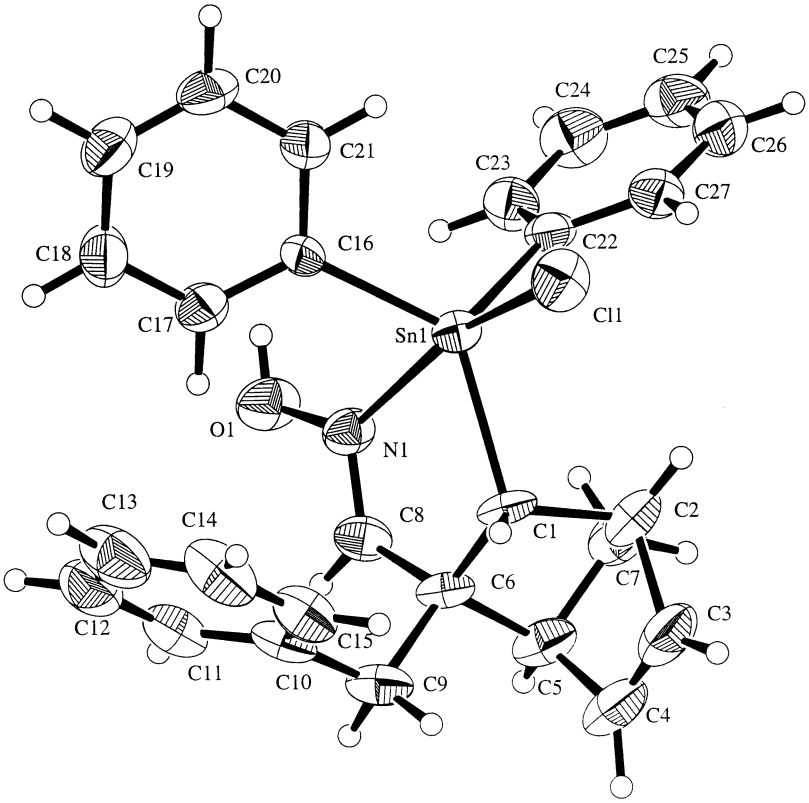


Figure 3. A projection of the structure of the oxime **23** as established by the X-ray crystal structure determination.

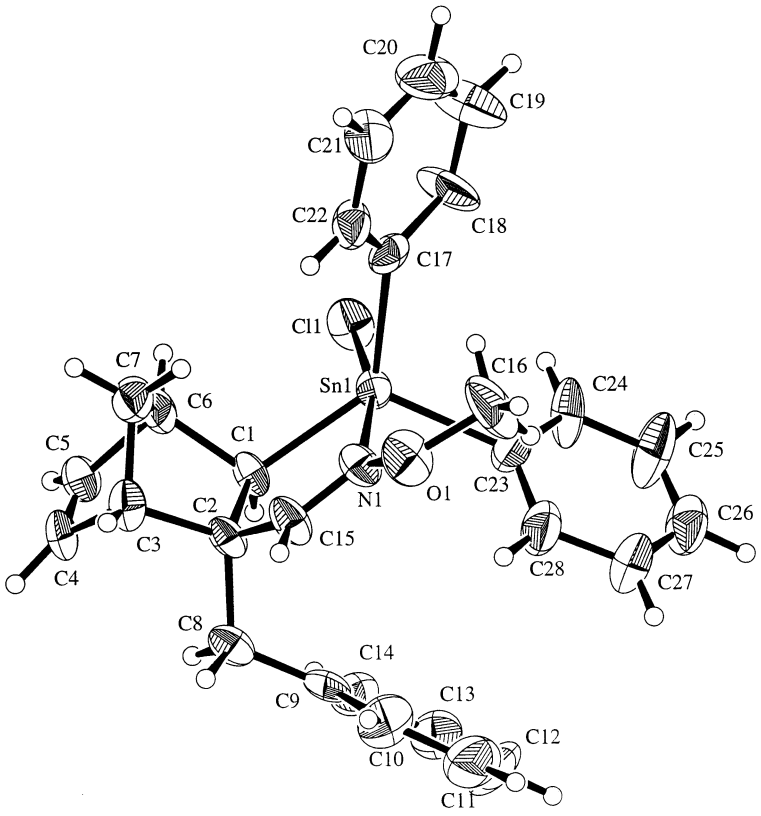
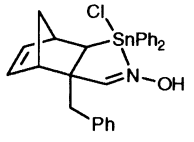


Figure 4. A projection of the structure of the oxime **25** as established by the X-ray crystal structure determination.

led to the formation of the oxime containing diphenyltin chloride **23** in a 62% isolated yield. The structure of this tin chloride was confirmed by X-ray crystallography, see Fig. 3. In this case the nitrogen–tin distance, 2.496(6) Å, was indicative of significant bonding. The tin has a nearly trigonal bipyramidal geometry with the chlorine and the nitrogen in the pseudo apical positions, the bond angle between the tin–nitrogen and tin–chlorine bonds being 165.6(1)°. When the formation of this oximyl tin chloride was monitored by TLC, an intermediate was detected which on further reaction was converted into the tin chloride **23**. Attempts to isolate and characterise this intermediate were unsuccessful since it had a tendency to decompose rapidly at room temperature, but it may have been the triphenyltin containing oxime.

On treatment with *O*-methyl hydroxylamine, the aldehyde **22** was converted first into the oxime methyl ether **24** in which the triphenylstannyl group is unchanged and subsequently into the corresponding diphenyltin chloride **25**. In this case both the triphenylstannyl- and diphenylchlorostannyl *O*-methyl oximes were isolated and characterised. The structure of the tin chloride **25** was again confirmed by X-ray diffraction, see Fig. 4. The structure of the compound as determined by the X-ray crystallographic study shows significant interaction between the nitrogen of the oxime and the tin with tin–nitrogen bond distances of 2.54(2) and 2.46(2) Å. The tin is almost a trigonal bipyramid with the chloro and nitrogen substituents in the apical positions, the nitrogen–tin–chlorine angles being 167.4(4) and 169.2(4)°.

