1 PERKIN

Synthesis of chiral organotin reagents: synthesis of enantiomerically enriched bicyclo[2.2.1]hept-2-yl tin hydrides from camphor. X-Ray crystal structures of (dimethyl)[(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]tin chloride and methyl(phenyl)bis[(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]stannane

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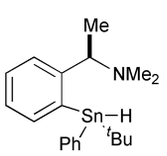
2-Iodo-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene **27** was prepared in two steps from camphor **23**. Halogen–metal exchange using butyllithium followed by addition of the appropriate tin halide gave the corresponding bicyclo[2.2.1]-hept-2-en-2-ylstannanes **26**, **35**–**38** and the (diphenyl)bis[1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]stannane **48**. Reduction of the 1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-ylstannanes **35**–**38** using diimide took place predominantly from the *exo*-face to give the *endo*-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylstannanes **18**, **43**–**45**, *endo*–*exo* = *ca.* 80 : 20 in all cases. The methyl(phenyl)bis[*endo*-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]stannane **51** was prepared from the diphenyl(methyl)[*endo*-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]stannane **40** by selective removal of one of the phenyl groups using iodine to give the dialkyl(phenyl)tin iodide **49** which was treated with the alkenyllithium reagent generated from the vinyl iodide **27** to give the bicyclo[2.2.1]hept-2-en-2-yl(dialkyl)phenylstannane **50**, as a mixture of epimers at the tin. Reduction using diimide then gave the methyl(phenyl)bis[*endo*-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl]stannane **51** whose structure was established by X-ray crystallography.

The major (trimethyl)[1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]stannane **39** was shown to be the *endo*-isomer by an X-ray crystal structure determination of the tin chloride **46** prepared by treatment of the trimethylstannane **39** with tin tetrachloride. The configurations of the other stannanes **40**–**42** were established by analogy and by comparison of their ^{1}H NMR spectra with those of **39**. The dimethyl[1-dimethylaminomethyl-7,7-dimethylbicyclo[2.2.1]hept-2-enyl](phenyl)stannane **56** was similarly prepared from the parent ketone **52**. The stannanes **41**/**44** and **51** were converted into the tin hydrides **59** and **61**, but these gave only very modest enantiomeric excesses when used to reduce the bromoketone **62**.

Introduction

Tin hydrides are widely used reducing agents in organic synthesis.[1] The introduction of chiral, non-racemic tin hydrides for the asymmetric reduction of alkyl halides and ketones is therefore of interest, especially as the tin hydride may be used in catalytic amounts along with a stoichiometric achiral reducing agent. Most studies in this area have involved tin hydrides with chiral ligands on the tin, although in some cases, if the tin itself was attached to four different ligands, this meant that mixtures of diastereoisomers were being used. Examples of chiral tin hydrides investigated to date for asymmetric synthesis include the *o*-[(*R*)-1-dimethylaminoethyl]-phenyltin hydride **1**,[2] as a mixture of epimers at the tin, the binaphthyltin hydrides **2**[3] and **3**,[4] and monoterpene derived tin hydrides including **4** and **5**.[5] The dimethylamino co-ordinated naphthyltin hydrides **6** and **7** have also been prepared and fully characterised.[6]



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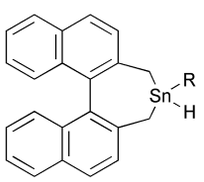
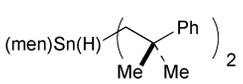


2 R = ^{t}Bu
3 R = Me



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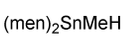

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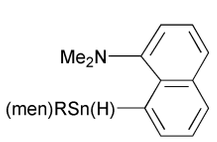
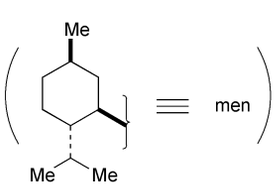


6 R = ^{t}Bu
7 R = Me



The enantiomeric excesses induced by reduction of alkyl halides using these chiral tin hydrides have, generally, been only modest by modern standards. This has been explained in terms of the large distance between the Sn atom and the radical bearing carbon atom in the transition structure for transfer of a hydrogen from a tin hydride to a prochiral carbon radical.[7] Exciting exceptions are, however, Lewis acid catalysed reductions of α-halocarbonyl compounds.[8] Extremely high enantiomeric excesses have been observed in these systems; for example, the reduction of the α-bromo-ester **8** using the tin hydride **10** in the presence of the salen complex **11** gave the reduced ester **9** with ≥96% enantiomeric excess.[9] Steroid based tin hydrides, in the presence of the salen complex **11**, similarly

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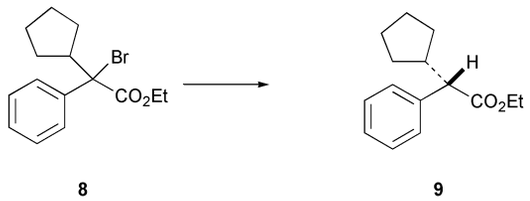
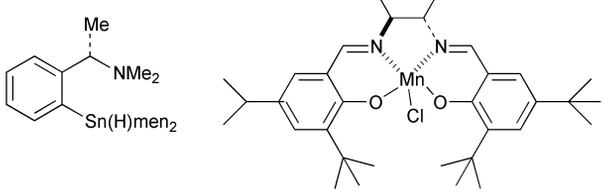
reduced the halo-ester **8** giving the product **9** with enantiomeric excesses of 62 and 90%.[10]

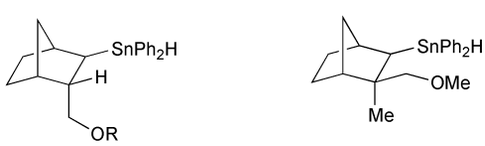


8 **9**



10 **11**

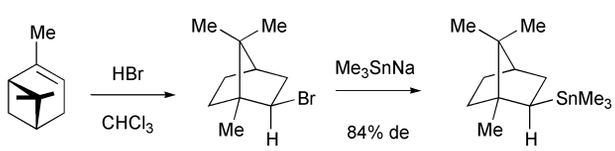
During the course of our own work, enantiomerically enriched bicyclo[2.2.1]hept-2-yl(diphenyl)tin hydrides were prepared using Diels–Alder reactions of (*E*)-3-triphenylacrylates to assemble the bicyclic nucleus.[11–13] Functional group transformations then led to the preparation of several bicyclo[2.2.1]heptyltin hydrides including the ethers **12**–**15**. These tin hydrides did not prove to be useful for asymmetric synthesis, although these preliminary studies were not carried out in the presence of a Lewis acid. Nevertheless, it was felt that further work on the chemistry of bicyclo[2.2.1]heptyl tin hydrides was justified; for example, it was hoped that by the incorporation of a suitably positioned nitrogen in the chiral ligand, the trajectory of the hydrogen to be transferred in the reduction step, *e.g.* of a prochiral radical, would be controlled.



