Synthesis of chiral organotin reagents: synthesis of bicyclo[2.2.1]heptan-2-yl(diphenyl)tin hydrides with *cis*-disposed, oxygen-containing substituents

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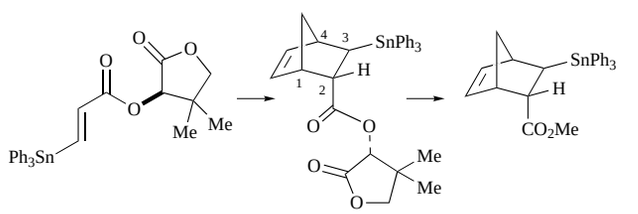
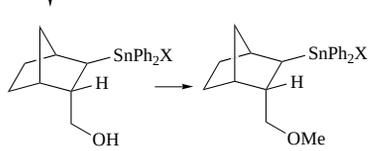
Alkylation of the methyl 3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate 3 using lithium diethylamide and either methyl iodide or benzyl bromide at −78 °C is stereoselective in favour of the *endo*-alkylated products 10 and 11. Methylation of the saturated ester 12 is also *endo*-selective in favour of 13. If the unsaturated ester 3 is deprotonated at 0 °C rather than at −78 °C, the rearranged stannane 17 is obtained as a side-product. The *endo*-triphenylstannylbicyclo[2.2.1]heptane-2-carboxylate 22 has been prepared from the ester 12 by phenylselenylation, oxidative elimination and reduction using diimide. The triphenylstannanes 13, 17 and 20 have been converted into the alkyl(diphenyl)tin hydrides 27, 28 and 29 and the methoxyalkyltin hydride 36 has also been prepared and characterized. These tin hydrides accelerate the reduction of aryl methyl ketones to 1-arylethanols by phenylsilane, but the reduction product is racemic. Syntheses of the aminobicycloalkyl(triphenyl)stannanes 44, 45 and 48 are described.

The (1*S*,2*S*,3*R*,4*R*)-*endo*-adduct **2** is the major product from the diethylaluminium chloride-catalysed Diels–Alder reaction between the chiral (*E*)-3-triphenylstannylacrylate **1** and cyclopentadiene.[1] The adduct **2** has been converted into the methyl ester **3** by transesterification and into the saturated alcohol **4**, ee 94%, by reduction using diisobutylaluminium hydride followed by hydrogenation. The alcohol was *O*-methylated to give the methyl ether **7**, and the alcohol **4** and methyl ether **7** were converted into the bicycloheptyl(diphenyl)tin hydrides **6** and **9** by



1 **2** **3**



4 X = Ph
5 X = I
6 X = H

7 X = Ph
8 X = I
9 X = H

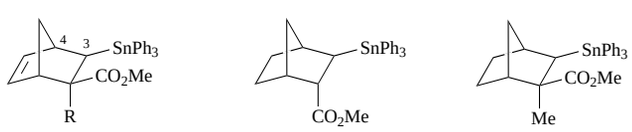
treatment with iodine followed by reduction of the iodides **5** and **8** using sodium borohydride. Analogous tin hydrides with different substituents on the oxygen (*tert*-butyldimethylsilyl, trityl and 1-naphthoyl) were also prepared. Spectroscopic data indicated that there is little interaction between the *trans*-disposed oxygen functionality and the tin substituents in these compounds.[1]

We now report syntheses of bicyclo[2.2.1]heptanyltin iodides and hydrides with *cis*-disposed, oxygen-containing, vicinal substituents together with preliminary studies into the preparation of amido- and amino-substituted stannanes. Bicyclo[2.2.1]heptanylstannanes with vicinal, oxygen-containing substituents *cis*-disposed to the tin have been prepared using Diels–Alder reactions of (*Z*)-3-(triphenylstannyl)acrylates and cyclopentadiene.[2] However, mixtures of *endo*- and *exo*-isomers were obtained with only modest diastereofacial selectivity being observed for addition of cyclopentadiene to the (*Z*)-isomer of the chiral dienophile **1**.[1]

Results and discussion

Alkylation of methyl 3-triphenylstannylbicyclo[2.2.1]heptane-2-carboxylates

Alkylation of the lithium enolate of the methyl ester **3** using methyl iodide or benzyl bromide gave the *endo*-alkylated products **10** and **11**, in which the methoxycarbonyl group is *cis*-disposed with respect to the tin, with stereoselectivities of ⩾97:3 and 85:15, respectively. Better yields were obtained in these reactions using lithium diethylamide rather than lithium diisopropylamide as the base, *e.g.* 98% rather than 17% for the methylation, perhaps because of steric interaction with the bulky, tin-containing, substituent. Hydrogenation of the ester **3** gave the saturated ester **12** which on methylation using lithium diethylamide and methyl iodide gave the *endo*-methylated product **13** with 95:5 stereoselectivity. The saturated ester **13**



10 R = Me
11 R = Bn

12

13

was also prepared by hydrogenation of the unsaturated methyl ester **10**.

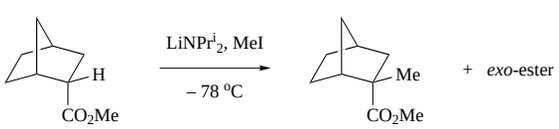
The structures of these alkylated products were assigned on the basis of spectroscopic data. In the ^{1}H NMR spectrum of the unsaturated *endo*-methylated product **10** the lack of coupling between 3-H and 4-H and the presence of a 'W'-coupling of 2.5 Hz between 3-H and the 7-H *syn* to the double bond confirmed the retained configuration at C(3).[3] The *endo*-selectivity of the methylation then followed from the ^{13}C NMR spectrum which showed three-bond couplings between the tin and the carboxy carbon and between the tin and the carbon of the 2-methyl group of 40.5 and 11 Hz, respectively. Since three-bond couplings to tin are known to follow a Karplus relation-

ship with respect to torsional angle,[4] it follows that the carboxy group is *exo*, with a torsional angle of *ca.* 0° with respect to the C(3)–Sn bond, and the 3-methyl group is *endo*, torsional angle *ca.* 110°. An NOE enhancement of 6-H of 1.3% on irradiation of the 3-methyl group is also consistent with the assigned stereochemistry. Similar features were observed in the NMR spectra of the other alkylation products **11** and **13**.

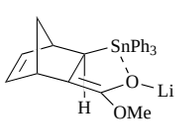
The carbonyl stretching frequency in the IR of the methylated ester **10** was at 1707 cm^{-1}, *cf.* 1731 cm^{-1} for the *endo*-methyl ester **3**. This shift suggests a small interaction between the tin and the oxygen of the carbonyl group. This interaction is consistent with the increases observed in the one-bond couplings between the tin and C(3) and between the tin and the *ipso*-aromatic carbon in the ^{13}C NMR spectra of the esters on methylation, $^{1}J_{C(3)^{119/117}Sn}$ 440/421 for **10**, *cf.* 398/381 for **3** and $^{1}J_{C(ipso)^{119/117}Sn}$ 503/481 for **10**, *cf.* 481/458 for **3**.[5]

Organostannanes containing suitably disposed oxygen-containing functional groups for coordination have been prepared and examined by X-ray crystallography.[6] The tetrahedral geometry of the tin in these compounds was found to be distorted slightly by interaction with the oxygen and increases in the one-bond coupling to the tin were observed similar to those reported here. No interaction between the tin and the carboxy group was indicated by the spectroscopic data obtained for the bicyclo[2.2.1]heptane carboxylates **2** and **3**.[1] The detection of this interaction is therefore indicative of a *cis*-relationship between the triphenyltin and methoxycarbonyl substituents as in the methylated ester **10**. Similar features were observed for the benzylated ester **11** and the saturated *endo*-methylated ester **13**.

The preference for *endo*-alkylation shown by the 3-triphenylstannyl esters **3** and **12** contrasts with the stereoselectivity of methylation of methyl bicyclo[2.2.1]heptane-3-carboxylate **14** which gives preferentially the *exo*-methylated product **15**.[7] Perhaps the tin in the lithium enolate, *e.g.* **16** derived from the



14 **15**



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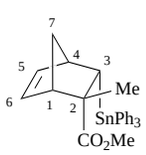
ester **3**, is coordinated by the negatively charged oxygen. This coordination would have to be disrupted if the alkylation took place from the *exo*-direction whereas it can translate into the weak interaction observed in the alkylated products if the alkylation takes place from the *endo*-direction.

When the alkylation of the ester **3** was carried out at 0 °C rather than at −78 °C, the yield of the *endo*-methylated product **10** was only 21% and an isomer of the alkylated product was isolated (8%) together with methyl(triphenyl)stannane (17%). The structure **17** was assigned to the new product on the basis



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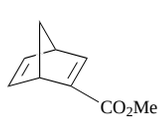

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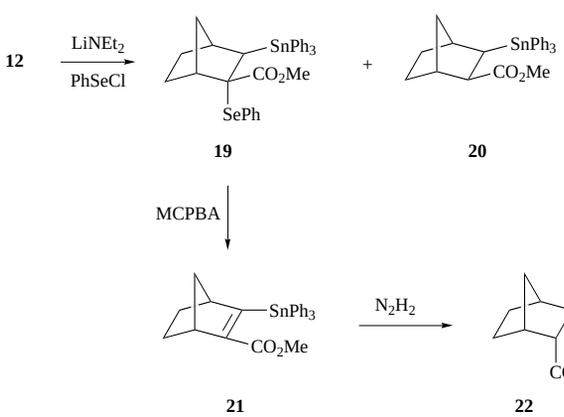
of spectroscopic data. In its ^{13}C NMR spectrum, three-bond couplings of 64 and 24 Hz were observed between the tin and C(7) and between the tin and C(5) suggesting that the tin is in the *endo*-position.[4,8] This was confirmed by the ^{1}H NMR spectrum which showed that 3-H was *exo* by a coupling of 2.9 Hz between 3-H and 4-H and no 'W'-coupling between 3-H and the *syn*-7-H. The configuration at C(2) was assigned on the basis of the three-bond couplings to tin of 30 and 14 Hz observed in the ^{13}C NMR spectrum for the carboxy carbon and the carbon of the 2-methyl group, respectively.[4] A carbonyl stretching frequency of 1715 cm^{-1} in the IR spectrum of the ester **17** was also consistent with a small interaction between the carbonyl group and the tin indicative of the *cis*-disposition of the methoxycarbonyl and triphenylstannyl substituents.

The formation of the *endo*-ester **17** may be due to partial elimination of triphenyltin lithium from the enolate **16** at 0 °C to generate the dienyl ester **18**. Readdition of the triphenyltin lithium to this conjugated ester could then either regenerate the enolate **16** or its epimer at C(3) which would be expected to react with the methyl iodide from the *exo*-face to preserve any interaction between the enolate oxygen and the tin in the transition structure for alkylation. The isolation of methyl(triphenyl)-stannane as a side-product is consistent with the involvement of triphenyltin lithium in this reaction.

Preliminary studies were carried out into an alternative route to bicyclo[2.2.1]heptanes with *endo*-methoxycarbonyl and triphenyltin substituents. Addition of benzeneselenenyl chloride to the lithium enolate of the ester **12** gave the *endo*-phenylselenenyl ester **19** (19%) together with unchanged ester **12** (11%) and the epimerised ester **20** (40%). Differences in the



21 **22**

NMR spectra of the ester **12** and its epimer **20** were consistent with the assigned structures. For example, the three-bond coupling between the tin and the carboxy carbon was 55 Hz for **20** consistent with a torsional angle between the C(3)–Sn and C(2)–CO_2Me bonds approaching 0°, *cf.* the coupling of 22 Hz observed for the *endo*-ester **12**.[4] One-bond tin–carbon couplings were larger for **17** than for **12** in line with some degree of coordination of the tin by the *cis*-methoxycarbonyl group.[5] The IR stretching frequency is lower for the *exo*-ester **20** than for the *endo*-ester **12**, 1715 *vs.* 1731 cm^{-1}.