The aldehyde **22** was converted into the hydrazone **26** by treatment with aqueous hydrazine. In this case loss of one of the phenyl rings under the conditions used to form the hydrazone was not observed. However, the reaction was accompanied by concomitant reduction of the carbon–carbon double-bond by di-imide generated in situ. Preliminary attempts to reduce the triphenyltin substituted *O*-methyl oxime **24** with sodium cyanoborohydride or the hydrazone **26** with lithium aluminium hydride in order to prepare the corresponding amines were unsuccessful.



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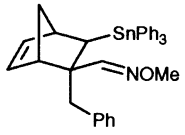

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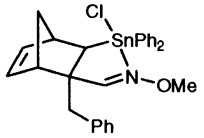

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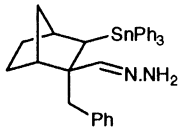

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3. Summary and conclusions

This work has developed a synthesis of diphenyltin halides attached to a bicyclo[2.2.1]heptyl system with *cis*-disposed nitrogen containing substituents which are co-ordinated to the tin. The X-ray studies of these tin halides show that there is significant tin–nitrogen bonding so that the nitrogen and halide substituents adopt apical positions on approximately trigonal bipyramidal tin atoms. Such strong co-ordination was not observed for structurally related triphenyltin substituted carbonyl compounds although there was evidence of weak tin–carbonyl interactions.

The congestion in these triphenyltin containing compounds led to reduced reactivity of the carbonyl groups. Nevertheless the isolation of the oxime **23** and *O*-methyl oxime **25** indicates that these may be useful intermediates for the preparation of nitrogen substituted tin hydrides. Present work is concerned with the preparation of enantiomerically enriched oximes and *O*-methyl oximes related to **23** and **25** and with investigations into the uses of these intermediates as catalysts for asymmetric synthesis.

4. Experimental

4.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 300, Varian Inova 300 and Varian Gemini 200 spectrometers in chloroform-d_1. Mass spectra were recorded on Kratos Concept 1S and Fisons VG Trio 2000 mass spectrometers using electron impact (EI) or chemical ionisation (CI) modes. Characteristic groups of isotope peaks were observed for compounds containing tin. Those quoted correspond to ^{120}Sn. IR spectra were recorded on an ATI Mattson Genesis FTIR spectrometer as evaporated films on sodium chloride plates unless otherwise stated. Flash column chromatography was carried out using Merck silica gel 60H (40–60 μ, 230–300 mesh) as the stationary phase. Optical rotations were measured on an Optical Activity AA-100 polarimeter operating at 589 nm. Light petroleum refers to the fraction with bp 40–60°C and was redistilled before use. Ether refers to diethyl ether. All solvents were distilled and purified by standard procedures. All products were obtained as colourless oils after chromatography.

4.1.1. (*E*)-3-Triphenylstannylprop-2-en-1-ol 11. AIBN (25 mg) followed by redistilled propargyl alcohol (0.6 cm^3, 10.3 mmol) were added to a deoxygenated (30 min with nitrogen) and stirred solution of triphenyltin hydride (4.1 g, 11.68 mmol) in toluene (20 cm^3). The mixture was heated at 110°C for 25 h. It was then cooled to ambient temperature, concentrated under reduced pressure and the residue flash chromatographed using 20% ether in light petroleum as eluent to give 2-triphenylstannylprop-2-en-1-ol **13** (R_f 0.31) as a white solid (413 mg, 10%), mp 108°C (Found: C, 62.30; H, 5.05; Sn, 28.85. $C_{21}H_{20}OSn$ requires C, 61.95; H, 4.95; Sn 29.15%); ν_{max}/cm^{-1} 699, 730, 930, 997, 1013, 1073, 1263, 1303, 1428, 1480, 2929, 3062 and 3368 (broad, OH); δ_H 1.69 (1H, t, J=5.9 Hz, OH), 4.51 (2H, dt, J=5.9, 1.8 Hz, $^3J_{SnH}$=41 Hz, CH_2), 5.54 (1H, td, J=1.8, 1.7 Hz, $^3J_{SnH}$=78 Hz, 3-H), 6.16 (1H, q, J=1.8 Hz, $^3J_{SnH}$=167 Hz, 3-H′), 7.35–7.55 (9H, m, ArH) and 7.55–7.75 (6H, m, $^3J_{SnH}$=49 Hz, *o*-ArH); δ_C 68.97, 126.74, 128.52, 128.95, 137.1, 138.07 and 152.55; *m*/*z* (CI) 331 (M$^+$−77, 85%), 348 (M$^+$−60, 100) and 368 (28). Next off the column was the *title compound* **11** (R_f 0.125) as a white solid (2.44 g, 58%), mp 120°C (Found: C, 62.8; H, 4.7. $C_{21}H_{20}OSn$ requires C, 61.95; H, 4.95%); ν_{max}/cm^{-1} 699, 730, 997, 1074, 1428, 1480, 3062 and 3393 (broad, OH); δ_H 1.68 (1H, t, J=5.9 Hz, OH), 4.34 (2H, ddd, J=5.9, 4.2, 1.4 Hz, CH_2), 6.46 (1H, dt, J=19.1, 4.0 Hz, $^3J_{SnH}$=73 Hz, 2-H), 6.62 (1H, dt, J=19.1, 1.5 Hz, $^2J_{SnH}$=92 Hz, 3-H), 7.35–7.54 (9H, m, ArH) and 7.54–7.76 (6H, m, $^3J_{SnH}$=49 Hz, *o*-ArH); δ_C 65.82, 123.71, 128.56, 129.06, 137.0, 137.95 and 150.78; *m*/*z* (CI) 331 (M$^+$−77, 70%), 348 (M$^+$−60, 100) and 368 (92).