12 R = CPh_3
13 R = Me
14 R = $SiMe_2{}^tBu$

15

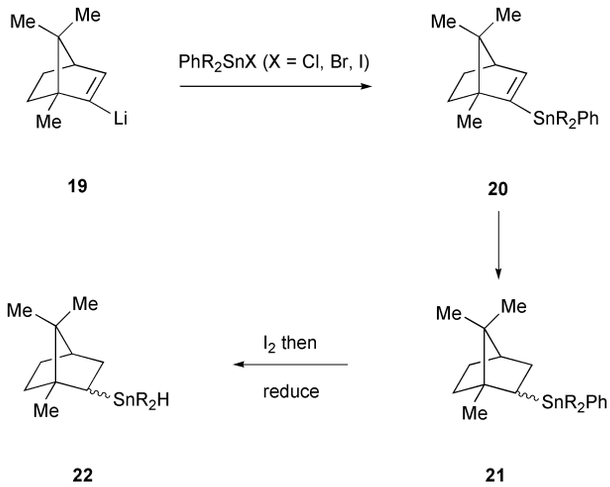
We now report the synthesis of enantiomerically enriched bicyclo[2.2.1]hept-2-ylstannanes from camphor, a readily available monoterpene. This work complements Diels–Alder approaches to stannanes of this type. Indeed, a synthesis of a stannane identified as the *exo*-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl(trimethyl)stannane **18** from α-pinene **16** *via exo*-2-bromobornane **17** was reported several years ago, an electron transfer mechanism being postulated for the reaction between the bromide **17** and trimethyltin sodium,[14] although the use of the corresponding tin hydride for asymmetric synthesis was not investigated.



16 **17** **18**

Results and discussion

The bicyclo[2.2.1]heptyltin hydrides **22** were to be prepared from the corresponding phenyl substituted stannanes **21** which were to be obtained by reaction of the appropriate tin halide with the 2-lithiated bicyclo[2.2.1]hept-2-ene **19** followed by reduction of the intermediate bicyclo[2.2.1]hept-2-enylstannane **20** by hydrogenation or reaction with diimide, see Scheme 1. At the onset of this work, it was expected that the

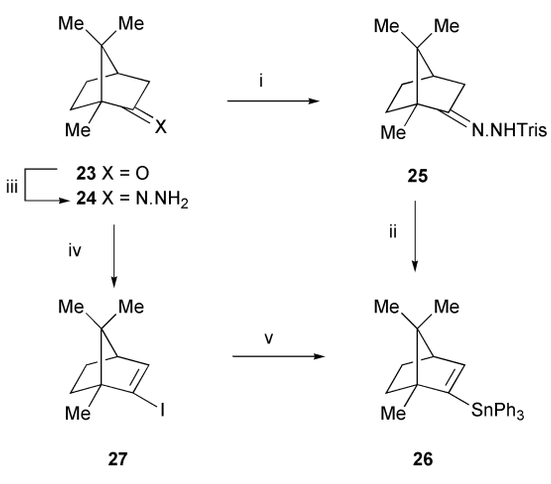


19 **20** **22** **21**

Scheme 1 Proposed synthesis of bicyclo[2.2.1]hept-2-yl(dialkyl)tin hydrides.

syn-7-methyl substituent would direct reduction of the double-bond to the *endo*-face giving more of the *exo*-isomers **22** but this remained to be established.

A Shapiro reaction was initially investigated for generation of the vinyllithium intermediate **19**. The 2,4,6-triisopropylphenyl hydrazone **25** was prepared from camphor **23**[15] but treatment with *sec*-butyllithium followed by triphenyltin chloride gave variable yields (19–57%) of the triphenylvinylstannane **26**, see Scheme 2. As an alternative route to a

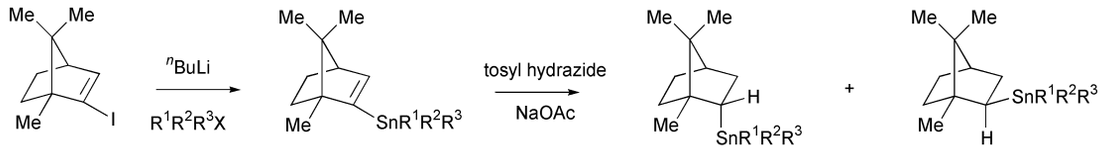


Scheme 2 *Reagents and conditions*: i, trisyl hydrazide,† MeCN, concentrated HCl, rt, 16 h (76%); ii, TMEDA, hexane, *s*-BuLi, 2 h, −55 °C to 0 °C then Ph_3SnCl, rt, 16 h (19–57%); iii, hydrazine hydrate, EtOH, reflux 18 h (90%); iv, I_2, 1,1,3,3-tetramethylguanidine, 1 h (49%); v, BuLi, Ph_3SnCl, 1 h, −78 °C (74%).

vinyllithium intermediate equivalent to **19**, the vinyl iodide **27** was prepared from camphor hydrazone **24**.[16,17] In this case, treatment with butyllithium followed by the addition of triphenyltin chloride gave a more reliable yield (74%) of the bicyclo[2.2.1]hept-2-en-2-yl(triphenyl)stannane **26**. However, attempts to reduce this vinylstannane to the corresponding saturated bicyclo[2.2.1]hept-2-ylstannane (**21**, R = Ph) were

† The IUPAC name for trisyl hydrazide is 2,4,6-triisopropylbenzenesulfonohydrazide.