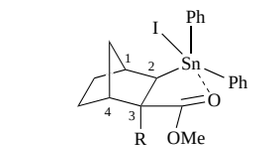
Similar data supported the assignment of stereochemistry to the phenylselenated ester **19**. Moreover, oxidation of the selenide using *m*-chloroperoxybenzoic acid[9] was accompanied by loss of phenylselenenic acid and gave the unsaturated ester **21**. The loss of the hydrogen from C(3) in this elimination confirmed the *cis*-orientation of the phenylselenyl group and 3-H. It would appear that reactions with other electrophiles of the enolate generated from the 3-triphenylstannylated ester **12** also take place *trans* with respect to the triphenyltin substituent. Finally reduction of the unsaturated ester **21** by diimide gave the *endo*-ester **22** the structure of which was supported by spectroscopic data. For example, in the ^{1}H NMR spectrum a 'W'-coupling of 1.5 Hz was observed between 2-H and the *exo*-

6-H and a vicinal coupling of 4.5 Hz was observed between 1-H and 2-H so showing the methoxycarbonyl group to be in the *endo*-position. The low carbonyl stretching frequency observed in its IR spectrum, 1719 cm^{-1} relative to 1731 cm^{-1} observed for the *endo*-ester **12**, indicates the *cis*-disposition of the triphenylstannyl and methoxycarbonyl substituents in **22**.

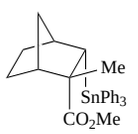
This study of the alkylation of esters **3** and **12** had led to the synthesis of several products **10**, **11**, **13**, **17**, **20** and **22**, in which a triphenyltin substituent is *cis*-disposed with respect to a methoxycarbonyl group. The conversion of these stannanes into *cis*-functionalized tin iodides and tin hydrides was then investigated.

Syntheses of *cis*-functionalized tin hydrides

The *exo*-3-triphenylstannylbicyclo[2.2.1]heptane-2-carboxylates **13** and **20** were treated with 1 mol equiv. of iodine to give the alkyl(diphenyl)tin iodides **23** and **24** in excellent yields.[2]



23 R = Me
24 R = H



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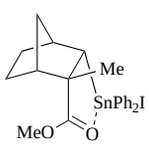

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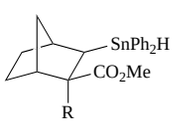
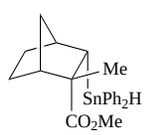


27 R = Me
28 R = H



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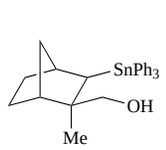
Hydrogenation of the *endo*-stannane **17** gave the saturated stannane **25** which was converted into the tin iodide **26** by treatment with iodine. Reduction of the tin iodides **23**, **24** and **26** with sodium borohydride gave the corresponding tin hydrides **27**, **28** and **29**.[2]

Structures were assigned to these products on the basis of spectroscopic data. Of interest was the degree of coordination of the methoxycarbonyl group to the tin.[6] For the tin iodides, a significant lowering of the carbonyl stretching frequency was observed in their IR spectra from 1709, 1715 and 1712 cm^{-1} for the triphenylstannanes **13**, **20** and **25** to 1664, 1665 and 1661 cm^{-1} for the tin iodides **23**, **24** and **26**, respectively, which is consistent with a significant coordination of the tin by the methoxycarbonyl substituent in these compounds. In the ^1H NMR spectra of the *exo*-tin iodides **23** and **24** a marked deshielding of the bridgehead proton 1-H was observed relative to the triphenylstannanes **13** and **20**, δ 3.00 and 3.15 for **23** and **24** *cf.* δ 2.67 and 2.77 for **13** and **20**. This may be due to pseudo trigonal bipyramidal geometry of the tin which would place the axial iodide close to this bridgehead proton as indicated for the iodides **23** and **24**.

As usually observed for chiral tin halides,[10,11] the diastereotopic phenyl rings in the diphenyltin iodide **8** for which intramolecular coordination of the tin by the methoxy group is not possible, were found to be equivalent by ^1H NMR consistent with rapid exchange on the NMR time-scale.[1] However, the two phenyl rings in each of the tin iodides **23**, **24** and **26** were found to be non-equivalent by both ^1H and ^{13}C NMR spectroscopy. For example, two *ipso*-aromatic carbons were observed for the tin iodides **23**, **24** and **26** at δ 140.36/142.37, 140.54/142.42 and 141.03/141.86, respectively.

The coordination of the tin by the methoxycarbonyl substituents in the tin iodides **23**, **24** and **26** which is indicated by the spectroscopic data discussed above, was not as apparent in the tin hydrides **27**, **28** and **29**. For example, the carbonyl stretching frequencies of 1708, 1713 and 1711 cm^{-1} observed for the tin hydrides **27**, **28** and **29** were similar to those observed for the corresponding triphenylstannanes,[1] Diastereotopic substituents attached to the tin of chiral tin hydrides can usually be distinguished by NMR spectroscopy[10,11] and the diastereotopic phenyl groups of the tin hydrides **27** and **29** gave rise to different peaks in their ^{13}C NMR spectra although only one set of aromatic peaks was apparent for the tin hydride **28**. The hydrogens bound to tin were detected in the ^1H NMR spectra of the tin hydrides **27**, **28** and **29** as doublets (*J* 1.5–2.5 Hz) at δ_H 6.98 ($^1J_{H^{119/117}Sn}$ 1906/1820), 6.89 ($^1J_{H^{119/117}Sn}$ 1906/1821) and 7.09 ($^1J_{H^{119/117}Sn}$ 1966/1889), respectively, the slightly increased one-bond coupling to tin for the *endo*-tin hydride **29** perhaps indicating a slightly stronger interaction between the tin and the methoxycarbonyl group than for the *exo*-isomer **27**.

Reduction of the methylated *exo*-ester **13** using diisobutylaluminium hydride gave the alcohol **30** which on treatment with iodine was converted into the tin iodide **31**. The one-bond coupling of C(2) to the tin observed in the ^{13}C NMR spectrum of the tin iodide **31**, $^1J_{C(2)^{119/117}Sn}$ 490/467, is larger than that observed for the hydroxyalkyltin iodide **5**, $^1J_{C(2)^{119/117}Sn}$ 440/418, which is consistent with some degree of coordination of the tin by the hydroxy group.[5,13] Moreover, the resonance observed in the ^{119}Sn NMR spectrum of the tin iodide **31**, at δ −102, is considerably more upfield than that observed for the iodide **5**, δ −38.8.[1] The diastereotopic phenyl groups in the tin iodide **31** gave rise to different peaks in its ^{13}C NMR spectrum, *e.g.* at δ 141.22 and 142.62 for the *ipso*-aromatic carbons.



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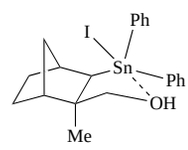

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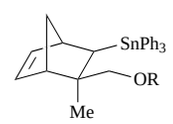
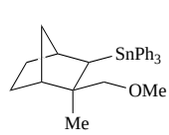


32 R = H
33 R = Me



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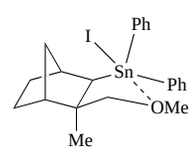

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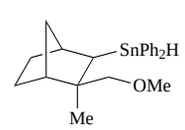

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However, reduction of the tin iodide **31** using sodium borohydride did not give a tin hydride which could be isolated or characterised and attempts to eliminate hydrogen iodide from **31** using sodium hydride, perhaps to give an oxastannocycle, gave only complex mixtures of products.[14]

Reduction of the unsaturated methylated ester **10** gave the alcohol **32** which was methylated using sodium iodide and methyl iodide to give the methyl ether **33**. Hydrogenation gave the saturated methyl ether **34** which was treated with iodine to give the tin iodide **35**. The iodide was reduced using sodium borohydride to give the tin hydride **36**.

The structures of the tin iodide **35** and hydride **36** were assigned on the basis of spectroscopic data. The bridgehead proton, 1-H, in the ^1H NMR spectrum of the iodide **35** was deshielded with respect to that of the triphenylstannane **34** by 0.72 ppm, and the diastereotopic phenyl groups in the iodide **35** were distinguishable in its ^{13}C NMR spectrum, *e.g.* two *ipso*-carbons were observed at δ 141.11 and 141.73. These observations are consistent with some degree of coordination of the tin by the methoxy group in the tin iodide **35**.

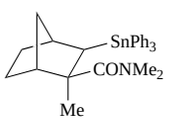
The one-bond tin–proton coupling observed in the ^1H NMR spectrum of the tin hydride **36** was larger than that observed for the tin hydride **9**, $^1J_{H^{119/117}Sn}$ 1850/1769 *cf.* 1763/1681, and the tin in its ^{119}Sn NMR spectrum was somewhat more shielded, δ −139 *cf.* −118 ppm. The diastereotopic phenyl rings of the tin

hydride **36** also gave rise to distinctly different peaks in its ^{1}H and ^{13}C NMR spectra.

Tin hydrides with substituents which can coordinate with the tin in the transition state for hydride transfer can act as hydride reducing agents. The tin hydrides **27**, **28**, **29** and **36** were found to accelerate the reduction of acetophenone and *o*-hydroxyacetophenone by phenylsilane, with better conversions being obtained for the hydroxyacetophenone. However the 1-arylethanol so obtained was racemic and reduction of methyl 2-bromo-2-phenylpropanoate using the tin hydride **36** gave racemic methyl 2-phenylpropanoate. Alkyltin hydrides with amino substituents which can coordinate with the tin have also been shown to be useful for the reduction of carbonyl compounds.[15] The preparation of amino-substituted bicyclo[2.2.1]heptyl(triphenyl)stannanes was therefore briefly investigated with the synthesis of *cis*-substituted (aminoalkyl)bicycloheptylstannanes in which the amino group can coordinate to the tin being of particular interest.[16]

Approaches to aminoalkylbicyclo[2.2.1]heptyl(triphenyl)stannanes

The *endo*-methylated methyl ester **13** was recovered unchanged from attempts to prepare the dimethylamide **37** by heating the



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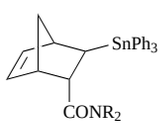
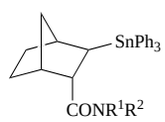
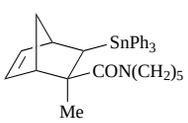


38 R = Me
39 R_2 = $(CH_2)_4$
40 R_2 = $(CH_2)_5$



41 R^1 = H, R^2 = Bn
42 R^1,R^2 = $(CH_2)_5$



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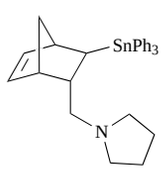
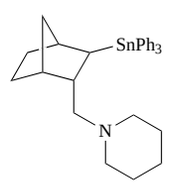


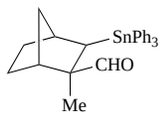
44



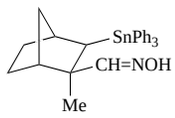
45

ester with trimethylaluminium and dimethylamine.[17] Analogous attempts to prepare the corresponding benzylamide were also unsuccessful. However, the esters **3** and **12** could be converted into the amides **38**–**40** and **41**, **42** by treatment with the appropriate aluminium amide.[18] The amide **40** was methylated by deprotonation using lithium diethylamide at −30 °C followed by the addition of methyl iodide at −78 °C, but the *endo*-methylated product **43** was only obtained in a modest yield (16%) together with unchanged starting material (36%) and methyl(triphenyl)tin (21%). Of note is the IR carbonyl stretching frequency of the amide **43** which was at 1588 cm^{-1}, *cf.* 1636 cm^{-1} for the amide **40**. This is indicative of some degree of coordination of the tin by the carbonyl oxygen consistent with the expected stereoselectivity of alkylation.[1] Attempts to reduce the methylated amide **43** to the corresponding tertiary amine using lithium aluminium hydride were unsuccessful, although the non-methylated amides **39** and **42** were cleanly reduced to the *endo*-dialkylaminomethylbicyclo[2.2.1]heptanylstannanes **44** and **45**. It would appear that the combination of a bulky triphenyltin substituent and a quaternary centre α to the carbonyl group makes the *endo*-alkylated amides, *e.g.* **43**, both relatively inaccessible and difficult to use.