Following the same procedure as above, redistilled propargyl alcohol (2.28 g, 40.67 mmol), triphenyltin hydride (14.46 g, 41.19 mmol) and AIBN (25 mg) in anhydrous benzene (80 cm^3) heated under reflux for 24 h followed by column chromatography of the crude product with gradient elution using 10–50% ether in light petroleum as eluent, gave *(Z)-3-triphenylstannylprop-2-en-1-ol* **12** (R_f 0.46, 30% ether in light petroleum) as a white crystalline solid (2.44 g, 15%), mp 89°C (Found: C, 61.9; H, 5.0; Sn, 28.85. $C_{21}H_{20}OSn$ requires C, 61.95; H, 4.95; Sn, 29.15%); ν_{max}/cm^{-1} 699, 728, 997, 1023, 1073, 1164, 1302, 1427, 1479, 1600, 2986, 3061, 3405 and 3561; δ_H 1.41 (1H, t, J=5.6 Hz, OH), 4.32 (2H, m, CH_2), 6.41 (1H, dt, J=12.8, 1.9 Hz, $^2J_{SnH}$=88 Hz, 3-H), 7.01 (1H, dt, J=12.8, 3.9 Hz, $^3J_{SnH}$=173 Hz, 2-H), 7.25–7.52 (9H, m, ArH) and 7.52–7.8 (6H, m, $^3J_{SnH}$=49 Hz, *o*-ArH); δ_C 64.24, 124.69, 128.38, 128.6, 136.7, 140.79 and 148.01; *m*/*z* (CI) 331 (M$^+$−77, 100%). Next a mixture of **12** and 2-triphenylstannylpropenol **13** (R_f 0.38, 2.7 g, 16%) was eluted followed by (*E*)-3-triphenylstannylprop-2-en-1-ol **11** (R_f 0.19; 9.01 g, 54%).

4.1.2. (*E*)-3-Triphenylstannylpropenal 14. Manganese dioxide (24.11 g, 0.277 mol; reactivated for 24 h at 115–130°C and cooled to ambient temperature in a desiccator) was added to a solution of the (*E*)-alcohol **11** (11.29 g, 27.73 mmol) in dichloromethane (100 cm^3) and the reaction mixture was stirred at ambient temperature for 24 h under argon then filtered through celite. After concentration under reduced pressure, column chromatography of the residue over silica using 20% ether in light petroleum as eluent gave the title compound **4** (R_f 0.55) as a white solid, mp 102°C (9.95 g, 88.6%) (Found: C, 62.6; H, 4.45; Sn, 29.5. $C_{21}H_{18}OSn$ requires C, 62.25; H, 4.5; Sn, 29.3%); ν_{max}/cm^{-1} 699, 730, 997, 1074, 1189, 1429, 1480, 1687, 3017 and 3064; δ_H 6.85 (1H, dd, J=19.1, 7.4 Hz, $^3J_{SnH}$=61 Hz, 2-H), 7.4–7.55 (9H, m, aromatic, ArH), 7.55–7.76 (6H, m, $^3J_{SnH}$=51 Hz, *o*-ArH), 8.01 (1H, d, J=19.1 Hz, $^2J_{SnH}$=68 Hz, 3-H) and 9.62 (1H, d, J=7.4 Hz, CHO); δ_C 128.90, 129.61, 136.12, 136.91, 149.45, 156.81 and 193.19; *m*/*z* (CI) 329 (M$^+$−77, 60%), 346 (M$^+$−60, 100) and 424 (M$^+$+18, 10).

4.1.3. (*E*)-3-Triphenylstannylpropenoic acid 15. A solution of $NaClO_2$ (80%; 19.0 g, 168 mmol) and sodium dihydrogen phosphate dihydrate (13.1 g, 84 mmol) in water (80 cm^3) was added dropwise to a solution of aldehyde **14** (4.54 g, 11.20 mmol) in a mixture of *tert*-butanol (180 cm^3)

and 2-methyl-2-butene (90 cm^3) over a period of 50 min at ambient temperature. After the addition was complete, the reaction mixture was stirred for 1 h at rt, diluted with ether (100 cm^3), the organic layer was separated, the aqueous layer was extracted with ether (2×100 cm^3), and the combined extract was washed with water (100 cm^3) followed by brine (100 cm^3), dried over magnesium sulfate and filtered through celite. The solvent was completely removed under reduced pressure, the residue was redissolved in diethyl ether (50 cm^3), and the solution was diluted with light petroleum (50 cm^3). When the solution was reduced in volume to about 20 cm^3 at rt, the acid precipitated as a white solid. After removing the liquor with a pipette, the solid mass was washed with light petroleum (2×20 cm^3) and dried under reduced pressure to give the title compound **15** (4.16 g, 88%) as a white solid, mp 138°C (Found: C, 59.90; H, 4.40; Sn, 28.05. $C_{21}H_{18}O_2Sn$ requires C, 59.90; H, 4.30; Sn, 28.0%); ν_{max}/cm^{-1} 697, 728, 997, 1075, 1253, 1290, 1412, 1428, 1480, 1591, 1688, 3015, 3064; δ_H 6.56 (1H, d, J=19.1 Hz, $^3J_{SnH}$=66 Hz, 2-H), 7.3–7.5 (9H, m, ArH), 7.5–7.74 (6H, m, $^3J_{SnH}$=50 Hz, *o*-ArH), 8.14 (1H, d, J=19.2 Hz, $^2J_{SnH}$=73 Hz, 3-H); δ_C 128.86, 129.53, 136.42, 136.99, 138.59, 150.94 and 169.61; *m/z* (CI) 326 (40%), 345 (M^+-77, 35) and 368 (100).