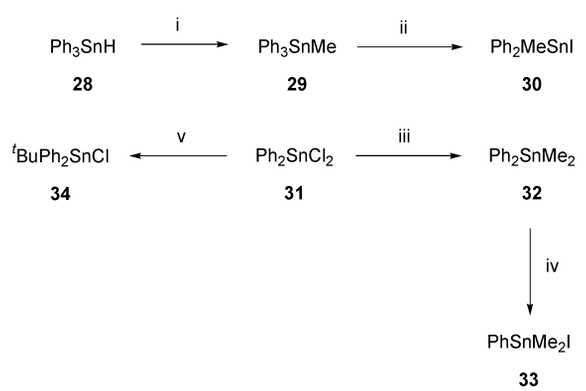
Table 1 Preparation of bicyclo[2.2.1]hept-2-yl[trialkyl(aryl)]stannanes



			Vinyl stannane		Bicyclo[2.2.1]heptylstannane			
R^1	R^2	R^3		Yield (%)	*endo*-isomer	*exo*-isomer	*endo*–*exo* ratio	Yield (%)
Ph	Ph	Ph	**26**	74	–	–	–	
Me	Me	Me	**35**	69	**39**	**18**	85 : 15	80
Me	Ph	Ph	**36**	70	**40**	**43**	78 : 22	89
Me	Me	Ph	**37**	71	**41**	**44**	78 : 22	97
Ph	Ph	^{t}Bu	**38**	65	**42**	**45**	82 : 18	67

unsuccessful. Only unchanged starting material was recovered from attempts at alkene hydrogenation (10% Pd/C, methanol, 1–5 atm H_2; 5% Rh/C, tetrahydrofuran, water, 5 atm H_2; PtO_2, ethanol, 5 atm H_2) and reduction using diimide was also unsuccessful.

To ascertain whether steric hindrance was responsible for the problems encountered in the reduction of the vinylstannane **26**, it was decided to prepare a series of structurally related alkenylstannanes to see whether any could be reduced to the corresponding alkylstannanes. For this purpose a series of tin halides had to be prepared. Diphenyl(methyl)tin iodide **30** was prepared from triphenyltin hydride **28** by deprotonation and alkylation using methyl iodide to give methyl(triphenyl)stannane **29**. Treatment of this with iodine gave the diphenyl(methyl)tin iodide **30**,[18] see Scheme 3. Dimethyl(phenyl)tin



Scheme 3 *Reagents and conditions*: i, LDA, THF, −78 °C, 1 h then MeI, −10 °C to 40 °C (99%); ii, I_2, CH_2Cl_2, rt, 10 min (89%); iii, MeMgBr, THF, −78 °C then rt, 2 h (97%); iv, I_2, CH_2Cl_2, rt, 30 min (83%); v, ^{t}BuMgCl, THF, −78 °C then 10 °C, 1 h, (87%).

iodide **33**[19] was obtained by reacting diphenyltin dichloride **31** with methyl magnesium bromide to give dimethyl(diphenyl)stannane **32** which gave the dimethyl(phenyl)tin iodide **33** on treatment with iodine. The *tert*-butyl(diphenyl)tin chloride **34** was prepared by treatment of diphenyltin dichloride **31** with one equivalent of *tert*-butyllithium.

Generation of a vinyllithium corresponding to **19** from the vinyl iodide **27** using butyllithium, and treatment of this intermediate with trimethyltin chloride and the tin halides **30**, **33** and **34** gave the corresponding bicyclo[2.2.1]hept-2-en-2-ylstannanes **35**–**38** in yields 65–71% based on the vinyl iodide **27**, see Table 1. Hydrogenation of the trimethyl vinylstannane **35** gave only unchanged starting material (5% Pd/C, ethanol, 5 atm of H_2; PtO_2, ethanol, 5 atm. of H_2). However, reduction of the vinylstannanes **35**–**38** using diimide was successful and gave the *endo*-bicyclo[2.2.1]hept-2-ylstannanes **39**–**42** in excellent yields together with *ca.* 15–20% of their *exo*-diastereoisomers.

The *endo*-configuration of the major bicyclo[2.2.1]hept-2-yl(trimethyl)stannane **39** was established by an X-ray crystal structure determination for the corresponding dimethyltin chloride **46** prepared by treatment of the trimethylstannane with one equivalent of tin(IV) chloride.[14] This gave a good yield of an 85 : 15 mixture of the *endo* and *exo*-isomers of the tin chlorides from which the major *endo*-chloride **46** was isolated by recrystallisation. Fig. 1 shows a projection of a molecule

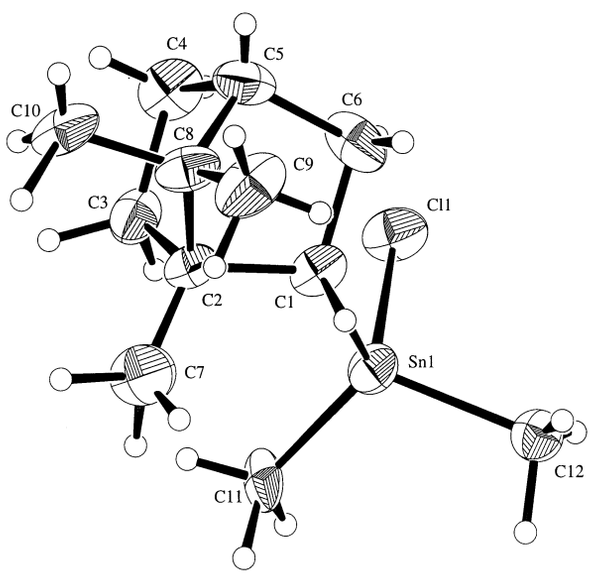
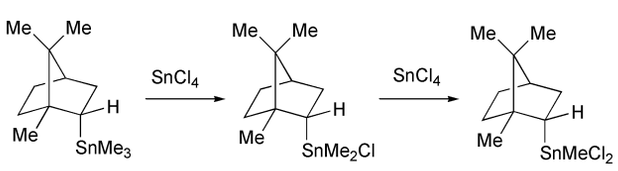


Fig. 1 Structure of the bicyclo[2.2.1]heptyltin chloride **46** as determined by X-ray crystallography.

of **46** as established by the X-ray crystal study which clearly illustrates the assigned *endo*-configuration.