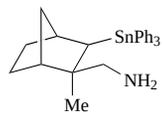
As a second approach to bicyclo[2.2.1]heptanylstannanes with *cis*-disposed amino groups, aspects of the chemistry of the aldehydes **46** and **49** were briefly investigated. The aldehyde **46** was prepared by oxidation of the alcohol **30** using TPAP[19] but reaction with hydroxylamine[20] gave only a low yield, 11%, of the oxime **47**. Nevertheless this oxime was reduced using lithium aluminium hydride to the amine **48**. The unsaturated aldehyde



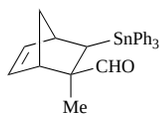
46



47



48



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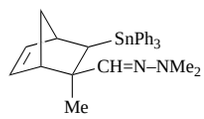

50

49 was similarly prepared by oxidation of the alcohol **32**. Treatment of this aldehyde with dimethylamine and sodium cyanoborohydride gave none of the required tertiary amine although the *N*,*N*-dimethylhydrazone **50** was prepared, albeit in low yield, by treatment with *N*,*N*-dimethylhydrazine.

Conclusions

The work described in this and the preceding papers has reported aspects of the chemistry of bicyclo[2.2.1]heptan-2-yl(diphenyl)stannanes. In the present paper, the influence of the triphenyltin substituent on the stereoselectivity of alkylation of the esters **3** and **12** is of note. The heteroatom functionality in the tin iodides **23**, **24**, **26**, **31** and **35** is believed to be associated with the tin of the tin iodide to a certain extent and the functionalized tin hydrides were found to behave as reducing agents towards ketones and alkyl halides although the products obtained were racemic.

It may be that better coordinating groups than the methoxycarbonyl and methoxy groups used to date will be required for effective asymmetric reduction of carbonyl compounds. It may also be necessary to use bulkier ligands on the tin. In the present work, the carbon skeleton of the enantiomerically enriched tin hydrides was assembled using an asymmetric Diels–Alder reaction. A completely different approach would start from readily available bicyclic monoterpenes and related natural products. This approach is presently being investigated.

Experimental

For general experimental details see the first paper in this series.[2]

Methyl (1*S*,2*R*,3*R*,4*R*)-2-methyl-3-(triphenylstannyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate 10

Butyllithium (1.5 mol dm^{-3} in hexanes; 2.10 cm^3) was added dropwise to a solution of diethylamine (0.41, 3.95 mmol) in tetrahydrofuran (16 cm^3) at 0 °C. The solution was stirred for 15 min, and then cooled to −78 °C before the addition of the ester **3** (0.99 g, 1.97 mmol) in tetrahydrofuran (4 cm^3). The mixture was stirred at −78 °C for 1 h and then methyl iodide (0.49 cm^3, 7.89 mmol) was added dropwise. After stirring for a further 1.5 h, the reaction mixture was warmed to ambient temperature, concentrated under reduced pressure and the residue diluted with ether (20 cm^3). The solution was washed with water (20 cm^3), then brine (20 cm^3), and the organic phase dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **10** (1.0 g, 98%), as an oil, used without further purification; $[\alpha]_D$ −10.9 (*c* 1.33 in $CHCl_3$) (Found: $M^+ - C_6H_5$, 439.0717. $C_{22}H_{23}O_2Sn$ requires *M*, 439.0720); ν_{max}/cm^{-1} 3062, 1707, 1428, 1291, 1273, 1250, 1216, 1100, 1072, 728 and 699; δ_H 1.20 (3 H, s, 2-CH_3), 1.20 (1 H, d, *J* 2.5, 3-H), 1.33 (1 H, dd, *J* 8.5, 1.5, 7-H), 1.37 (1 H, d, *J* 8.5, 7-H′), 3.13 (1 H, m, 1-H), 3.18 (1 H, m, 4-H), 3.58 (3 H, s, OCH_3), 6.10 (1 H, dd, *J* 5.5, 3, 6-H), 6.39 (1 H, dd, *J* 5.5, 3, 5-H), 7.4 (9 H, m, ArH) and 7.6 (6 H, m, ArH); δ_C 24.97 ($^3J_{CSn}$ 11), 38.92 ($^1J_{CSn}$ 440/421), 47.06,

48.36, 52.26 ($^3J_{CSn}$ 12.5), 52.85, 52.89, 128.11 ($^3J_{CSn}$ 48), 128.22, 131.63, 137.44 ($^2J_{CSn}$ 35), 140.45 ($^3J_{CSn}$ 55.5), 142.55 ($^1J_{CSn}$ 503/481) and 181.34 ($^3J_{CSn}$ 40.5); *m*/*z* 439 ($M^+ - 77$, 100%), 368 (10) and 351 (10).

Chromatography, using light petroleum–ether (100 : 1) as eluent, of the mixture of products obtained when 3.0 mol equiv. of lithium diethylamide at 0 °C was used to deprotonate the ester **3** gave methyl(triphenyl)tin (0.225 g, 17%) as a white solid (Found: C, 62.9; H, 5.3. $C_{19}H_{18}Sn$ requires C, 62.5; H, 5.0%); ν_{max}/cm^{-1} 3063, 3047, 3014, 1428, 1075, 726 and 698; δ_H 0.88 (3 H, s, $^2J_{HSn}$ 56.0/54.0, CH_3), 7.5 (9 H, m, ArH) and 7.7 (6 H, m, ArH); δ_C −10.36 ($^1J_{CSn}$ 375/358), 128.62 ($^3J_{CSn}$ 49.5), 129.03 ($^4J_{CSn}$ 11), 136.91 ($^2J_{CSn}$ 37.0) and 139.30 ($^1J_{CSn}$ 510/487); *m*/*z* 351 ($M^+ - 15$, 20%), 307 (100) and 289 (30). Further elution gave the methylated ester **10** (0.42 g, 21%) followed by *methyl* (1S,2S,3S,4R)-2-*methyl*-3-*triphenylstannylbicyclo*[2.2.1]*heptan*-2-*yl-carboxylate* **17** (0.15 g, 8%) as an oil (Found: M^+, 516.1110. $C_{28}H_{28}O_2Sn$ requires *M*, 516.1111); $[\alpha]_D$ +65.8 (*c* 2.37 in CH_2Cl_2); ν_{max}/cm^{-1} 3062, 1715, 1428, 1331, 1297, 1275, 1212, 1123, 1072, 729 and 700; δ_H 1.60 (3 H, s, CH_3), 1.69 and 1.73 (each 1 H, d, *J* 8.5, 7-H), 2.00 (1 H, d, *J* 2.5, $^2J_{HSn}$ 50, 3-H), 3.02 (1 H, m, 1-H), 3.27 (1 H, m, 4-H), 3.57 (3 H, s, OCH_3), 6.11 (1 H, dd, *J* 5.5, 3, 6-H), 6.16 (1 H, dd, *J* 5.5, 3, 5-H), 7.37 (9 H, m, ArH) and 7.65 (6 H, m, ArH); δ_C 27.32 ($^3J_{CSn}$ 14), 41.88 ($^1J_{CSn}$ 498/487), 47.28 ($^2J_{CSn}$ 9), 49.59 ($^3J_{CSn}$ 64), 51.66 ($^3J_{CSn}$ 22.5), 52.46, 52.78 ($^2J_{CSn}$ 16), 128.07 ($^3J_{CSn}$ 48), 128.12, 135.67, 137.48 ($^2J_{CSn}$ 35.0), 139.07 ($^3J_{CSn}$ 24), 142.86 ($^1J_{CSn}$ 506/483) and 179.95 ($^3J_{CSn}$ 30); *m*/*z* (EI) 516 (M^+, 10%), 439 (60) and 351 (100).

Methyl (1*S*,2*R*,3*R*,4*R*)-2-benzyl-3-triphenylstannylbicyclo-[2.2.1]hept-5-ene-2-carboxylate 11

Following the procedure outlined for the synthesis of the methylated ester **10**, but using benzyl bromide as the alkylating agent, the ester **3** (0.15 g, 0.3 mmol) gave, after chromatography using light petroleum–ether (20 : 1) as eluent, the *title compound* **11** (91 mg, 51%) as a white solid (Found: $M^+ - C_6H_5$, 515.1034. $C_{28}H_{27}O_2Sn$ requires *M*, 515.1033); mp 90–94 °C; $[\alpha]_D$ +10.1 (*c* 3.60 in $CHCl_3$); ν_{max}/cm^{-1} 3061, 1707, 1427, 1330, 1247, 1212, 1179, 1072, 728 and 699; δ_H 1.26 and 1.40 (each 1 H, d, *J* 8.5, 7-H), 1.71 (1 H, d, *J* 2.5, $^2J_{HSn}$ 49, 3-H), 2.65 and 3.12 (each 1 H, d, *J* 13, C*H*HPh), 3.19 (1 H, m, 4-H), 3.28 (1 H, m, 1-H), 3.52 (3 H, s, OCH_3), 6.27 (1 H, dd, *J* 5, 2.5, 6-H), 6.51 (1 H, dd, *J* 5, 2.5, 5-H), 7.03 (5 H, m, ArH), 7.3 (9 H, m, ArH) and 7.5 (6 H, m, ArH); δ_C 37.1 ($^1J_{CSn}$ 445/425), 45.44 (J_{CSn} 10), 46.68, 48.09, 51.54 (J_{CSn} 11.5), 52.43, 59.9 ($^3J_{CSn}$ 11.5), 126.67, 127.95 ($^3J_{CSn}$ 48.5), 128.01, 128.35, 129.10, 132.36, 137.47 ($^2J_{CSn}$ 34), 140.90 ($^3J_{CSn}$ 55.5), 142.25 ($^1J_{CSn}$ 503/481) and 180.01 ($^3J_{CSn}$ 40.5); *m*/*z* 515 ($M^+ - 77$, 100%).

Methyl (1*R*,2*S*,3*R*,4*S*)-3-triphenylstannylbicyclo[2.2.1]heptane-2-carboxylate 12

Palladium (10% on charcoal; 0.21 g, 0.20 mmol Pd) was added to a solution of the alkene **3** (0.96 g, 1.92 mmol) in ethanol (45 cm^3). The mixture was stirred vigorously for 20 h under an atmosphere of hydrogen then filtered through Celite and the retained solids washed with ether (4 × 20 cm^3). The combined filtrates were concentrated under reduced pressure to give the *title compound* **12** (0.91 g, 95%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 427.0720. $C_{21}H_{23}O_2Sn$ requires *M*, 427.0700); $[\alpha]_D$ −39.0 (*c* 3.6 in $CHCl_3$); ν_{max}/cm^{-1} 1731, 1428, 1197, 728 and 699; δ_H 1.36 (1 H, d, *J* 9.5, 7-H), 1.42–1.58 (5 H, m, 5-H_2, 6-H_2 and 7-H′), 2.34 (1 H, dd, *J* 6.5, 2, 3-H), 2.62 (2 H, m, 1-H and 4-H), 3.20 (1 H, dd, *J* 6.5, 3, 2-H), 3.70 (3 H, s, OCH_3), 7.36–7.48 (9 H, m, ArH) and 7.6 (6 H, m, ArH); δ_C 24.74, 31.12 ($^1J_{CSn}$ 419/396), 33.31 ($^3J_{CSn}$ 66.5), 40.61, 41.09 ($^2J_{CSn}$ 7), 41.65 ($^2J_{CSn}$ 15), 51.1 ($^3J_{CSn}$ 18), 51.63, 128.59 ($^3J_{CSn}$ 47), 128.95 ($^4J_{CSn}$ 8.5), 137.38 ($^2J_{CSn}$ 34), 138.48 ($^1J_{CSn}$ 474/453) and 175.21 ($^3J_{CSn}$ 22); δ_{Sn} −99.5; *m*/*z* (EI) 427 ($M^+ - 77$, 25%), 351 (40) and 197 (100).