4.1.4. Methyl (*E*)-3-triphenylstannylpropenoate 8. Trimethylsilyldiazomethane (2.0 M in hexane, 0.4 cm^3, 0.8 mmol) was added to a solution of the acid **15** (181 mg, 0.431 mmol) in anhydrous methanol (3.5 cm^3) and benzene (7 cm^3) at 0°C. After 5 min, ether (10 cm^3) was added, the mixture was concentrated under reduced pressure, and chromatography of the residue using 5% ether in light petroleum as eluent gave the title compound **8** (171 mg, 91%) as a white solid, mp 61°C; ν_{max}/cm^{-1} 699, 730, 998, 1023, 1075, 1158, 1217, 1261, 1315, 1429, 1480, 1586, 1723, 2950, 3015 and 3062; δ_H 3.82 (3H, s, OCH_3), 6.55 (1H, d, J=19.2 Hz, $^3J_{SnH}$=67 Hz, 2-H), 7.4–7.5 (9H, m, ArH), 7.5–7.8 (6H, m, $^2J_{SnH}$=49 Hz, *o*-ArH) and 8.02 (1H, d, J=19.2 Hz, $^3J_{SnH}$=75 Hz, 3-H); δ_C 51.70, 128.74, 129.39, 136.58, 136.93, 138.86, 147.38 and 165.0; *m/z* (CI) 359 (M^+-77, 100%), 376 (42) and 454 (M^++18, 35).

4.1.5. (*R*)-4,4-Dimethyl-2-oxotetrahydrofuran-3-yl (*E*)-3-triphenylstannylpropenoate 16.[13] 4-Dimethylaminopyridine (13 mg, 0.1 mmol) and dicyclohexylcarbodiiide (207 mg, 1.00 mmol) dissolved in dichloromethane (1 cm^3) were added to a solution of the acid **8** (209 mg, 0.497 mmol) and (*R*)-pantolactone (88 mg, 0.676 mmol) in dichloromethane (2 cm^3) at ambient temperature. Precipitation was observed within a few seconds. After stirring at ambient temperature for 1 h, the reaction mixture was diluted with ether (5 cm^3), filtered through glass-wool, and the precipitate was washed repeatedly with ether. Concentration under reduced pressure and chromatography of the residue with gradient elution using 20–40% ether in light petroleum gave the title compound **6** (225 mg, 85%) as a white solid, mp 129–130°C. $[\alpha]_D^{21}$=+4.07 (Found: C, 60.9; H, 5.1; Sn, 22.05. $C_{27}H_{26}O_4Sn$ requires C, 60.8; H, 4.9; Sn, 22.25%); ν_{max}/cm^{-1} 699, 730, 997, 1013, 1077, 1148, 1200, 1249, 1301, 1370, 1429, 1481, 1731, 1799, 2932, 2968, 3016 and 3065; δ_H 1.18 and 1.28 (each 3H, s, Me), 4.08 and 4.12 (each 1H, d, J=9.1 Hz, 5′-H), 5.49 (1H, s, 3′-H), 6.63 (1H, d, J=19.2 Hz, $^3J_{SnH}$=64.5 Hz, 2-H), 7.35–7.54 (9H, m, ArH), 7.54–7.75 (6H, m, $^3J_{SnH}$=50 Hz, *o*-ArH) and 8.17 (1H, d, J=19.2 Hz, $^2J_{SnH}$=71.1 Hz, 3-H); δ_C 19.93, 23.03, 40.36, 75.33, 76.21, 128.88, 129.54, 136.33, 136.99, 137.25, 150.79, 163.12 and 172.33; *m/z* (CI) 457 (M^+-77, 30%) and 552 (M^++18, 65).

4.1.6. (*E*)-*N*-Benzyl-3-triphenylstannylpropenamide 17. Benzylamine (125 μl, 1.144 mmol) followed by dicyclohexylcarbodiimide (242 mg, 1.173 mmol) in dichloromethane (1 cm^3) were added to the acid **15** (241 mg, 0.573 mmol) and 4-dimethylaminopyridine (15 mg, 0.123 mmol) in dichloromethane (1 cm^3) at room temperature. The reaction mixture was stirred for 22 h before being diluted with ether (5 cm^3), filtered through glass-wool, and the precipitate washed repeatedly with ether. Concentration under reduced pressure and column chromatography of the residue using 20% ether in light petroleum as eluent, gave the title compound **17** (182 mg, 62%) as a white solid, mp 148°C (Found: C, 65.75; H, 4.9; N, 2.75; Sn, 22.65. $C_{28}H_{25}NOSn$ requires C, 65.9; H, 4.95; N, 2.75; Sn, 23.25%); ν_{max}/cm^{-1} 698, 728, 996, 1023, 1075, 1250, 1333, 1428, 1453, 1480, 1548, 1642, 2850, 2919, 3063 and 3275; δ_H 4.43 (2H, d, J=5.6 Hz, CH_2), 5.78 (1H, broad, NH), 6.33 (1H, d, J=18.8 Hz, $^3J_{SnH}$=69 Hz, 2-H), 7.1–7.36 (14H, m, ArH), 7.36–7.6 (6H, m, $^3J_{SnH}$=50 Hz, *o*-ArH), 7.73 (1H, d, J=18.8 Hz, $^2J_{SnH}$=77 Hz, 3-H); δ_C 43.8, 127.58, 127.97, 128.69, 129.32, 136.84, 137.96, 141.58, 141.69 and 163.98; *m/z* (CI) 434 (M^+-77, 35%) and 512 (M^++H, 42).