The bicyclo[2.2.1]hept-2-yl(dimethyl)tin chloride **46** was converted into the corresponding monomethyltin dichloride **47**[14] using a second equivalent of tin(IV) chloride, and back into the *endo*-trimethylstannane **39** on reaction with methyllithium. In this case the product obtained was identical to the major product from the diimide reduction of the vinylstannane **35** so confirming that no epimerisation had taken place during these reactions. This sequence also provided a stereochemically homogeneous sample of the *endo*-stannane **39**.

Table 2 ^{13}C NMR data for the bicyclo[2.2.1]heptylstannanes **18**, **39**–**42**

	δ_C(ppm) ($^nJ_{CSn}$/Hz)								
Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9/10)
39	49.0	35.1 (426/408)	32.9	45.7 (18.2)	28.5	36.8 (41.9)	48.0 (48.8)	16.2	19.5/18.8
40	49.1	36.9 (449/428)	33.1	45.5 (20.0)	28.2	37.7 (42.5)	48.1 (57.8)	16.3	19.5/18.9
41	48.5	35.5 (437/412)	32.4	45.2	27.8	36.8 (46.6)	47.4 (52)	15.6	19.0/18.4
42	49.0	38.0 (368/361)	33.5	45.4 (16.2)	28.2	38.04 (31.0)	48.0 (53.4)	16.7	19.7/18.9
18	48.8	37.9	34.0	45.8	27.8	41.8	47.1	17.5	20.6/19.8

The *endo* configuration assigned to the monomethyltin dichloride **47** was consistent with the three-bond carbon to tin couplings observed in its ^{13}C NMR spectrum. Such couplings vary with torsional angle according to a Karplus relationship and so in conformationally rigid structures are a reliable guide to stereochemistry.[20] In bicyclo[2.2.1]hept-2-ylstannanes, $^3J_{CSn}$ between the tin and C(7) is diagnostic of the *endo* or *exo* orientation of the tin, being *ca.* 50–60 Hz if the tin is *endo* and very small, *ca.* 0 Hz, if the tin is *exo*, see Fig. 2.[21] The three bond

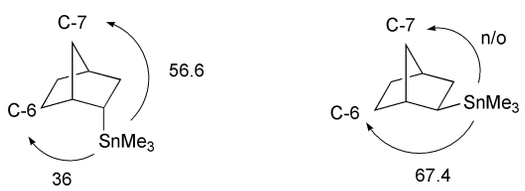
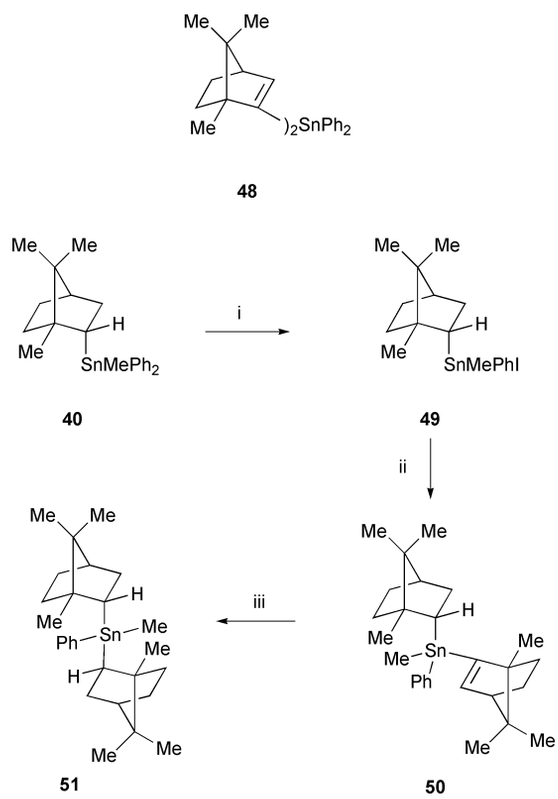


Fig. 2 Some ^{13}C NMR couplings (Hz) observed for *endo* and *exo*-bicyclo[2.2.1]hept-2-yl(trimethyl)stannanes.

coupling between the tin and C(6) also depends on the orientation of the tin substituent with couplings of *ca.* 36 and 67 Hz being recorded for *endo* and *exo*-stannanes, respectively, see Fig. 2.[21] For the tin dichloride **47** the three-bond coupling between the tin and C(7), $^3J_{C(7)Sn}$, was 94 Hz, fully supportive of the *endo* position of the tin. A $^3J_{C(7)Sn}$ of 48.8 Hz was also observed for the major bicyclo[2.2.1]hept-2-yl(trimethyl)-stannane **39** consistent with the *endo*-configuration assigned on the basis of the X-ray crystal structure of **46**.

The other major bicyclo[2.2.1]hept-2-ylstannanes **40**–**42** were assigned the *endo*-configuration by analogy and on the basis of comparison of their ^{13}C NMR data with those of the *exo*- and *endo*-isomers **18** and **39**. The *endo*-assignments for the major isomers were also supported by their $^3J_{C(7)Sn}$ couplings, see Table 2. The minor products had similar ^{13}C NMR spectra but no observable three bond Sn–C(7) coupling, the data for the minor *exo*-trimethylstannane **18** being given in Table 2. ‡

Having prepared a series of mono-bicyclo[2.2.1]hept-2-ylstannanes by reduction of the corresponding vinylstannanes, it was decided to see whether this approach could be extended to the synthesis of bis[bicyclo[2.2.1]hept-2-yl]stannanes. The reaction of diphenyltin dichloride **31** with two equivalents of the vinyllithium species generated by treatment of the vinyl iodide **27** with butyllithium gave the bis[bicyclo[2.2.1]hept-2-en-2-yl](diphenyl)stannane **48** but attempts to reduce this with diimide were unsuccessful. However, reaction of the *endo*-bicyclo[2.2.1]hept-2-yl(diphenyl)(methyl)stannane **40** (containing *ca.* 20% of its *exo*-isomer **43**) with one equivalent of iodine gave the dialkyl(phenyl)tin iodide **49** (Scheme 4). Treatment of this with the vinyllithium reagent generated from the vinyl iodide **27** gave the vinylstannane **50** together with *ca.* 20% of its *exo*-isomer, as a mixture of diastereoisomers at the tin. This mixture was not separated but was successfully reduced using diimide to give the bis-*endo*-bicyclo[2.2.1]hept-2-yl(methyl)-(phenyl)stannane **51** again containing minor amounts of the mono- and bis-*exo*-isomers. Recrystallisation of this mixture gave pure samples of the bis-*endo*-stannane **51** the structure of which was confirmed by X-ray crystallography. Fig. 3 shows the structure of this bis-bicyclo[2.2.1]hept-2-ylstannane as determined by crystallography which illustrates the bis-*endo*-stereochemistry. Again this crystal structure determination confirms that the diimide reductions of the bicyclo[2.2.1]hept-2-en-2-ylstannanes take place selectively from the *exo*-direction to give rise to the formation of the *endo*-stannanes as the major products.