Methyl (1*R*,2*R*,3*R*,4*S*)-2-methyl-3-triphenylstannylbicyclo-[2.2.1]heptane-2-carboxylate 13

Following the procedure outlined for the synthesis of the ester **10**, the saturated ester **12** (0.45 g, 0.89 mmol) and methyl iodide (0.22 cm^3, 3.58 mmol) gave the *title compound* **13** (0.47 g, 98%), as an oil, used without further purification (Found: $M^+ - C_6H_5$, 441.0875. $C_{22}H_{25}O_2Sn$ requires *M*, 441.0877); $[\alpha]_D$ −4.2 (*c* 6.6 in $CHCl_3$); ν_{max}/cm^{-1} 3062, 1709, 1428, 1300, 1277, 1222, 1072, 728 and 699; δ_H 1.24 (1 H, d, *J* 10.5, 7-H), 1.40 (3 H, s, 2-CH_3), 1.45 (1 H, d, *J* 2, 3-H), 1.50–1.90 (5 H, m, 5-H_2, 6-H_2 and 7-H′), 2.63 (1 H, m, 1-H), 2.67 (1 H, m, 4-H), 3.65 (3 H, s, OCH_3), 7.35–7.48 (9 H, m, ArH) and 7.58–7.78 (6 H, m, ArH); δ_C 22.86, 22.92, 33.62 ($^3J_{CSn}$ 66), 38.69, 41.92, 43.69 ($^1J_{CSn}$ 455/435), 46.10 (J_{CSn} 14), 52.91, 53.33 (J_{CSn} 30.5), 128.00 ($^3J_{CSn}$ 47.5), 128.07, 137.44 ($^2J_{CSn}$ 34), 142.99 ($^1J_{CSn}$ 498/476) and 181.55 ($^3J_{CSn}$ 55.5); *m*/*z* 441 ($M^+ - 77$, 100%).

Phenylselenation of the ester 12

Butyllithium (1.6 mol dm^{-3} in hexanes; 0.47 cm^3) was added dropwise to a solution of diethylamine (0.085 cm^3, 0.84 mmol) in tetrahydrofuran (2 cm^3) at 0 °C. The solution was stirred for 15 min then cooled to −78 °C before the addition of the ester **12** (0.21 g, 0.42 mmol) in tetrahydrofuran (2 cm^3). The mixture was stirred at −78 °C for 2 h then a solution of benzeneselenenyl chloride (0.105 g, 0.545 mmol) in tetrahydrofuran (1 cm^3) was added dropwise. After stirring for a further 2 h, the reaction mixture was warmed to ambient temperature and concentrated under reduced pressure. The residue was diluted with ether (10 cm^3) then washed with saturated aqueous ammonium chloride (10 cm^3) and brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum–ether (40 : 1) as eluent gave *methyl* (1R,2R, 3R,4S)-3-*triphenylstannylbicyclo*[2.2.1]*heptane*-2-*carboxylate* **20** (84 mg, 40%) as an oil (Found: $M^+ - C_6H_5$, 427.0715. $C_{21}H_{23}O_2Sn$ requires *M*, 427.0720); ν_{max}/cm^{-1} 3062, 1715, 1428, 1215, 1201, 1176, 1073, 728 and 699; δ_H 1.16 (1 H, d, *J* 10, 7-H), 1.4–1.6 (3 H, m, CH_2 and 7-H′), 1.65–1.8 (2 H, m, CH_2), 2.05 (1 H, dd, *J* 9, 2, $^2J_{HSn}$ 55, 3-H), 2.66 (1 H, m, 1-H), 2.77 (1 H, m, 4-H), 2.88 (1 H, d, *J* 9, $^3J_{HSn}$ 50, 2-H), 3.55 (3 H, s, OCH_3), 7.38–7.46 (9 H, m, ArH) and 7.60–7.80 (6 H, m, ArH); δ_C 29.67, 33.10 ($^3J_{CSn}$ 66.5), 34.47 ($^1J_{CSn}$ 442), 36.33, 40.65 (J_{CSn} 11.5), 43.03, 50.18 ($^2J_{CSn}$ 30.5), 52.32, 128.11 ($^3J_{CSn}$ 47.5), 128.24 ($^4J_{CSn}$ 11), 137.43 ($^2J_{CSn}$ 34.5), 142.18 ($^1J_{CSn}$ 497/475) and 178.74 ($^3J_{CSn}$ 55); *m*/*z* 427 ($M^+ - 77$, 100%). Further elution gave *methyl* (1R,2S,3R,4S)-2-*phenylselenyl*-3-*triphenylstannyl-bicyclo*[2.2.1]*heptane*-2-*carboxylate* **19** (52 mg, 19%) as an oil (Found: $M^+ - C_6H_5$, 583.0193. $C_{27}H_{27}O_2SeSn$ requires *M*, 583.0198); ν_{max}/cm^{-1} 3061, 1702, 1428, 1299, 1264, 1219, 1072, 1053, 1022, 728 and 699; δ_H 1.15 and 1.38 (each 1 H, d, *J* 10.5, 7-H), 1.47 (2 H, m), 1.72 (3 H, m), 2.65 (1 H, m, 4-H), 2.88 (1 H, m, 1-H), 3.29 (3 H, s, OCH_3), 7.20–7.40 (12 H, m, ArH) and 7.53–7.74 (8 H, m, ArH); δ_C 25.74, 33.48 ($^3J_{CSn}$ 61.5), 37.78, 41.39, 42.46 ($^1J_{CSn}$ 438/419, $^2J_{SeC}$ 20), 45.07 (J_{CSn} 12), 52.54, 63.33 ($^2J_{CSn}$ 32, $^1J_{SeC}$ 75), 127.96, 128.11, 128.70, 128.98, 137.33 ($^2J_{CSn}$ 35), 137.51 ($^2J_{SeC}$ 7.5), 142.13, 142.60 ($^1J_{CSn}$ 512/489) and 177.11 ($^3J_{CSn}$ 49); *m*/*z* 583 ($M^+ - 77$, 3%), 503 (3), 444 (5) and 368 (30). Further elution gave starting material **12** (25 mg, 11%).

Methyl (1*R*,4*S*)-3-triphenylstannylbicyclo[2.2.1]hept-2-ene-2-carboxylate 21

3-Chloroperbenzoic acid (*ca.* 75% in water; 36 mg, 0.155 mmol) was added to the selenide **19** (45 mg, 0.07 mmol) in dichloromethane (2 cm^3). The solution was stirred at ambient temperature for 5 h then washed with aqueous sodium thiosulfate (5 cm^3) and brine (5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum–ether (20 : 1) as eluent gave the *title compound* **21** (18 mg, 53%) as an oil (Found: $M^+ - C_6H_5$, 425.0565. $C_{21}H_{21}O_2Sn$ requires *M*, 425.0564); ν_{max}/cm^{-1} 3063, 1715, 1698,

1429, 1330, 1276, 1255, 1162, 1096, 1075, 729 and 699; δ_H 1.04–1.32 (3 H, m, CH_2 and 7-H), 1.57 (1 H, d, *J* 9, 7-H′), 1.8 (2 H, m, CH_2), 3.22 (1 H, d, *J* 1.5, 4-H), 3.31 (3 H, s, OCH_3), 3.48 (1 H, m, 1-H), 7.4 (9 H, m, ArH) and 7.45–7.68 (6 H, m, ArH); δ_C 24.04, 24.53 (J_{CSn} 10.5), 43.48, 47.91 (J_{CSn} 28), 49.25 (J_{CSn} 40.5), 50.73, 128.4, 128.77, 136.86 ($^2J_{CSn}$ 38), 139.13, 151.97, 163.03 and 165.36; *m*/*z* 425 ($M^+ - 77$, 100%).

Methyl (1*R*,2*S*,3*S*,4*S*)-3-triphenylstannylbicyclo[2.2.1]heptane-2-carboxylate 22

Sodium acetate (5.5 mg, 0.065 mmol) and toluene-*p*-sulfonohydrazide (12 mg, 0.065 mmol) were added to the α,β-unsaturated ester **21** (16 mg, 0.03 mmol) in ethanol (2 cm^3) at 65 °C. Further portions of base and hydrazide were added every 30 min until all the starting material had disappeared (TLC). After 3 h at reflux the mixture was cooled to ambient temperature and partitioned between ether (5 cm^3) and water (5 cm^3). The organic phase was separated, washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum–ether (2:1) as eluent gave the *title compound* **22** (6.0 mg, 38%) as an oil (Found: $M^+ - C_6H_5$, 427.0724. $C_{21}H_{23}O_2Sn$ requires *M*, 427.0720); ν_{max}/cm^{-1} 3062, 1719, 1428, 1206, 1071, 1029, 728 and 699; δ_H 0.9 (2 H, m), 1.3 (2 H, m), 1.42–1.65 (2 H, m), 2.34 (1 H, d, *J* 11.5, $^2J_{HSn}$ 60, 3-H), 2.70 and 2.76 (each 1 H, m), 3.28 (1 H, ddd, *J* 11.5, 4.5, 1.5, 2-H), 3.62 (3 H, s, OCH_3), 7.37 (9 H, m, ArH) and 7.64 (6 H, m, ArH); δ_C 25.32, 29.73, 30.08, 36.11, 40.94, 42.67, 48.51, 52.22, 128.02 ($^3J_{CSn}$ 47.5), 128.06, 137.30 ($^2J_{CSn}$ 35.5), 142.76 and 177.81; *m*/*z* 427 ($M^+ - 77$, 100%).

(1*S*,2*R*,3*R*,4*R*)-3-Methoxycarbonyl-3-methylbicyclo[2.2.1]-heptan-2-yl(diphenyl)tin iodide 23

Iodine (27 mg, 0.105 mmol) was added to a solution of the triphenylstannane **13** (57 mg, 0.110 mmol) in dichloromethane (1 cm^3) and the mixture stirred for 30 min at ambient temperature. Concentration under reduced pressure then gave the *title compound* **23** (63 mg, 100%), as an oil, used without further purification (Found: $M^+ - C_6H_5$, 490.9528. $C_{16}H_{20}IO_2Sn$ requires *M*, 490.9530); ν_{max}/cm^{-1} 3065, 3047, 1664, 1430, 1311, 730 and 696; δ_H 1.10 (1 H, d, *J* 10.5, 7-H), 1.24 (1 H, dd, *J* 10, 1.5, 7-H′), 1.34 (3 H, s, CH_3), 1.38–1.85 (4 H, m, 5-H_2 and 6-H_2), 1.60 (1 H, d, *J* 2, 2-H), 2.67 (1 H, m, 4-H), 3.00 (1 H, m, 1-H), 3.84 (3 H, s, CH_3), 7.4 (6 H, m, ArH) and 7.8 and 7.9 (each 2 H, m, ArH); δ_C 22.59, 23.23, 33.18, 39.06, 41.60, 47.53, 52.91, 54.39, 55.37, 128.81, 129.62, 136.62, 137.51, 140.36, 142.37 and 187.38; *m*/*z* 491 ($M^+ - 77$, 70%) and 441 (100).

(1*S*,2*R*,3*R*,4*R*)-3-Methoxycarbonylbicyclo[2.2.1]heptan-2-yl(diphenyl)tin iodide 24

Iodine (31 mg, 0.12 mmol) was added to a solution of the triphenylstannane **20** (65 mg, 0.13 mmol) in dichloromethane (2 cm^3) and the mixture stirred for 5 min at ambient temperature. Concentration under reduced pressure gave the *title compound* **24** (72 mg, 100%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 476.9378. $C_{15}H_{18}IO_2Sn$ requires *M*, 476.9374); ν_{max}/cm^{-1} 3046, 1665, 1441, 1429, 1298, 1241, 1129, 730 and 696; δ_H 1.1, 1.46 and 1.7 (each 2 H, m), 2.09 (1 H, dd, *J* 9, 1.5, 2-H), 2.79 (2 H, m, 3-H and 4-H), 3.15 (1 H, m, $^3J_{HSn}$ 44, 1-H), 3.84 (3 H, s, OCH_3), 7.38 (6 H, m, ArH) and 7.8 and 7.9 (each 2 H, m, ArH); δ_C 29.85, 32.64 ($^3J_{CSn}$ 87.5), 36.96 (J_{CSn} 15.5), 40.62 (J_{CSn} 17.5), 43.49 ($^1J_{CSn}$ 520/498), 44.56 (J_{CSn} 7), 50.99 ($^2J_{CSn}$ 37.5), 55.05, 128.83 and 128.87 (each $^3J_{CSn}$ 61.0), 129.59, 129.67, 136.84 and 137.50 (each $^2J_{CSn}$ 45), 140.54, 142.42 and 183.95; *m*/*z* 477 ($M^+ - 77$, 90%) and 427 (100).