4.1.7. (1*RS*,2*RS*,3*SR*,4*SR*)-Methyl 3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate 18.[12] Freshly prepared cyclopentadiene (20 cm^3, 281 mmol) was added to a deoxygenated (15 min with nitrogen) solution of ester **8** (6.07 g, 13.95 mmol) in benzene (100 cm^3), and the reaction mixture was heated under reflux for 24 h. On cooling to room temperature, concentration under reduced pressure and column chromatography of the residue using 10% ether in light petroleum as eluent gave a mixture of the title compound **18** and a minor isomer (88:12; 6.66 g, 95%) as a white solid, mp 100°C; ν_{max}/cm^{-1} 699, 728, 1021, 1074, 1197, 1255, 1332, 1428, 1480, 1731, 2987, 3063; δ_H 1.33 and 1.39 (each 1H, d, J=8.5 Hz, 7-H), 1.95 (1H, dd, J=5.0, 2.4 Hz, $^2J_{SnH}$=38 Hz, 3-H), 3.21 (1H, br s, $^3J_{SnH}$=24 Hz, 4-H), 3.3–3.4 (2H, m, 1-H and 2-H), 3.66 (3H, s, OCH_3), 5.93 (1H, dd, J=5.6, 2.4 Hz, 6-H), 6.36 (1H, dd, J=5.6, 3 Hz, 5-H), 7.33–7.52 (9H, m, ArH), 7.52–7.6 (6H, m, $^3J_{SnH}$=42 Hz, *o*-ArH); δ_C 27.31, 46.0, 46.69, 47.07, 49.30, 51.49, 128.53, 128.92, 130.40, 137.24, 138.29, 138.88 and 174.97; *m/z* (CI) 351 (5%), 368 (10), 425 (M^+-77, 35) and 442 (100).

4.1.8. (1*RS*,2*RS*,3*SR*,4*SR*)-3-Triphenylstannylbicyclo-[2.2.1]hept-5-ene-2-carboxaldehyde 19. Freshly prepared cyclopentadiene (4.9 cm^3, 69 mmol) was added to a deoxygenated (1 h with nitrogen) solution of aldehyde **14** (1.4 g, 3.45 mmol) in benzene (50 cm^3), and the reaction mixture was heated under reflux for 22 h then cooled to room temperature. Concentration under reduced pressure and column chromatography using 10% ether in light petroleum as eluent gave the adduct **19** together with a minor isomer (85:15) as a viscous oil. Crystallization gave the title compound **19** (1.50 g, 92%) as a white solid, mp 90–92°C

(Found: C, 66.2; H, 5.20; Sn, 25.25. $C_{26}H_{24}OSn$ requires C, 66.3; H, 5.15; Sn, 25.2%); ν_{max}/cm^{-1} 699, 728, 997, 1073, 1331, 1428, 1480, 1714, 2715, 2809, 2867, 2971, 3062; δ_H 1.32 (1H, d, J=8.7 Hz, 7-H), 1.39 (1H, d, J=8.5 Hz, 7-H′), 1.97 (1H, dd, J=5.2, 2.3 Hz, $^2J_{SnH}$=36 Hz, 3-H), 3.28 (1H, br s, 4-H), 3.30 (1H, m, 2-H), 3.37 (1H, br s, 1-H), 5.93 (1H, dd, J=5.6, 2.7 Hz), 6.36 (1H, dd, J=5.4, 3 Hz), 7.3–7.5 (9H, m, ArH), 7.5–7.7 (6H, m,$^3J_{SnH}$=46 Hz, *o*-ArH) and 9.84 (1H, d, J=2.1 Hz, CHO); δ_C 24.73, 46.44, 49.2, 55.81, 128.73, 129.05, 129.51, 137.27, 137.97, 139.22 and 203.86; *m/z* (CI) 368 (12%), 395 (M^+−77, 6), 412 (100), 490 (M^++18, 23).

4.1.9. (1*RS*,2*SR*,3*SR*,4*SR*)-Methyl 2-benzyl-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate 20.[14] *n*-Butyllithium (1.34 mol dm^{-3} in hexane, 5.9 cm^3, 7.906 mmol) was added slowly to a stirred solution of diethylamine (1.0 cm^3, 9.67 mmol) in tetrahydrofuran (40 cm^3) at 0°C. The solution was stirred for 15 min, and then cooled to −78°C before addition of the ester **18** (3.03 g, 6.046 mmol) in tetrahydrofuran (20 cm^3). The mixture was stirred at −78°C for 1 h and then benzyl bromide (1.4 cm^3, 11.8 mmol) was added dropwise. After stirring for a further 1.5 h, the reaction mixture was warmed up to ambient temperature over a period of 1 h then concentrated under reduced pressure. The residue was diluted with ethyl acetate (100 cm^3) and the solution washed with water (50 cm^3) and brine (50 cm^3) then dried over magnesium sulfate. Column chromatography using light petroleum and 10% ether in light petroleum as eluent gave the title compound **20** (2.64 g, 74%) as a white solid, mp 131°C (Found: C, 68.95; H, 5.5; Sn, 19.95. $C_{34}H_{32}O_2Sn$ requires C, 69.05; H, 5.45; Sn, 20.05%); ν_{max}/cm^{-1} 699, 728, 1073, 1181, 1213, 1247, 1331, 1428, 1480, 1708, 2950 and 3061; δ_H 1.28 and 1.41 (each 1H, d, J=8.9 Hz, 7-H), 1.74 (1H, d, J=2.5 Hz, $^2J_{SnH}$=49 Hz, 3-H), 2.68 and 3.14 (each 1H, d, J=13.3 Hz, PhHC*H*), 3.22 (1H, br s, $^3J_{SnH}$=28 Hz, 4-H), 3.31 (1H, br s, 1-H), 3.55 (3H, s, OMe), 6.30 (1H, dd, J=5.1, 3.02 Hz, 6-H), 6.54 (1H, dd, J=5.1, 3.0 Hz, 5-H), 7.0–7.2 (5H, m, ArH), 7.2–7.4 (9H, m, ArH) and 7.4–7.65 (6H, m, $^3J_{SnH}$=46 Hz, *o*-ArH); δ_C 37.04, 45.34, 46.60, 48.00, 51.43, 52.30, 59.80, 126.56, 127.83, 128.22, 128.99, 132.25, 137.35, 137.85, 140.79, 142.14, and 179.88; *m/z* (CI) 449 (10%), 368 (10), 515 (M^+−77, 100).