Scheme 4 *Reagents and conditions*: i, I_2, CH_2Cl_2, 20 min (99%); ii, **27**, BuLi, −78 °C, 1 h, then add **49** (60%); iii, toluene-*p*-sulfonyl hydrazide, NaOAc, $(MeOCH_2)_2$ (93%).

En route to an amino-substituted tin hydride, 8-dimethylaminocamphor **52** was prepared from camphor following the literature procedure.[22] This was converted into the hydrazone **53** which on treatment with tetramethylguanidine and iodine, following the procedure used to prepare the iodide **27**, gave the

‡ Comparison of the literature ^{13}C NMR data for the *exo*-stannane **18** with the data obtained for the *exo*- and *endo*-bicyclo[2.2.1]hept-2-yl(trimethyl)stannanes prepared during the course of our work,[14] suggest that the major stannane prepared from the *exo*-bromide **17** was in fact the *endo*-isomer **39** and not the *exo*-isomer **18** as reported. This revision of structure is supported by comparison of the ^{13}C data for the corresponding tin chloride **46** and tin dichloride **47** which suggest that our *endo* compounds are the same as those described as being *exo* in the literature.[14]

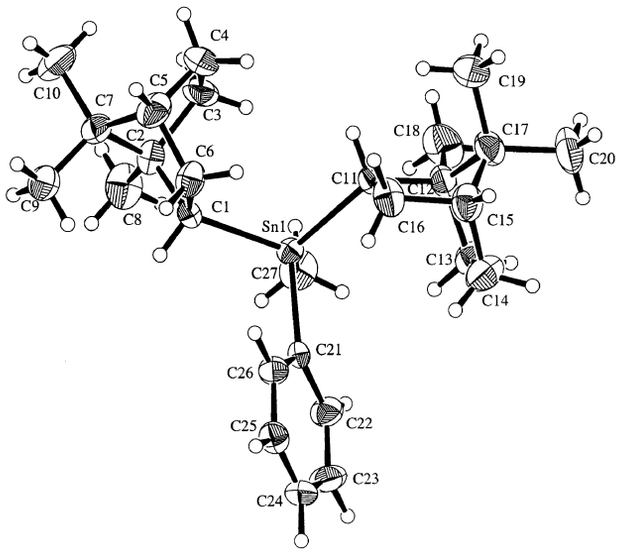


Fig. 3 Structure of the bis-bicyclo[2.2.1]heptylstannane **51** as determined by X-ray crystallography.

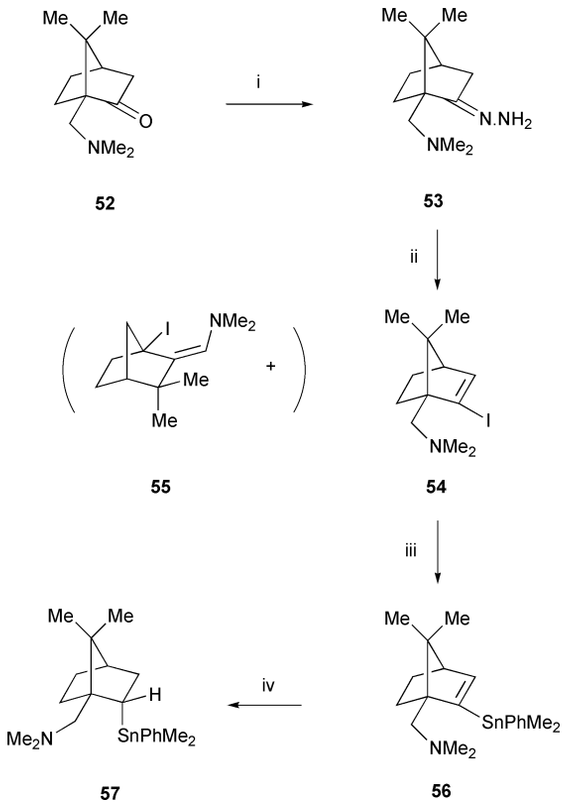
vinyl iodide **54** but only in a rather low yield (19%), together with a minor product which may have been the rearranged product **55** but which was not isolated sufficiently pure for full identification. Treatment of the iodide **54** with butyllithium followed by the addition of dimethyl(phenyl)tin iodide **33** gave the vinylstannane **56**. The spectroscopic data obtained for **56** didn't indicate any significant nitrogen–tin co-ordination. For example, the two diastereotopic methyl groups gave rise to peaks in its ^{1}H NMR spectrum at δ 0.03 and δ 0.00 ppm with $^2J_{SnH}$ couplings of 56.4/54 and 55.9/53.4 Hz which are very similar to the corresponding peaks in the ^{1}H NMR spectrum of the vinylstannane **37**. Nevertheless, this vinylstannane was reduced using di-imide to give a stannane believed to be the *endo*-dimethyl(phenyl)stannane **57** but this was not fully characterised because of insufficient material (Scheme 5).

Finally, the mixture of the phenyldimethylstannanes **41**–**44** (**41**–**44** = 78 : 22) was taken through to the tin hydride **59** (containing *ca.* 20% of its *exo*-isomer) by cleavage of the phenyl group using iodine and reduction of the iodide **58** so obtained using sodium borohydride. The bis-bicyclo[2.2.1]-heptylstannane **51** was similarly converted *via* the iodide **60** into the stannane **61**. However, preliminary studies of the reduction of bromoketone **62** using these tin hydrides, albeit in the absence of a Lewis acid, gave the debrominated product **63** with less than 5% ee.