Methyl (1*R*,2*S*,3*S*,4*S*)-2-methyl-3-triphenylstannylbicyclo-[2.2.1]heptane-2-carboxylate 25

Palladium (10% on charcoal; 24 mg, 0.025 mmol Pd) was added to the unsaturated ester **17** (0.118 g, 0.23 mmol) in ethanol (5 cm^3). The resultant suspension was stirred vigorously under an atmosphere of hydrogen for 66 h then filtered through Celite, and the retained solids washed with ether (4 × 10 cm^3). The combined filtrates were concentrated under reduced pressure to give the *title compound* **25** (0.117 g, 99%) as an oil, used without further purification (Found: $M^+ - 77$, 441.0876. $C_{22}H_{25}O_2Sn$ requires *M*, 441.0877); ν_{max}/cm^{-1} 3062, 1712, 1428, 1118, 1072, 728 and 699; δ_H 1.35 (3 H, s, CH_3), 1.25–1.6 (5 H, m, 5-H_2, 6-H_2 and 7-H), 1.77 (1 H, d, *J* 8.5, 7-H′), 1.86 (1 H, m, 3-H), 2.38 and 2.68 (each 1 H, m), 3.69 (3 H, s, OCH_3), 7.37 (9 H, m, ArH) and 7.65 (6 H, m, ArH); δ_C 26.52, 27.54, 28.35, 39.42, 41.82, 45.69, 46.69, 52.43, 53.41, 127.86 ($^3J_{CSn}$ 48), 127.89, 137.31 ($^2J_{CSn}$ 35), 143.11 and 180.39; *m*/*z* 441 ($M^+ - 77$, 100%) and 351 (15).

(1*S*,2*S*,3*S*,4*R*)-3-Methoxycarbonyl-3-methylbicyclo[2.2.1]-heptan-2-yl(diphenyl)tin iodide 26

Iodine (36 mg, 0.14 mmol) was added to a solution of the triphenylstannane **25** (78 mg, 0.15 mmol) in dichloromethane (2 cm^3) and the mixture stirred for 1 h at ambient temperature. Concentration under reduced pressure gave the *title compound* **26** (86 mg, 100%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 490.9525. $C_{16}H_{20}IO_2Sn$ requires *M*, 490.9530); $[\alpha]_D$ +42.6 (*c* 6.2 in $CHCl_3$); ν_{max}/cm^{-1} 1661, 1429, 1323, 1306, 1126, 730 and 697; δ_H 0.95 (1 H, m, 5-H), 1.28–1.40 (4 H, m, 6-H and CH_3), 1.45–1.64 (3 H, m, 5-H′, 6-H′ and 7-H), 1.80 (1 H, d, *J* 10, 7-H′), 2.16 (1 H, m, $^2J_{HSn}$ 67, 2-H), 2.53 (1 H, m, 4-H), 3.03 (1 H, m, 1-H), 3.89 (3 H, s, OCH_3), 7.33–7.50 (6 H, m, ArH) and 7.65–7.78 and 7.94–8.19 (each 2 H, m, ArH); δ_C 26.22, 26.64 ($^3J_{CSn}$ 21.5), 28.62 ($^3J_{CSn}$ 49), 38.93 ($^3J_{CSn}$ 94), 41.14 ($^2J_{CSn}$ 20), 47.38 ($^3J_{CSn}$ 28.5), 54.35 ($^1J_{CSn}$ 562/538), 54.66, 128.35, 128.43, 129.02, 129.16, 135.96 ($^2J_{CSn}$ 44.5), 137.05 ($^2J_{CSn}$ 49), 141.03, 141.86 and 185.79 ($^3J_{CSn}$ 40.5); δ_{Sn} −113.98; *m*/*z* 586 (M^+, 2%), 491 (100) and 441 (80).

(1*S*,2*R*,3*R*,4*R*)-3-Methoxycarbonyl-3-methylbicyclo[2.2.1]-heptan-2-yl(diphenyl)tin hydride 27

Sodium borohydride (4.6 mg, 0.12 mmol) in ethanol (1 cm^3) was added to the tin iodide **23** (63 mg, 0.11 mmol) in dry ethanol (1 cm^3) at ambient temperature. After 30 min, the mixture was concentrated under reduced pressure and the residue partitioned between saturated aqueous ammonium chloride (5 cm^3) and ether (5 cm^3). The aqueous phase was extracted with ether (3 × 10 cm^3) and the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **27** (50 mg, 100%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 365.0569. $C_{16}H_{21}O_2Sn$ requires *M*, 365.0564); ν_{max}/cm^{-1} 3063, 1836, 1708, 1428, 1301, 1276, 1222, 1171, 1137, 1121, 1092, 1072, 728 and 699; $\delta_H(C_6D_6)$ 0.97 (1 H, d, *J* 8.5, 7-H), 1.12 (3 H, s, CH_3), 1.16–1.60 (6 H, overlapping m, 2-H, 5-H_2, 6-H_2 and 7-H′), 2.5 (2 H, m, 1-H and 4-H), 3.18 (3 H, s, OCH_3), 6.98 (1 H, d, *J* 1.5, $^1J_{HSn}$ 1906/1820, SnH), 7.10–7.38 (6 H, m, ArH) and 7.70–8.05 (4 H, m, ArH); $\delta_C(C_6D_6)$ 23.08 (J_{CSn} 15), 23.36, 33.82 (J_{CSn} 64.5), 39.19, 42.75 (J_{CSn} 9.5), 43.51 ($^1J_{CSn}$ 452/433), 46.76 (J_{CSn} 12.5), 52.86, 53.78, 128.50, 128.92, 138.31, 142.92, 143.13 and 182.36; *m*/*z* 441 ($M^+ - 1$, 100%) and 365 (30).

(1*S*,2*R*,3*R*,4*R*)-3-Methoxycarbonylbicyclo[2.2.1]heptan-2-yl-(diphenyl)tin hydride 28

Sodium borohydride (5.5 mg, 0.145 mmol) in ethanol (1 cm^3) was added to a solution of the tin iodide **24** (71 mg, 0.13 mmol) in ethanol (1 cm^3) at ambient temperature. After 15 min the mixture was concentrated under reduced pressure and the residue partitioned between saturated aqueous ammonium chloride (10 cm^3) and ether (10 cm^3). The aqueous phase was extracted with ether (3 × 10 cm^3) and the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **28** (54 mg, 98%) as an oil, used without further purification; ν_{max}/cm^{-1} 3061, 3045, 1837, 1713, 1428, 1217, 1202, 1176, 1033, 729 and 699; $\delta_H(C_6D_6)$ 0.83

(1 H, m), 1.1 (2 H, m), 1.25–1.6 (4 H, m), 2.4 (2 H, m, 3-H and 4-H), 2.51 (1 H, m, 1-H), 3.20 (3 H, s, OCH_3), 6.89 (1 H, d, *J* 1.5, $^1J_{HSn}$ 1906/1821, SnH), 7.10–7.35 (6 H, m, ArH) and 7.70–7.95 (4 H, m, ArH); $\delta_C(C_6D_6)$ 30.13, 33.22, 34.13, 36.80, 41.44, 43.61, 50.58, 52.34, 128.64, 128.94, 138.31 ($^2J_{CSn}$ 36), 142.34 and 179.24; *m*/*z* 427 ($M^+ - 1$, 100%) and 351 (90).

(1*S*,2*S*,3*S*,4*R*)-3-Methoxycarbonyl-3-methylbicyclo[2.2.1]-heptan-2-yl(diphenyl)tin hydride 29

Sodium borohydride (6.3 mg, 0.165 mmol) in ethanol (1 cm^3) was added to the tin iodide **26** (86 mg, 0.15 mmol) in ethanol (1 cm^3) at ambient temperature. After 15 min, the mixture was concentrated under reduced pressure and the residue partitioned between saturated aqueous ammonium chloride (10 cm^3) and ether (10 cm^3). The aqueous phase was extracted with ether (3 × 10 cm^3) and the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **29** (62 mg, 93%), as an oil, used without further purification (Found: $M^+ - C_6H_5$, 365.0564. $C_{16}H_{21}O_2Sn$ requires *M*, 365.0564); $[\alpha]_D$ +6.4 (*c* 4.9 in C_6H_6); ν_{max}/cm^{-1} 3061, 1839, 1711, 1428, 1287, 1249, 1118, 729 and 699; $\delta_H(C_6D_6)$ 1.22 (3 H, s, CH_3), 1.30–1.55 (4 H, m), 1.60–1.74 (3 H, m), 2.28 and 2.50 (each 1 H, m), 3.29 (3 H, s, OCH_3), 7.09 (1 H, d, *J* 2.5, $^1J_{HSn}$ 1966/1879, SnH), 7.27–7.39 (6 H, m, ArH) and 7.80–7.92 and 7.92–8.50 (each 2 H, m, ArH); $\delta_C(C_6D_6)$ 26.53, 27.22 ($^3J_{CSn}$ 14.5), 28.10 ($^3J_{CSn}$ 41), 39.10 ($^3J_{CSn}$ 70.5), 41.85 ($^2J_{CSn}$ 12.5), 44.21 ($^1J_{CSn}$ 478/462), 46.79 ($^3J_{CSn}$ 28.5), 51.71, 53.48 ($^2J_{CSn}$ 11), 127.46–128.27 (overlapping peaks, not resolved), 137.44 ($^2J_{CSn}$ 36), 137.62 ($^2J_{CSn}$ 38.5), 141.57, 143.26 ($^1J_{CSn}$ 430/408) and 180.54 ($^3J_{CSn}$ 28.5); *m*/*z* 441 ($M^+ - 1$, 100%) and 365 (20).

(1*S*,2*R*,3*R*,4*R*)-3-Hydroxymethyl-3-methyl-2-triphenylstannylbicyclo[2.2.1]heptane 30

Diisobutylaluminium hydride (1 mol dm^{-3} in dichloromethane; 1.17 cm^3) was added dropwise to a solution of the ester **13** (0.24 g, 0.47 mmol) in dichloromethane (5 cm^3) at 0 °C. The solution was warmed to ambient temperature over 19 h before quenching with methanol (1 cm^3) at 0 °C. Saturated aqueous Rochelle's salt (10 cm^3) was added followed by extraction with dichloromethane (4 × 15 cm^3). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **30** (0.23 g, 100%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 413.0933. $C_{21}H_{25}OSn$ requires *M*, 413.0927); ν_{max}/cm^{-1} 3569, 3411, 3062, 3046, 1427, 1073, 1018, 728 and 699; δ_H 1.25 (3 H, s, CH_3), 1.38 (1 H, m, OH), 1.46 (1 H, d, *J* 2.5, 2-H), 1.3–1.9 (6 H, overlapping m, 5-H_2, 6-H_2 and 7-H_2), 1.96 (1 H, d, *J* 2.5, 4-H), 2.62 (1 H, d, *J* 3, $^3J_{HSn}$ 37.0, 1-H), 3.27 (1 H, dd, *J* 10.5, 5, C*H*HOH), 3.36 (1 H, dd, *J* 10, 2, C*H*HOH), 7.33–7.43 (9 H, m, ArH) and 7.54–7.72 (6 H, m, ArH); δ_C 23.27, 24.19, 33.61, ($^3J_{CSn}$ 69), 38.64, 42.48, 43.16 ($^1J_{CSn}$ 425/406), 45.00 (J_{CSn} 12.5), 46.74 (J_{CSn} 27), 70.67 ($^3J_{CSn}$ 65), 128.14 ($^3J_{CSn}$ 46), 136.98 ($^2J_{CSn}$ 34) and 141.91 ($^1J_{CSn}$ 462/444); δ_{Sn} −109.1; *m*/*z* 413 ($M^+ - 77$, 100%).