4.1.10. (1*RS*,2*RS*,3*RS*,4*SR*)-3-Benzyl-3-hydroxymethyl-2-triphenylstannylbicyclo[2.2.1]hept-5-ene 21. Di-isobutylaluminium hydride (1.0 M in dichloromethane, 35 cm^3, 35 mmol) was added to a solution of the ester **20** (5.11 g, 8.64 mmol) in dichloromethane (100 cm^3) at room temperature. After stirring for 2.5 h at this temperature the reaction mixture was cooled to 0°C, methanol (20 cm^3) was added, and the mixture allowed to warm to room temperature. Saturated aqueous Rochelle's salt (75 cm^3) was added and the mixture stirred for 3 h. The organic phase was separated and the aqueous phase was extracted with dichloromethane (3×50 cm^3). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. Column chromatography using 10% ether in light petroleum as eluent gave the title compound **21** (4.19 g, 7.44 mmol, 86%) as a white solid, mp 126°C (Found: C, 70.5; H, 5.55; Sn, 20.35. $C_{33}H_{32}OSn$ requires C, 70.35; H, 5.75; Sn, 21.05%); ν_{max}/cm^{-1} 700, 728, 908, 996, 1023, 1073, 1257, 1327, 1427, 1453, 1480, 1494, 2882, 2964, 3061 and 3561; δ_H 1.24 (1H, dd, J=4.9, 2.6 Hz, OH), 1.31 (2H, m, 2-H and 7-H), 1.58 (1H, d, J=9.1 Hz, 7-CH′), 2.43 (1H, br s, 4-H), 2.48 and 2.74 (each 1H, d, J=13.3 Hz, PhCH*H*), 3.07 (1H, br s, $^3J_{SnH}$=28 Hz, 1-H), 3.21 (1H, dd, J=10.0, 4.9 Hz, HC*H*OH), 3.37 (1H, dd, J=10.0, 2.6 Hz, *H*CHOH), 6.24 (1H, dd, J=5.5, 2.9 Hz, 5-H), 6.31 (1H, dd, J=5.5, 2.9 Hz, 6-H), 7.0–7.34 (14H, m, ArH), 7.34–7.6 (6H, m, $^3J_{SnH}$=44 Hz, *o*-ArH); δ_C 35.80, 42.72, 46.64, 47.50, 48.35, 51.41, 66.96, 126.07, 128.25, 128.31, 129.87, 133.41, 137.10, 138.76, 139.32 and 141.77; *m/z* (CI) 368 (5%) and 487 (M^+−77, 100).

4.1.11. (1*RS*,2*SR*,3*SR*,4*SR*)-2-Benzyl-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde 22. Dimethylsulfoxide (2.5 cm^3, 35.2 mmol) was added to a solution of oxalyl chloride (1.5 cm^3, 17.2 mmol) in dichloromethane (80 cm^3) at −78°C. After 5 min, the alcohol **21** (4.52 g, 8.02 mmol) in dichloromethane (50 cm^3) was added and the reaction mixture was stirred for 15 min before adding triethylamine (10.1 cm^3, 72.46 mmol). After 5 min at −78°C, the reaction mixture was allowed to warm to 0°C, and was stirred at this temperature for 30 min then for 1 h at room temperature. Water (100 cm^3) was added and the organic phase separated, washed with water (4×50 cm^3) and dried over magnesium sulfate. After concentration under reduced pressure, the residue was dissolved in ether (250 cm^3) and the solution diluted with light petroleum (50 cm^3) then concentrated to 50 cm^3 under reduced pressure. It was refrigerated to give the title compound **22** as a white crystalline solid which was washed repeatedly with light petroleum then dried under vacuum (4.17 g, 92.6%), mp 140°C (Found: C, 70.35; H, 5.3; Sn, 20.7. $C_{33}H_{30}OSn$ requires C, 70.6; H, 5.4; Sn, 21.15%); ν_{max}/cm^{-1} 699, 728, 907, 1072, 1328, 1427, 1454, 1480, 1711, 2961, 3061; δ_H 1.02 and 1.26 (each 1H, d, J= 9.1 Hz, 7-H), 1.45 (1H, d, J=2.8 Hz, $^2J_{SnH}$=45 Hz, 3-H), 2.63 (1H, d, J=13.9 Hz, PhHC*H*), 3.09 (1H, br s, 1-H), 3.20 (1H, d, J=13.9 Hz, Ph*H*CH), 3.21 (1H, br s, 4-H), 6.29 (1H, dd, J=5.5, 3.0 Hz, 6-H), 6.60 (1H, dd, J=5.5, 3.0 Hz, 5-H), 6.9–7.2 (5H, m, ArH), 7.2–7.4 (9H, m, ArH), 7.4–7.6 (6H, m, $^3J_{SnH}$=44 Hz, *o*-ArH), 9.74 (1H, s, CHO); δ_C 30.95, 42.93, 46.44, 46.79, 48.69, 63.70, 126.70, 127.92, 127.98, 128.5, 129.07, 130.9, 136.68, 137.19, 141.52, 141.82 and 205.93; *m/z* (CI) 368 (48%), 419 (77), 485 (M^+−77, 100).