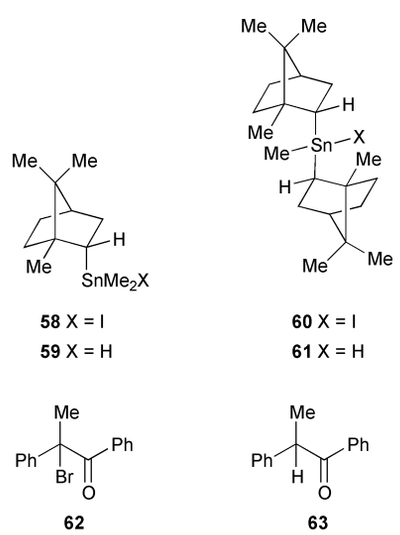
Conclusion

This work has shown that *endo*-bicyclo[2.2.1]hept-2-ylstannanes can be prepared by coupling bicyclo[2.2.1]hept-2-en-2-yllithium with tin halides followed by reductive removal of the double-bond using diimide. This approach has been used to prepare both mono- and bis-bicyclo[2.2.1]hept-2-ylstannanes and is also useful for the preparation of dialkylamino-substituted stannanes. The selective formation of *endo*-isomers during the diimide reduction of the vinylstannanes was unexpected since a *syn*-7-methyl substituent usually directs bidentate attack on a bicyclo[2.2.1]hept-2-ene to the *endo*-face giving rise to the formation of *exo*-products. The selectivity observed here may well be due to the bulk of the tin and its substituents. The steric interaction between a *exo*-2-tin substituent and the 7-*syn*-methyl group in the transition structure for *endo*-reduction may be substantial and lead to a lower energy transition structure for *exo*-attack.

The lack of success in attempts to reduce the bicyclo[2.2.1]-hept-2-en-2-yl(triphenyl)stannane **26** using diimide cannot be attributed *solely* to steric effects since analogous more hindered



Scheme 5 *Reagents and conditions*: i, hydrazine hydrate (50%); ii, I_2, 1,1,3,3-tetramethylguanidine (19%); iii, BuLi, −78 °C, then $PhSnMe_2I$ (66%); iv, tosyl hydrazide, NaOAc.



stannanes were reduced, *e.g.* the *tert*-butyldiphenylstannane **38** was reduced to the *endo*- and *exo*-bicyclo[2.2.1]heptylstannanes **42** and **45**. Perhaps electronic effects involving increased electron withdrawal by the triphenyltin group are also involved although this observation was not examined further.

Further work in this area will be to evaluate further the potential of enantiomerically enriched bicyclo[2.2.1]heptyltin hydrides and related tin reagents for asymmetric synthesis, specifically the possible advantages of having a suitably positioned nitrogen substituent.

Experimental

^{1}H and ^{13}C NMR were recorded on Varian INOVA 300 (300 MHz) or Varian Unity 500 (500 MHz) spectrometers in chloroform-d_1 at 300 MHz for protons and at 75 MHz for carbon unless otherwise stated. Coupling constants J are given

in Hz. Coupling constants for $^{119/117}$Sn–^{13}C ($^{n}J_{CSn}$) and $^{119/117}$Sn–^{1}H ($^{n}J_{HSn}$) are quoted when observed. When couplings to ^{119}Sn and ^{117}Sn are discrete they are quoted with the value for ^{119}Sn given first. Infrared spectra were recorded on an ATI Mattson Genesis Series FTIR spectrometer as thin films (produced by evaporation of a dichloromethane solution) on a sodium chloride plate. Low resolution chemical ionisation (CI) and electron impact (EI) mass spectra were recorded on a Fisons TRIO 2000 quadrupole mass spectrometer. All high resolution mass spectra were recorded on a Kratos Concept-1S mass spectrometer coupled to a Mach 3 data system. Compounds containing tin showed characteristic clusters of peaks in their mass spectra, only those corresponding to ^{120}Sn are quoted.

Optical rotations were recorded at ambient temperature (22 °C) on an Optical Activity AA-100 polarimeter at 589 nm using either chloroform or hexane as solvent and are given in 10^{-1} deg cm^2 g^{-1}.

Preparative high performance liquid chromatography was carried out using a Gilson 303 pump (with manometric module) attached to a Dynamax 83–121-C, 60 Å, 300 × 10 mm column. The packed column contained a SiO 8 μ stationary phase. The mobile phase consisted of hexane. Detection was by ultraviolet (UV) absorption at 255 nm monitored by a Gilson 115 UV detector. Chromatography refers to flash column chromatography and was performed using Merck silica gel 60H (40–63 μ, 230–300 mesh) as the stationary phase. Thin layer chromatography was performed using Machery Nagel DC-Fertigplatten SIL G-25 UV_{254} silica gel glass plates. Visualisation was by UV absorption at 254 nm and by treatment with 10% w/v methanolic dodecamolybdophosphoric acid and subsequent heating.

Petrol refers to the fraction with bp 40–60 °C and was redistilled prior to use. Tetrahydrofuran was dried over sodium–benzophenone and distilled under an atmosphere of nitrogen. Dichloromethane was dried over calcium hydride and distilled under an atmosphere of nitrogen. Diethyl ether and hexane were dried over sodium wire. All other commercially available reagents were purified following standard procedures.