{(1*S*,2*R*,3*R*,4*R*)-3-Hydroxymethyl-3-methylbicyclo[2.2.1]-heptan-2-yl}(diphenyl)tin iodide 31

Iodine (50 mg, 0.2 mmol) was added to a solution of the diphenylstannane **30** (0.1 g, 0.2 mmol) in dichloromethane (2 cm^3) and the mixture stirred for 5 min at ambient temperature. Concentration under reduced pressure gave the *title compound* **31** (0.11 g, 100%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 463.9658. $C_{15}H_{21}IOSn$ requires *M*, 463.9659); ν_{max}/cm^{-1} 3404, 1428, 998 , 729 and 696; δ_H 1.20 (3 H, s, CH_3), 1.25–1.90 (6 H, overlapping m, 5-H_2, 6-H_2 and 7-H_2), 1.50 (1 H, d, *J* 2.5, 2-H), 1.95 (1 H, d, *J* 2.5, 4-H), 2.72 (1 H, br s, OH), 3.19 (1 H, d, *J* 3.5, 1-H), 3.24 (1 H, dd, *J* 10, 3.5, C*H*HOH), 3.50 (1 H, d, *J* 10, CH*H*OH), 7.35–7.50 (6 H, m, ArH) and 7.70–7.95 (4 H, m, ArH); δ_C 23.68, 23.87 ($^3J_{CSn}$ 26), 33.24 ($^3J_{CSn}$ 92.5), 38.83, 42.30 (J_{CSn} 14), 46.56 (J_{CSn} 17.5), 47.04 (J_{CSn} 31), 48.43 ($^1J_{CSn}$ 490/467), 70.40 ($^3J_{CSn}$ 68), 128.41, 128.49, 129.00, 129.10, 135.73, 136.16, 141.22 and 142.62; δ_{Sn} −102; *m*/*z* 463 ($M^+ - 77$, 65%) and 413 (80).

(1*R*,2*R*,3*R*,4*S*)-3-Hydroxymethyl-3-methyl-2-triphenylstannylbicyclo[2.2.1]hept-5-ene 32

Diisobutylaluminium hydride (1 mol dm^{-3} in dichloromethane; 4.70 cm^3) was added dropwise to a solution of the unsaturated ester **3** (0.97 g, 1.88 mmol) in dichloromethane (20 cm^3) at 0 °C. The solution was warmed to ambient temperature over 19 h before quenching with methanol (6 cm^3) at 0 °C. Saturated aqueous Rochelle's salt (30 cm^3) was added followed by extraction with dichloromethane (4 × 30 cm^3). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **32** (0.915 g, 99%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 411.0766. $C_{21}H_{23}OSn$ requires *M*, 411.0771); $[\alpha]_D$ −19.2 (*c* 1.9 in $CHCl_3$); ν_{max}/cm^{-1} 3571, 3425, 3061, 1427, 1073, 1022, 1008, 717 and 699; δ_H 1.10 (3 H, s, CH_3), 1.32 (1 H, d, *J* 2.5, $^2J_{HSn}$ 51, 2-H), 1.41 (1 H, d, *J* 9, 7-H), 1.50 (1 H, br t, *J* 5, OH), 1.72 (1 H, d, *J* 9, 7-H′), 2.58 (1 H, m, 4-H), 3.18 (1 H, m, 1-H), 3.55 (2 H, m, CH_2OH), 6.15 (1 H, dd, *J* 5.5, 3, vinylic-H), 6.33 (1 H, dd, *J* 5.5, 2.5, vinylic-H), 7.4 (9 H, m, ArH) and 7.65 (6 H, m, ArH); δ_C 24.56 ($^3J_{CSn}$ 13.5), 36.94 ($^1J_{CSn}$ 413/394), 46.76, 47.36, 47.91, 50.10 (J_{CSn} 12), 72.06 ($^3J_{CSn}$ 50.5), 128.39 ($^3J_{CSn}$ 47), 128.48, 133.14, 137.18 ($^2J_{CSn}$ 34.5), 138.48 ($^3J_{CSn}$ 59) and 141.63 ($^1J_{CSn}$ 476/455); *m*/*z* 411 ($M^+ - 77$, 50%).

(1*R*,2*R*,3*R*,4*S*)-3-Methoxymethyl-3-methyl-2-triphenylstannylbicyclo[2.2.1]hept-5-ene 33

The alcohol **32** (0.215 g, 0.44 mmol) in tetrahydrofuran (2 cm^3) was added dropwise to a suspension of sodium hydride (60% in mineral oil; 26 mg, 0.66 mmol) in tetrahydrofuran (3 cm^3) at ambient temperature. The solution was stirred for 1.5 h before the addition of methyl iodide (0.22 cm^3, 3.53 mmol) and further stirring at ambient temperature for 15 h. After concentration under reduced pressure, the residue was partitioned between dichloromethane (10 cm^3) and brine (10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **33** (0.207 g, 94%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 425.0936. $C_{22}H_{25}OSn$ requires *M*, 425.0927); ν_{max}/cm^{-1} 3062, 1480, 1428, 1098, 1073, 717 and 699; δ_H 1.10 (3 H, s, CH_3), 1.15–1.45 (2 H, m, 2-H and 7-H), 1.86 (1 H, d, *J* 7-H′), 2.50 (1 H, m, 4-H), 2.85 (4 H, m, 1-H and OCH_3), 3.13 and 3.29 (each 1 H, d, *J* 9, C*H*HOCH$_3$), 6.10 (1 H, dd, *J* 5.5, 3, vinylic-H), 6.25 (1 H, dd, *J* 5.5, 2.5, vinylic-H), 7.28–7.50 (9 H, m, ArH) and 7.6 (6 H, m, ArH); *m*/*z* 425 ($M^+ - 77$, 100%).

(1*S*,2*R*,3*R*,4*R*)-3-Methoxymethyl-3-methyl-2-triphenylstannylbicyclo[2.2.1]heptane 34

Palladium (10% on charcoal; 44 mg, 0.04 mmol Pd) was added to a solution of the alkene **33** (0.207 g, 0.41 mmol) in ethanol (8 cm^3). The resultant suspension was stirred vigorously under an atmosphere of hydrogen for 66 h then filtered through Celite and the retained solids washed with ether (4 × 10 cm^3). The combined filtrates were concentrated under reduced pressure to give the *title compound* **34** (0.193 g, 93%) as an oil, used without further purification (Found: $M^+ - 77$, 427.1079. $C_{22}H_{27}OSn$ requires *M*, 427.1084); ν_{max}/cm^{-1} 1427, 1104, 1073, 727 and 699; δ_H 1.25 (3 H, s, CH_3), 1.42 (1 H, d, *J* 2.5, 2-H), 1.38–1.95 (7 H, overlapping m, 4-H, 5-H_2, 6-H_2 and 7-H_2), 2.55 (1 H, m, 1-H), 2.80 (3 H, s, OCH_3), 2.91 and 3.36 (each 1 H, d, *J* 9, C*H*HOCH$_3$), 7.29–7.50 (9 H, m, ArH) and 7.6 (6 H, m, ArH); *m*/*z* 444 (15%), 427 (100) and 306 (30).

(1*S*,2*R*,3*R*,4*R*)-3-Methoxymethyl-3-methylbicyclo[2.2.1]heptan-2-yl(diphenyl)tin iodide 35

Iodine (91 mg, 0.36 mmol) was added to a solution of the triphenylstannane **34** (0.19 g, 0.38 mmol) in dichloromethane

(5 cm^3) and the mixture stirred for 1 h at ambient temperature. Concentration under reduced pressure gave the *title compound* **35** (0.203 g, 97%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 477.9821. $C_{16}H_{23}IOSn$ requires *M*, 477.9816); $[\alpha]_D$ +14.5 (*c* 4.0 in $CHCl_3$); ν_{max}/cm^{-1} 3064, 3047, 1429, 1075, 729 and 697; δ_H 1.31 (3 H, s, CH_3), 1.37–1.95 (7 H, m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.03 (1 H, m, 4-H), 2.99 (3 H, s, OCH_3), 3.09 (1 H, d, *J* 8, C*H*HOCH$_3$), 3.23–3.31 (2 H, m, CH*H*OCH$_3$ and 1-H), 7.35–7.51 (6 H, m, ArH) and 7.66 and 7.86 (each 2 H, m, ArH); δ_C 23.64, 24.57 ($^3J_{CSn}$ 27), 33.40 ($^3J_{CSn}$ 93), 39.16, 42.56 (J_{CSn} 14), 46.41 ($^2J_{CSn}$ 17.5), 47.06 J_{CSn} 18.5), 49.40 ($^1J_{CSn}$ 500/478), 58.88, 80.74 ($^3J_{CSn}$ 64.5), 128.54 ($^3J_{CSn}$ 58), 129.19, 129.24, 136.05 ($^2J_{CSn}$ 39.5), 136.47 ($^2J_{CSn}$ 46.5), 141.11 and 141.73; δ_{Sn} −114.7; *m*/*z* 477 ($M^+ - 77$, 100%) and 427 (20).

(1*S*,2*R*,3*R*,4*R*)-3-Methoxymethyl-3-methylbicyclo[2.2.1]heptan-2-yl(diphenyl)tin hydride 36

Sodium borohydride (12 mg, 0.32 mmol) in ethanol (2 cm^3) was added to the tin iodide **35** (0.16 g, 0.29 mmol) in ethanol (2 cm^3) at ambient temperature. After 15 min, the mixture was concentrated under reduced pressure and the residue partitioned between saturated aqueous ammonium chloride (10 cm^3) and ether (10 cm^3). The aqueous phase was extracted with ether (3 × 15 cm^3) and the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **36** (0.118 g, 95%) as an oil, used without further purification (Found: $M^+ - H$, 427.1083. $C_{22}H_{27}OSn$ requires *M*, 427.1084); ν_{max}/cm^{-1} 3062, 1818, 1428, 1104, 728 and 699; $\delta_H(C_6D_6)$ 1.22 (3 H, s, CH_3), 0.95–1.90 (8 H, m, 2-H, 4-H, 5-H_2, 6-H_2 and 7-H_2), 2.48 (1 H, d, *J* 4, $^3J_{HSn}$ 38, 1-H), 2.86 (1 H, d, *J* 8.5, C*H*HOCH$_3$), 2.93 (3 H, s, OCH_3), 3.10 (1 H, d, *J* 8.5, CH*H*OCH$_3$), 6.49 (1 H, d, *J* 4, $^1J_{HSn}$ 1850/1769, SnH), 7.22–7.36 (6 H, m, ArH) and 7.7 and 7.86 (each 2 H, m, ArH); $\delta_C(C_6D_6)$ 24.06 ($^3J_{CSn}$ 20.5), 24.33, 32.92 ($^3J_{CSn}$ 71.5), 39.24, 42.83 (J_{CSn} 7), 42.99 ($^1J_{CSn}$ 449/429), 45.43 ($^2J_{CSn}$ 28), 46.08 (J_{CSn} 12), 57.24, 81.26 ($^3J_{CSn}$ 62.5), 128.01–128.33 (overlapping peaks, not resolved), 128.48, 128.59, 137.63 ($^2J_{CSn}$ 34.5), 137.99 ($^2J_{CSn}$ 37.5), 141.29 and 142.79; $\delta_{Sn}(C_6D_6)$ −139.0 (d, $^1J_{SnH}$ 1860); *m*/*z* 427 ($M^+ - 1$, 100%) and 368 (30).