4.1.12. (1*RS*,2*RS*,3*RS*,4*SR*)-3-Benzyl-2-chlorodiphenylstannylbicyclo[2.2.1]hept-5-ene-3-carbaldehyde oxime 23. Sodium acetate (211 mg, 2.57 mmol) and hydroxylamine hydrochloride (167 mg, 2.40 mmol) were added in portions to a solution of aldehyde **22** (73 mg, 0.131 mmol) in anhydrous methanol (1.5 cm^3) and benzene (2 cm^3) over a period of 13 days at ambient temperature. An intermediate was detected by TLC (R_f 0.29; 10% ether in light petroleum). After 13 days neither the aldehyde (R_f 0.49) nor the intermediate could be detected and the solvent was removed under reduced pressure. The residue was dissolved in water, extracted with dichloromethane, and the extracts were dried over magnesium sulfate. After concentration under reduced pressure, short column chromatography of the residue, using 20% ether in light petroleum as eluent,

gave the title compound **23** (44 mg, 63%; R_f 0.11) as a solid, mp 106°C; ν_{max}/cm^{-1} 699, 732, 756, 906, 959, 1072, 1268, 1326, 1429, 1454, 1481, 2918, 2963, 3053, 3254, 3431, 3610; δ_H 1.47 and 1.52 (each 1H, d, J=9.2 Hz, 7-H), 1.66 (1H, d, J=2.5 Hz, $^2J_{SnH}$=61 Hz, 2-H), 2.69 (1H, d, J=13.5 Hz, PhHC*H*), 2.97 (1H, s, 4-H), 3.04 (1H, d, J=13.5 Hz, Ph*H*CH), 3.52 (1H, s, $^3J_{SnH}$=35 Hz, 1-H), 6.31 (1H, dd, J=5.5, 3.0 Hz, 5-H), 6.57 (1H, dd, J=5.5, 3.0 Hz, 6-H), 6.93 (1H, s, OH), 7.0–7.5 (13H, m, ArH), 7.6–7.85 (2H, m, ArH) and 7.92 (1H, s, CH=N); δ_C 39.68, 45.25, 45.7, 47.24, 51.32, 54.62, 126.98, 128.59, 128.79, 128.83, 128.97, 129.26, 129.77, 131.50, 135.53, 135.83, 136.65, 140.58 and 162.92; *m/z* (ES) 500 ($M^+-{}^{35}Cl$, 100%); (CI) 212 (100%), 458 (M^+-77, 3), 500 (M^+-35, 35) and 535 (M^+, 2).

4.1.13. (1*RS*,2*RS*,3*RS*,4*SR*)-3-Benzyl-2-triphenylstannylbicyclo[2.2.1]hept-5-ene-3-carbaldehyde *O*-methyloxime 24 and (1*RS*,2*RS*,3*RS*,4*SR*)-3-Benzyl-2-chlorodiphenylstannylbicyclo[2.2.1]hept-5-ene-3-carbaldehyde *O*-methyloxime 25. Sodium acetate (147 mg, 1.79 mmol) and methoxylamine hydrochloride (138 mg, 1.65 mmol) were added in portions to a solution of the aldehyde **22** (107 mg, 0.190 mmol) in anhydrous methanol (2.5 cm^3) and benzene (2.5 cm^3) at ambient temperature over a period of 13 days. Concentration under reduced pressure then gave a residue, which was dissolved in water. The aqueous solution was extracted with dichloromethane and the extracts dried over magnesium sulfate then concentrated under reduced pressure. Column chromatography of the residue with gradient elution using 10–30% ether in light petroleum gave the title compound **24** (62 mg, 55%) as a white solid, mp 115°C (Found: C, 68.95; H, 5.80; N, 2.45; Sn, 19.70. $C_{34}H_{33}NOSn$ requires C, 69.2; H, 5.65; N, 2.35; Sn, 20.1%); ν_{max}/cm^{-1} 700, 729, 908, 1045, 1072, 1427, 1453, 1480, 1494, 2963 and 3061; δ_H 1.48–1.55 (2H, m, 2-H and 7-CH), 1.81 (1H, d, J=7.8 Hz, 7-CH′), 2.80 and 2.87 (each 1H, d, J=13.3 Hz, PhHC*H*), 2.93 (1H, s, 4-H), 3.21 (3H, s, OCH_3), 3.25 (1H, s, $^3J_{SnH}$=41 Hz, 1-H), 6.31 (1H, dd, J=5.4, 2.9 Hz, 5-H), 6.45 (1H, dd, J=5.4, 2.9 Hz, 6-H), 7.15–7.6 (20H, m, ArH) and 7.62 (1H, s, CH=N); δ_C 36.15, 46.31, 46.58, 47.45, 50.86, 52.08, 60.92, 126.59, 128.03, 128.47, 128.56, 130.00, 131.33, 136.80, 137.13, 137.83, 140.11, 142.79 and 158.13; *m/z* (CI) 514 (M^+-77, 100%); (ES) 447 (100%) and 393 (20).

Further elution gave the title compound **25** (18 mg, 17%) as a white solid (Found: H, 5.15; N, 2.1; Cl, 6.6. $C_{28}H_{28}NOClSn$ requires H, 5.15; N, 2.55; Cl, 6.45%); ν_{max}/cm^{-1} 701, 733, 788, 908, 998, 1038, 1072, 1266, 1326, 1430, 1454, 1481, 1495, 2874, 2968 and 3052; δ_H 1.52 (1H, dd, J=9.2, 2.2 Hz, 7-CH), 1.58 (1H, d, J=9.2 Hz, 7-H′), 1.65 (1H, d, J=2.5 Hz, $^2J_{SnH}$=60 Hz, 2-H), 2.75 (1H, d, J=13.6 Hz, PhHC*H*), 2.99 (1H, s, 4-H), 3.00 (1H, d, J=13.6 Hz, Ph*H*CH), 3.25 (3H, s, OCH_3), 3.51 (1H, s, $^3J_{SnH}$=35 Hz, 1-H), 6.32 (1H, dd, J=5.5, 3.0 Hz, 5-H), 6.56 (1H, dd, J=5.5, 3.0 Hz, 6-H), 7.1–7.5 (13H, m, ArH), 7.8–7.88 (2H, m, ArH) and 7.93 (1H, s, CH=N); δ_C 39.02, 45.58, 45.84, 47.41, 51.41, 54.12, 62.03, 127.01, 128.39, 128.57, 128.82, 128.86, 129.26, 130.01, 131.46, 135.55, 136.39, 136.72, 140.42, 140.79, 142.98 and 163.01; *m/z* (CI), 514 ($M^+-{}^{35}Cl$, 100%); (ES) 513 ($M^+-H^{35}Cl$, 100%) and 514 ($M^+-{}^{35}Cl$, 98).