[(1*R*,4*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl]-(triphenyl)stannane 26

From trisylhydrazone 25. A solution of the trisylhydrazone **25**[15] (1.0 g, 2.31 mmol) and TMEDA (5 cm^3) in hexane (12 cm^3) was cooled to −55 °C before the addition of *sec*-butyllithium (1.3 M in hexanes; 3.91 cm^3, 5.08 mmol) over 15 min. The mixture was stirred at −55 °C for 2 h before being warmed slowly to 0 °C. The evolution of nitrogen gas was observed. On cessation of nitrogen evolution a solution of triphenyltin chloride (1.07 g, 2.77 mmol) in THF (5 cm^3) was added. The reaction mixture was warmed to ambient temperature and was stirred for 16 h before being poured into distilled water (10 cm^3). The solution was extracted using diethyl ether (3 × 10 cm^3), and the combined organic phases were washed with water (3 × 10 cm^3) before being dried over magnesium sulfate, filtered and concentrated under reduced pressure. Column chromatography of the residue using petrol–triethylamine (100 : 1) as eluent afforded the *title compound* **26** (639 mg, 57%) as a colourless oil, $[\alpha]_D$ −23.3 (*c* 1.7, $CHCl_3$) (Found: M$^+$, 486.1366. $C_{28}H_{30}Sn$ requires *M*, 486.1368); ν_{max}/cm^{-1} 3062, 3048, 3015, 2950, 1479, 1428 and 1074; δ_H 7.67 (6 H, m, Ar–H), 7.45 (9 H, m, Ar–H), 6.59 (1 H, d, *J* 3, $^3J_{HSn}$ 46.6, 3-H), 2.52 (1 H, t, *J* 3, 4-H), 1.17–1.95 (4 H, m, 5-H_2 and 6-H_2) and 1.12, 1.04 and 0.89 (each 3 H, s, 1-CH_3 and 2 × 7-CH_3); *m*/*z* (CI) 486 (M$^+$, 3%), 426 (100) and 368 (92).

From vinyl iodide 27. A solution of vinyl iodide **27** (200 mg, 0.75 mmol) in THF (1 cm^3) at −78 °C was treated with butyllithium (1.5 M in hexanes; 0.52 cm^3, 0.79 mmol). The solution was stirred at −78 °C for 30 min before the addition of triphenyltin chloride (303 mg, 0.79 mmol) in THF (5 cm^3), stirred at −78 °C for 3 h then methanol (1 cm^3) was added. The solution was warmed to ambient temperature and partitioned between water and diethyl ether. The aqueous phase was extracted with diethyl ether (3 × 5 cm^3) and the combined extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Flash column chromatography of the residue using petrol–triethylamine (100 : 1) as eluent afforded the stannane **26** (270 mg, 74%) as a colourless oil.

(1*R*,4*R*)-2-Iodo-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene 27[16,17]

A nitrogen flushed three-necked flask was fitted with a mechanical stirrer, condenser and gas outlet. The flask was charged with the hydrazone **24** (22.76 g, 137 mmol) and diethyl ether (200 cm^3) containing 1,1,3,3-tetramethylguanidine (60.1 cm^3, 479 mmol). A solution of iodine (72.96 g, 287 mmol) in diethyl ether (600 cm^3) was added over a period of 1 h, during which time the pale yellow solution turned deep pink and then brown in colour. On completion of the addition, the mixture was stirred for a further 15 min at ambient temperature. The mixture was washed with hydrochloric acid (3.5 M, 3 × 150 cm^3), saturated aqueous sodium thiosulfate (3 × 150 cm^3) and saturated aqueous sodium bicarbonate (3 × 100 cm^3) before being dried over magnesium sulfate, filtered and concentrated under reduced pressure. Repeated chromatography of the residue using petrol as eluent gave the title compound **27** (17.75 g, 49%) as a colourless oil, $[\alpha]_D$ −15.5 (*c* 0.62 in $CHCl_3$) (lit.[17] $[\alpha]_D$ −8.8 in $CHCl_3$) (Found: M$^+$, 262.0219. $C_{10}H_{15}I$ requires *M*, 262.0220); ν_{max}/cm^{-1} 2986, 2955, 2872 and 812; δ_H 6.33 (1 H, d, *J* 3.5, 3-H), 2.30 (1 H, t, *J* 3.5, 4-H), 1.72 (1 H, m), 1.38 (1 H, m), 0.95 (2 H, m), 0.90 (3 H, s, 1-CH_3), 0.78 and 0.77 (each 3 H, s, 2 × 7-CH_3); δ_C 142.9, 106.6, 57.9, 55.6. 54.5, 30.5, 25.1, 20.2, 19.4 and 15.1; *m*/*z* (EI) 262 (M$^+$, 38%), 247 (14), 135 (9) and 49 (100).

Methyl(triphenyl)stannane 29

Butyllithium (1.5 M in hexanes; 10.1 cm^3, 15.1 mmol) was added to a solution of diisopropylamine (2.31 cm^3, 16.4 mmol) in THF (2 cm^3) at 0 °C. The mixture was stirred for 20 min before being cooled to −78 °C. A solution of triphenyltin hydride **28** (4.81 g, 13.7 mmol) in THF (4 cm^3) was added and the pale yellow solution immediately darkened to a custard yellow colour. The solution was stirred at −78 °C for 1 h before being warmed to −10 °C. Methyl iodide (0.94 cm^3, 15.1 mmol) was added and the mixture was heated at 45 °C for 1 h during which time the solution adopted a dark brown colour. After cooling to ambient temperature, saturated aqueous ammonium chloride (6 cm^3) was added and the mixture was extracted using diethyl ether (3 × 8 cm^3). The combined organic extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford the stannane **29** (4.93 g, 99%) as a pale cream solid, used without further purification, mp 61–63 °C (Found: M$^+$, 366.0429. $C_{19}H_{18}Sn$ requires *M*, 366.0429); ν_{max}/cm^{-1} 3048, 3004, 1479, 1427, 1075 and 996; δ_H 7.50 (15 H, m, Ar–H) and 0.78 (3 H, s, $^2J_{HSn}$ 56.3/54.0, Sn–CH_3); δ_C 139.1, 136.7, 128.8, 128.4 and −10.6; *m*/*z* (EI) 366 (M$^+$, 2%) and 351 (100).

Diphenyl(methyl)tin iodide 30[18]

Iodine (3.37 g, 13.3 mmol) was added in small portions to methyl(triphenyl)stannane **29** (4.85 g, 13.3 mmol) dissolved in dry dichloromethane (30 cm^3) over 10 min. The mixture was stirred for a further 20 min before being concentrated. The residue was distilled under reduced pressure to furnish the tin iodide **30** (2.61 g, 89%) as a yellow oil, bp 158–164 °C, 1.0 mmHg (lit.[18] 115–116 °C, 0.008 mmHg) (Found: M$^+$ + NH_4,

433.9429. $C_{13}H_{17}INSn$ requires *M*, 433.9428); ν_{max}/cm^{-1} 3064, 3047, 1480, 1429, 1073, 997 and 756; δ_H 7.44–7.74 (10 H, m, Ar–H) and 1.29 (3 H, s, $^2J_{HSn}$ 57.5, Sn–CH_3); δ_C 137.3, 135.8, 130.0, 128.9 and −3.0; *m*/*z* (CI) 434 (M^+ + 18, 3%), 418 (10), 373 (14) and 356 (100).