Reduction of 2-hydroxyacetophenone

The tin hydride **27** (31 mg, 0.075 mmol) in methanol (0.5 cm^3) was added to a solution of 2-hydroxyacetophenone (0.10 g, 0.725 mmol) in methanol (1.5 cm^3) followed by phenylsilane (0.27 cm^3, 2.18 mmol). The reaction mixture was stirred at ambient temperature until all of the ketone had disappeared (4 d, TLC). After concentration of the mixture under reduced pressure, chromatography of the residue using light petroleum–ether (1:1) as eluent gave 1-(2-hydroxyphenyl)ethanol (95 mg, 95%) as an oil. In a control experiment, 2-hydroxyacetophenone (71 mg, 0.52 mmol), on being mixed with phenylsilane (0.195 cm^3, 1.56 mmol) in methanol (2 cm^3) in the absence of tin hydride gave only a trace of 1-(2-hydroxyphenyl)ethanol after 7 d.

***N*,*N*-Dimethyl (1*S*,2*S*,3*R*,4*R*)-3-triphenylstannylbicyclo[2.2.1]-hept-5-ene-2-carboxamide 38**

Dimethylamine (2 mol dm^{-3} in tetrahydrofuran; 2.45 cm^3) was added to a solution of trimethylaluminium (2 mol dm^{-3} in hexanes; 2.39 cm^3) in benzene (4 cm^3) and the mixture heated at 80 °C for 20 min. The ester **3** (0.3 g, 0.6 mmol) in benzene (1 cm^3) was added and the mixture heated for 15 h. After cooling to ambient temperature, the reaction mixture was quenched by the slow addition of aqueous hydrogen chloride (0.5 mol dm^{-3}; 5 cm^3) and extracted with ether (4 × 10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **38** (0.312 g, 100%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 438.0882. $C_{22}H_{24}NOSn$ requires *M*, 438.0880); ν_{max}/cm^{-1} 3062, 1642, 1428, 1395, 1143, 1073, 997, 729 and 699; δ_H 1.29 (2 H, m, 7-H_2), 2.21 (1 H, dd, *J* 5.5, 2.0, $^2J_{HSn}$ 34, 3-H), 2.85 and 2.90 (each 3 H, s, NCH_3), 3.13 (1 H, m, 1-H), 3.17 (1 H, m, 4-H), 3.36 (1 H, dd, *J* 5.5, 3.5, $^3J_{HSn}$ 75, 2-H), 5.71 (1 H, dd, *J* 5.5, 3, vinylic-H), 6.36 (1 H, dd, *J* 5.5, 2.5, vinylic-H), 7.35 (9 H, m, ArH) and 7.45–7.62 (6 H, m, ArH); δ_C 27.36, 36.09, 36.92, 43.86, 46.32, 46.96, 50.28, 128.40, 128.75, 137.12 ($^2J_{CSn}$ 34.5), 138.54 and 172.85; *m*/*z* 438 ($M^+ - 77$, 12%) and 166 (100).

1-{(1*S*,2*S*,3*R*,4*R*)-3-Triphenylstannylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl}pyrrolidine 39

Sodium diethyldihydroaluminate (2 mol dm^{-3} in toluene; 0.15 cm^3) and pyrrolidine (99.5%; 0.055 cm^3, 0.66 mmol) were heated in toluene (4 cm^3) at 110 °C for 1 h. A solution of the ester **3** (0.15 g, 0.3 mmol) in toluene (1 cm^3) was then added and the mixture heated for a further 24 h. After cooling to ambient temperature, the reaction mixture was quenched by the slow addition of saturated aqueous ammonium chloride (2 cm^3) and extracted with ether (4 × 10 cm^3). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using dichloromethane as eluent gave the *title compound* **39** (96 mg, 60%) as an oil (Found: $M^+ - C_6H_5$, 464.1028. $C_{24}H_{26}NOSn$ requires *M*, 464.1036); ν_{max}/cm^{-1} 3062, 1638, 1428, 1333, 1321, 1073, 728 and 699; δ_H 1.26 (1 H, d, *J* 8, 7-H), 1.31 (1 H, dd, *J* 8, 1.5, 7-H′), 1.66–1.90 (4 H, m, 2 × CH_2), 2.17 (1 H, dd, *J* 6, 2, $^2J_{HSn}$ 34, 3-H), 3.0 (1 H, m, C*H*HN), 3.14 and 3.17 (each 1 H, m), 3.21 (1 H, dd, *J* 6, 3.5, 2-H), 3.4 (3 H, m, CH_2N and C*H*HN), 5.77 (1 H, dd, *J* 5.5, 3, vinylic-H), 6.38 (1 H, dd, *J* 5.5, 2.5, vinylic-H), 7.36 (9 H, m, ArH) and 7.55 (6 H, m, ArH); δ_C 24.25, 26.28, 27.47, 38.17, 45.68, 46.12, 46.32, 46.64, 50.31, 128.41, 128.69, 128.77, 137.13 ($^2J_{CSn}$ 34.5), 138.38, 138.60 ($^1J_{CSn}$ 471) and 171.66; *m*/*z* 542 ($M^+ + 1$, 2%), 464 (10) and 192 (100).

1-{(1*S*,2*S*,3*R*,4*R*)-3-Triphenylstannylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl}piperidine 40

Sodium diethyldihydroaluminate (2 mol dm^{-3} in toluene; 0.15 cm^3) and piperidine (99.5%; 0.66 mmol) in toluene (4 cm^3) were heated at 110 °C for 1.5 h. A solution of the ester **3** (0.15 g, 0.30 mmol) in toluene (1 cm^3) was then added and the mixture heated for a further 24 h. After cooling to ambient temperature, the reaction mixture was quenched by the slow addition of saturated aqueous ammonium chloride (2 cm^3) and extracted with ether (4 × 10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using dichloromethane as the eluent gave the *title compound* **40** (0.11 g, 66%) as an oil (Found: $M^+ - C_6H_5$, 478.1191. $C_{25}H_{28}NOSn$ requires *M*, 478.1193); ν_{max}/cm^{-1} 3062, 1636, 1428, 1254, 1222, 1073, 1020, 728 and 699; δ_H 1.27 (2 H, m), 1.46 (4 H, m), 1.57 (2 H, m), 2.31 (1 H, d, *J* 5, $^2J_{HSn}$ 35, 3-H), 3.07 (1 H, m, 1-H), 3.16 (1 H, m, $^3J_{HSn}$ 35, 4-H), 3.30–3.45 (4 H, m, 2-H, CH_2N and C*H*HN), 3.65 (1 H, m, C*H*HN), 5.71 (1 H, dd, *J* 5.5, 3, vinylic-H), 6.35 (1 H, dd, *J* 5.5, 2.5, vinylic-H), 7.35 (9 H, m, ArH) and 7.55 (6 H, m, ArH), δ_C 24.78, 25.84, 26.70, 26.91, 43.47, 43.82, 46.28, 46.43, 47.43, 50.12, 128.31, 128.40, 128.72, 137.16 ($^2J_{CSn}$ 34.3), 138.59 ($^1J_{CSn}$ 480) and 170.82; *m*/*z* 556 ($M^+ + 1$, 10%), 478 (50), 206 (100) and 204 (40).

***N*-Benzyl (1*R*,2*S*,3*R*,4*S*)-3-triphenylstannylbicyclo[2.2.1]-heptane-2-carboxamide 41**

Sodium diethyldihydroaluminate (2 mol dm^{-3} in toluene; 0.15 cm^3) and benzylamine (99.5%; 0.065 cm^3, 0.595 mmol) were heated in toluene (3 cm^3) at 110 °C for 75 min. The ester **12** (0.15 g, 0.30 mmol) in toluene (1 cm^3) was then added and the mixture heated for a further 2 h. After cooling to ambient temperature, the reaction mixture was quenched by the slow addition of saturated aqueous ammonium chloride (2 cm^3) and extracted with ether (4 × 10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chroma-

tography of the residue using dichloromethane–light petroleum (9:1) as eluent gave the *title compound* **41** (0.15 g, 87%) as an oil (Found: $M^+ - C_6H_6$, 502.1194. $C_{27}H_{28}NOSn$ requires *M*, 502.1193); ν_{max}/cm^{-1} 3299, 3062, 1644, 1545, 1428, 1238, 1073, 728 and 698; δ_H 1.32 (1 H, d, *J* 10, 7-H), 1.39 (1 H, m), 1.45 (1 H, d, *J* 10, 7-H′), 1.6 (3 H, m), 2.39 (1 H, m, 1-H), 2.42 (1 H, dd, *J* 6.5, 2, $^2J_{HSn}$ 42, 3-H), 2.55 (1 H, m, $^3J_{HSn}$ 37, 4-H), 2.97 (1 H, ddd, *J* 6, 4, 1.5, $^3J_{HSn}$ 103, 2-H), 4.33 and 4.47 (each 1 H, dd, *J* 15, 5.5, C*H*HN), 5.51 (1 H, br t, *J* 5.5, NH), 7.22 (5 H, m, ArH), 7.35 (9 H, m, ArH) and 7.42–7.65 (6 H, m, ArH); δ_C 24.24, 30.68, 33.25, 41.14, 41.17, 42.51, 43.66, 52.54, 127.22, 127.61, 128.12, 128.43, 128.52, 128.74, 137.23 ($^2J_{CSn}$ 33.5), 138.42 and 173.07; *m*/*z* 590 (M^+ + 18, 10%) and 502 (100).

1-{(1*R*,2*S*,3*R*,4*S*)-3-Triphenylstannylbicyclo[2.2.1]heptan-2-ylcarbonyl}piperidine 42

Sodium diethyldihydroaluminate (2 mol dm^{-3} in toluene; 0.15 cm^3) and piperidine (99.5%; 0.065 cm^3, 0.66 mmol) in toluene (4 cm^3) were heated at 110 °C for 1 h. A solution of the ester **12** (0.15 g, 0.30 mmol) in toluene (1 cm^3) was then added and the mixture heated for a further 2 h. After cooling to ambient temperature, the reaction mixture was quenched by the slow addition of saturated aqueous ammonium chloride (2 cm^3) and extracted with ether (4 × 10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using dichloromethane–light petroleum (20:1) as eluent gave the *title compound* **42** (69 mg, 45%) as an oil (Found: $M^+ - C_6H_5$, 480.1343. $C_{25}H_{30}NOSn$ requires *M*, 480.1349); ν_{max}/cm^{-1} 3062, 1633, 1428, 1223, 1073, 728 and 699; δ_H 1.10–1.65 (12 H, m), 2.38 (1 H, m, 1-H), 2.56 (1 H, m, $^3J_{HSn}$ 35.5, 4-H), 2.75 (1 H, dd, *J* 6, 2, $^2J_{HSn}$ 30, 3-H), 3.20–3.74 (3 H, m, 2 × C*H*HN and 2-H), 3.47 (1 H, m, C*H*HN), 3.68 (1 H, m, C*H*HN), 7.4 (9 H, m, ArH) and 7.65 (6 H, m, ArH); *m*/*z* 557 (M^+, 1%), 480 (100) and 208 (100).

1-{(1*S*,2*R*,3*R*,4*R*)-2-Methyl-3-triphenylstannylbicyclo[2.2.1]-hept-5-en-2-ylcarbonyl}piperidine 43

Butyllithium (1.5 mol dm^{-3} in hexanes; 0.58 cm^3) was added dropwise to a solution of diethylamine (0.10 cm^3, 0.92 mmol) in tetrahydrofuran (4.5 cm^3) at 0 °C. The solution was stirred for 15 min then cooled to −78 °C before the addition of the amide **40** (0.10 g, 0.185 mmol) in tetrahydrofuran (2 cm^3). The mixture was stirred at −78 °C for 2.5 h and then methyl iodide (0.115 cm^3, 1.84 mmol) was added dropwise. After stirring for a further 2 h, the reaction mixture was warmed to ambient temperature, concentrated under reduced pressure and the residue diluted with ether (10 cm^3). The solution was washed with water (10 cm^3) then brine (10 cm^3), and the organic phase dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using light petroleum–ether (1:1) as eluent gave methyl(triphenyl)tin (14 mg, 21%). Further elution gave the *title compound* **43** (17 mg, 16%) as an oil (Found: $M^+ - C_6H_5$, 492.1345. $C_{20}H_{30}NOSn$ requires *M*, 492.1349); ν_{max}/cm^{-1} 3059, 1588, 1428, 1280, 1249, 1069, 1012, 728 and 699; δ_H 1.19 (3 H, s, CH_3), 1.30 (3 H, m, 3-H and CH_2), 1.50–1.80 (6 H, overlapping m, 3 × CH_2), 3.12 (2 H, m, 1-H and 4-H), 3.50–3.80 (4 H, overlapping m, 2 × CH_2N), 6.08 (1 H, dd, *J* 5.5, 3, vinylic-H), 6.42 (1 H, dd, *J* 5.5, 2.5, vinylic-H), 7.20–7.45 (9 H, m, ArH) and 7.5–7.80 (6 H, m, ArH); *m*/*z* 570 (M^+ + 1, 1%) and 492 (5). Further elution gave starting material **40** (37 mg, 36%).