4.1.14. (1*RS*,2*RS*,3*RS*,4*SR*)-3-Benzyl-2-triphenylstannylbicyclo[2.2.1]heptane-3-carbaldehyde hydrazone 26. Hydrazine hydrate (5 cm^3) was added to a solution of aldehyde **22** (323 mg, 0.575 mmol) in anhydrous ethanol (10 cm^3) and benzene (6 cm^3). The reaction mixture was heated under reflux for 47 h, then concentrated under reduced pressure. The residue was diluted with water and extracted with ether (4×50 cm^3). The combined extracts were washed with brine and dried over magnesium sulfate. Column chromatography using 10% ether in light petroleum as eluent gave the title compound **26** (230 mg, 69%) as a white solid, mp 60°C (Found: C, 68.60; H, 6.0; N, 4.8; Sn, 19.95; $M^+-C_6H_5$, 501.1359. $C_{33}H_{34}N_2Sn$ requires C, 68.65; H, 5.95; N, 4.85; Sn, 20.55%; $C_{27}H_{29}N_2Sn$ requires M, 501.1352); ν_{max}/cm^{-1} 701, 730, 1071, 1264, 1426, 1452, 1479, 1495, 1603, 2870, 2938 and 3059; δ_H 1.21 (1H, d, J=9.8 Hz, 7-H), 1.48–1.65 (3H, m, 5-H, 6-H and 7-H′), 1.65–1.88 (2H, m, 5-H′ and 6-H′), 2.11–2.33 (2H, m, 2-H and 4-H), 2.63 (1H, s, $^3J_{SnH}$=39 Hz, 1-H), 2.87 and 3.14 (each 1H, d, J=13.5 Hz, PhHC*H*), 4.67 (2H, s, NH_2), 6.90 (1H, s, CH=N), 7.1–7.4 (14H, m, ArH) and 7.4–7.6 (6H, m, $^3J_{SnH}$=43 Hz, *o*-ArH); δ_C 23.71, 34.24, 37.19, 41.31, 42.08, 43.18, 44.82, 53.15, 126.31, 127.63, 127.91, 128.35, 129.79, 136.89, 138.41, 144.55 and 152.61; *m/z* (CI) 501 (M^+-77, 100%); (ES) 501 (M^+-77, 100%), 527 (72), 541 (42) and 619 (12).

4.2. X-Ray crystal structure determinations

4.2.1. Crystal data for methyl 2-benzyl-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate 20. $C_{34}H_{32}O_2Sn$, M=591.32, C-centred monoclinic, space group *Cc* (#9), a=9.692(5), b=67.57(4), c=9.795(5) Å, U=5575(5) Å^3 β=119.63(3)° (by least squares refinement on diffractometer angles of 17 carefully centred reflections in the range 28.84<2θ<31.28°), Z=8, D_c=1.409 g cm^{-3}, μ=75.14 cm^{-1}, F(000)=2416.00, colourless needle, crystal dimensions 0.25×0.10×0.05 mm^3.[17]

4.2.2. Crystal data for 2-benzyl-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde 22. $C_{33}H_{30}OSn$, M=561.29, primitive triclinic, space group *P*1 (#2), a=13.912(7), b=16.820(8), c=11.615(6) Å, U=2659(2) Å^3, α=91.10(4)°, β=90.07(4)°, γ=78.13(4) ° (by least squares refinement using setting angles of 22 carefully centred reflections in the range 14.53<2θ<20.68°), Z=4, D_c=1.402 g cm^{-3}, μ=9.85 cm^{-1}, F(000)=1144.00, colourless block, crystal dimensions 0.20×0.30×0.40 mm^3.[18]

4.2.3. Crystal data for 3-benzyl-2-chlorodiphenylstannylbicyclo[2.2.1]hept-5-ene-3-carbaldehyde oxime 23. $C_{31}H_{36}NO_2SnCl$, M=608.77, primitive monoclinic, space group $P2_1/n$ (#14), a=11.870(7), b=14.311(3), c=17.597(6) Å, U=2960(2) Å^3, β=98.02(4)° (by least squares refinement using setting angles of 25 carefully centred reflections in the range 40.79<2θ<49.42°), Z=4, D_c=1.366 g cm^{-3}, μ=79.07 cm^{-1}, F(000)=1248.00, colourless block, crystal dimensions 0.30×0.20×0.20 mm^3.[19]

4.2.4. Crystal data for 3-benzyl-2-chlorodiphenylstannylbicyclo[2.2.1]hept-5-ene-3-carbaldehyde *O*-methyloxime 25. $C_{28}H_{28}NOSnCl$, M=548.68, primitive monoclinic, space group $P2_1$ (#4), a=9.128(2), b=30.712(6), c=

9.907(2) Å, U=2529.3(8) Å^3, β=114.39(1)° (by least squares refinement using setting angles of 24 carefully centred reflections in the range $28.50<2\theta<31.32°$), Z=4, D_c=1.441 g cm^{-3}, μ=91.62 cm^{-1}, $F(000)$=1112.00, colourless needle, crystal dimensions 0.25×0.12×0.15 mm^3.[20]

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