(1*R*,2*R*,3*S*,4*S*)-3-(Pyrrolidin-1-ylmethyl)-2-triphenylstannylbicyclo[2.2.1]hept-5-ene 44

Lithium aluminium hydride (1 mol dm^{-3} in ether; 1.02 cm^3) was added to a solution of the amide **39** (55 mg, 0.10 mmol) in ether (2 cm^3) at ambient temperature. The solution was stirred for 18 h, then quenched with saturated aqueous ammonium chloride (10 cm^3) and partitioned between ether (10 cm^3) and saturated aqueous Rochelle's salt (10 cm^3). The two-phase mixture was filtered through Celite and the filter washed with ether (4 × 10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **44** (46 mg, 85%) as an oil (Found: $M^+ - C_6H_5$, 450.1249. $C_{24}H_{28}NSn$ requires *M*, 450.1244); ν_{max}/cm^{-1} 3061, 1428, 1073, 727 and 699; δ_H 1.03 (1 H, dd, 2-H), 1.20–1.45 (2 H, m, 7-H_2), 1.65–1.90 (4 H, m), 2.15 (1 H, dd, *J* 11.5, 8, 3-CH), 2.25–2.50 (5 H, overlapping m, 3-CH′ and 2 × CH_2N), 2.65 (1 H, m), 3.08 (1 H, m, 1-H and 4-H), 5.95 and 6.24 (each 1 H, m, vinylic-H), 7.4 (9 H, m, ArH) and 7.54–7.72 (6 H, m, ArH); δ_C 24.33, 29.09, 29.75, 30.35, 42.16, 45.73, 45.83, 49.45, 54.79, 61.21, 128.48, 128.84, 130.83, 137.42, 137.68 and 139.13; *m*/*z* 528 (M^+ + 1, 10%), 450 (15), 178 (100) and 176 (80).

(1*S*,2*R*,3*S*,4*R*)-3-(Piperidin-1-ylmethyl)-2-triphenylstannylbicyclo[2.2.1]heptane 45

Lithium aluminium hydride (12 mg, 0.315 mmol) was added to a solution of the amide **42** (44 mg, 0.08 mmol) in ether (2 cm^3) at ambient temperature. The solution was stirred for 18 h then quenched with saturated aqueous ammonium chloride (10 cm^3) and partitioned between ether (10 cm^3) and saturated aqueous Rochelle's salt (10 cm^3). The two-phase mixture was filtered through Celite and the filter washed with ether (4 × 10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using dichloromethane–methanol (20:1) as eluent gave the *title compound* **45** (31 mg, 72%) as an oil (Found: $M^+ - C_6H_5$, 466.1553. $C_{25}H_{32}NSn$ requires *M*, 466.1557); ν_{max}/cm^{-1} 3062, 1428, 1073, 727 and 699; δ_H 1.2–1.8 (12 H, overlapping m, 5-H_2, 6-H_2, 7-H_2 and 3 × CH_2), 2.05–2.55 (10 H, overlapping m, 1-H, 2-H, 3-H, 4-H and 3 × CH_2N), 7.35 (9 H, m, ArH) and 7.55 (6 H, m, ArH); δ_C 22.71, 24.53, 25.85, 33.73, 36.78, 40.59, 40.65, 41.02, 42.40, 55.23, 62.64, 128.20, 128.50, 137.32 ($^2J_{CSn}$ 33) and 139.14; *m*/*z* 544 (M^+ + 1, 25%), 466 (25), 194 (70) and 192 (65).

(1*R*,2*R*,3*R*,4*S*)-2-Methyl-3-triphenylstannylbicyclo[2.2.1]-heptane-2-carbaldehyde 46

N-Methylmorpholine *N*-oxide (0.11 g, 0.94 mmol) and tetrapropylammonium perruthenate (8.5 mg, 0.025 mmol) were added to a solution of the alcohol **30** (0.24 g, 0.48 mmol) and 4 Å molecular sieves (0.5 g) in dichloromethane (3 cm^3) at ambient temperature. The mixture was stirred for 2 h, then filtered through Celite and the filtrate concentrated under reduced pressure. Chromatography of the residue using dichloromethane as eluent gave the *title compound* **46** (0.17 g, 73%) as an oil (Found: $M^+ - C_6H_5$, 411.0770. $C_{21}H_{23}OSn$ requires *M*, 411.0771); ν_{max}/cm^{-1} 3061, 1715, 1427, 1072, 727 and 699; δ_H 1.14 (2 H, m, 7-H_2), 1.24 (3 H, s, CH_3), 1.29 (1 H, s, 3-H), 1.40–1.90 (4 H, overlapping m, 5-H_2 and 6-H_2), 2.28 (1 H, d, *J* 3.5, 1-H), 2.60 (1 H, m, $^3J_{HSn}$ 37.5, 4-H), 7.4 (9 H, m, ArH), 7.50–7.80 (6 H, m, ArH) and 9.43 (1 H, s, CHO); *m*/*z* 488 (M^+, 2%) and 411 (100).

(1*S*,2*R*,3*R*,4*R*)-3-Aminomethyl-3-methyl-2-triphenylstannylbicyclo[2.2.1]heptane 48

Sodium acetate (22 mg, 0.27 mmol) was added to a solution of hydroxylamine hydrochloride (10 mg, 0.15 mmol) in ethanol (4 cm^3) and the mixture stirred for 30 min. The aldehyde **46** (60 mg, 0.125 mmol) in a mixture of ethanol (1.5 cm^3) and ether (1.5 cm^3) was added. The reaction mixture was stirred at ambient temperature for 4 d and then extracted with ether (4 × 15 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using dichloromethane as eluent gave the oxime **47** (7 mg, 11%) as an oil; δ_H 1.28 (3 H, s, CH_3), 1.36 (1 H, *J* 2, 2-H), 1.45–1.90 (7 H, overlapping m, OH, 5-H_2, 6-H_2 and 7-H_2), 2.09 (1 H, m, 4-H), 2.55 (1 H, m, $^3J_{HSn}$ 40, 1-H), 6.20 (1 H, s, CH=N), 7.35 (9 H, m, ArH) and 7.5 (6 H, m, ArH).

Lithium aluminium hydride (1 mol dm^{-3} in ether; 0.08 cm^3) was added to a solution of the oxime **47** (7 mg, 0.014 mmol) in

ether (1 cm^3). The solution was stirred for 1.5 h, then saturated aqueous ammonium chloride (2 cm^3) was added and the mixture extracted with ether (3 × 10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **48** (4 mg, 59%) as an oil (Found: $M^+ - C_6H_5$, 412.1094. $C_{21}H_{26}NSn$ requires *M*, 412.1087); ν_{max}/cm^{-1} 3634, 3384, 3315, 3060, 1579, 1479, 1427, 1260, 1071, 1021, 909, 803, 728 and 700; δ_H 1.07 (3 H, s, CH_3), 1.10–1.50 (3 H, overlapping m, 7-H_2 and 2-H), 1.5–1.9 (5 H, overlapping m, 4-H, 5-H_2 and 6-H_2), 2.2 (2 H, br s, NH_2), 2.55 (3 H, m, 1-H and CH_2N), 7.20–7.40 (9 H, m, ArH) and 7.50–7.70 (6 H, m, ArH), *m*/*z* 412 ($M^+ - 77$, 100%).

(1*S*,2*R*,3*R*,4*R*)-2-Methyl-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde 49

N-Methylmorpholine *N*-oxide (0.44 g, 3.76 mmol) and tetrapropylammonium perruthenate (66 mg, 0.19 mmol) were added to a solution of the alcohol **32** (0.92 g, 1.88 mmol) and 4 Å molecular sieves (2 g) in dichloromethane (15 cm^3) at ambient temperature. The mixture was stirred for 1.5 h, then filtered through Celite and the filtrate concentrated under reduced pressure. Chromatography of the residue using dichloromethane–light petroleum (3:2) as eluent gave the *title compound* **49** (0.58 g, 64%) as an oil (Found: C, 66.85; H, 5.35. $C_{27}H_{26}OSn$ requires C, 66.85; H, 5.4%. Found: $M^+ - C_6H_5$, 409.0605. $C_{21}H_{21}OSn$ requires *M*, 409.0614); $[\alpha]_D$ −12.0 (*c* 3.0 in $CHCl_3$); ν_{max}/cm^{-1} 3061, 1714, 1427, 1072, 727 and 699; δ_H 1.15 (5 H, m, 3-H, 7-H and CH_3), 1.29 (1 H, d, *J* 9, 7-H′), 2.94 (1 H, m, 1-H), 3.23 (1 H, m, 4-H), 6.12 (1 H, dd, *J* 5.5, 3, vinylic-H), 6.52 (1 H, dd, *J* 5.5, 3, vinylic-H), 7.4 (9 H, m, ArH), 7.65 (6 H, m, ArH) and 9.60 (1 H, s, CHO); δ_C 20.67 ($^3J_{CSn}$ 12.5), 32.79 ($^1J_{CSn}$ 423/403), 47.13, 47.19, 49.04 ($^3J_{CSn}$ 14.5), 57.86, 128.19 ($^3J_{CSn}$ 49.5), 128.31, 130.00, 137.28 ($^2J_{CSn}$ 35.0), 141.44 ($^3J_{CSn}$ 55.5), 142.03 ($^1J_{CSn}$ 506/483) and 205.17 ($^3J_{CSn}$ 37.5); *m*/*z* 486 (M^+, 5%) and 409 (100).

(1*S*,2*R*,3*R*,4*R*,*E*)-2-Methyl-3-triphenylstannylbicyclo[2.2.1]-hept-5-ene-2-carbaldehyde *N*,*N*-dimethylhydrazone 50

N,*N*-Dimethylhydrazine (0.04 cm^3, 0.86 mmol) was added to the aldehyde **49** (0.105 g, 0.215 mmol) in ethanol (2 cm^3) and ether (2 cm^3). The solution was stirred at 60 °C for 18 h, then cooled to ambient temperature and concentrated under reduced pressure. Chromatography of the residue using dichloromethane–light petroleum (4:1) gave the *title compound* **50** as an 80:20 mixture of geometric isomers (12 mg, 11%) (Found: $M^+ - C_6H_5$, 451.1191. $C_{23}H_{27}N_2Sn$ requires *M*, 451.1196); ν_{max}/cm^{-1} 3060, 1480, 1427, 1072, 728 and 700; δ_H(major isomer) 1.22 (4 H, m, 3-H and CH_3), 1.45 and 1.86 (each 1 H, d, *J* 8.5, 7-H), 2.33 (6 H, s, 2 × NCH_3), 2.76 (1 H, m, 1-H), 3.26 (1 H, m, 4-H), 6.10 and 6.28 (each 1 H, dd, *J* 5, 3, vinylic-H), 6.86 (1 H, s, CH=N), 7.35 (9 H, m, ArH) and 7.6 (6 H, m, ArH); *m*/*z* 529 (M^+ + 1, 10%), 451 (90), 179 (100) and 177 (30).

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