Dimethyl(diphenyl)stannane 32[19]

Methylmagnesium bromide (3.0 M in diethyl ether; 2.04 cm^3, 6.1 mmol) was added dropwise to a solution of dichloro-(diphenyl)stannane **31** (1.0 g, 2.9 mmol) in THF (2 cm^3) at −78 °C. The mixture was warmed to ambient temperature and was stirred for 2 h before the addition of saturated aqueous ammonium chloride (2 cm^3). The mixture was extracted using diethyl ether (3 × 5 cm^3) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to yield the stannane **32** (856 mg, 97%) as a pale yellow oil used without further purification (Found: M^+ − CH_3, 289.0041. $C_{13}H_{13}Sn$ requires *M*, 289.0038); ν_{max}/cm^{-1} 3063, 2916, 1428, 1075 and 752; δ_H 7.23 (4 H, m, Ar–H), 7.06 (6 H, m, Ar–H) and 0.22 (6 H, s, $^2J_{HSn}$ 55.9/53.4, 2 × Sn–CH_3); δ_C 140.6, 136.2, 128.5, 128.2 and −10.1; *m*/*z* (CI) 304 (M^+, 10%), 289 (4) and 244 (100).

Dimethyl(phenyl)tin iodide 33[19]

Iodine (4.31 g, 17.0 mmol) dissolved in dichloromethane (25 cm^3) was added dropwise to a solution of dimethyl-(diphenyl)stannane **32** (5.14 g, 17.0 mmol) in dichloromethane (25 cm^3) over a period of 30 min. The mixture was stirred at ambient temperature for 3 h before being concentrated under reduced pressure. Distillation of the residue under reduced pressure afforded the stannane **33** (4.96 g, 83%) as a colourless oil, bp 100–101 °C, 1.4 mmHg (lit.[19] bp 100–101 °C, 1.4 mmHg) (Found: M^+, 353.8928. $C_8H_{11}ISn$ requires *M*, 353.8928); ν_{max}/cm^{-1} 3064, 3048, 1429, 1073 and 763; δ_H 7.63 (2 H, m, Ar–H), 7.47 (3 H, m, Ar–H) and 1.12 (6 H, s, $^2J_{HSn}$ 58.1/55.6, 2 × Sn–CH_3); δ_C 137.4, 135.2, 129.8, 128.7 and −2.3; *m*/*z* (CI) 354 (M^+, 4%), 294 (100), 244 (23) and 202 (18).

tert-Butyl(diphenyl)tin chloride 34

Dichlorodiphenylstannane **31** (4.00 g, 11.6 mmol) was dissolved in dry THF (15 cm^3) before being cooled to −78 °C. *tert*-Butylmagnesium chloride (1.0 M in THF; 11.6 cm^3, 11.6 mmol) was added dropwise and the stirred mixture was warmed to −10 °C over 1 h before the addition of saturated aqueous ammonium chloride (10 cm^3). The mixture was filtered through Celite and the filtrate was extracted using diethyl ether (3 × 10 cm^3). The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to yield the *title compound* **34** (3.69 g, 87%) as a cream coloured oil (Found: M^+ − $C(CH_3)_3$, 308.9496. $C_{12}H_{10}ClSn$ requires *M*, 308.9492); ν_{max}/cm^{-1} 3585, 3066, 3049, 2955, 2922, 2852, 1480, 1466, 1430, 1367, 1166, 1073 and 997; δ_H 7.32–7.85 (10 H, m, Ar–H) and 1.49 [9 H, s, $^3J_{HSn}$ 97.1/92.8, $SnC(CH_3)_3$]; δ_C 138.4, 136.1, 129.9, 128.9, 35.2 and 29.5; *m*/*z* (EI) 366 (M^+, 3%), 353 (6), 309 (100), 197 (25) and 154 (29).

Preparation of the bicyclo[2.2.1]hept-2-en-2-ylstannanes general procedure: trimethyl[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]stannane 35

Butyllithium (1.6 M in hexanes; 1.25 cm^3, 2.00 mmol) was added to a solution of iodide **27** (500 mg, 1.91 mmol) in THF (5 cm^3) at −78 °C. After stirring for 45 min, trimethyltin chloride (1.0 M in THF; 2.00 cm^3, 2.00 mmol) was added and the mixture was stirred at −78 °C for a further 1 h before the addition of methanol (3 cm^3). The solution was warmed to ambient temperature and was poured into water (5 cm^3). The mixture was extracted using diethyl ether (3 × 10 cm^3) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Chromatography of the pale brown residue using petrol–triethylamine (100 : 1) afforded the stannane **35** (380 mg, 67%) as a colourless oil, $[\alpha]_D$ −26.5 (*c* 0.34 in $CHCl_3$); ν_{max}/cm^{-1} 2985, 2950, 2868 and 767; δ_H (500 MHz) 6.04 (1 H, d, *J* 3, $^3J_{HSn}$ 44, 3-H), 2.17 (1 H, t, *J* 3.3, 4-H), 1.66 and 1.37 (each 1 H, m), 0.94 (3 H, s, 1-CH_3), 0.74 (2 H, m), 0.68 and 0.65 (each 3 H, s, 2 × 7-CH_3) and 0.00 [9 H, s, $^2J_{HSn}$ 55.0/53.0, $Sn(CH_3)_3$]; δ_C (125 MHz) 152.4 ($^1J_{CSn}$ 458, 2-C), 145.1 ($^2J_{CSn}$ 24.2, 3-C), 57.2 (1-C), 56.2 (7-C), 53.7 ($^3J_{CSn}$ 48.6, 4-C), 31.3 (6-C), 24.4 (5-C), 19.84 and 19.76 (9-C and 10-C), 15.0 (8-C) and −9.6 [$^1J_{CSn}$ 344/330, $Sn(CH_3)_3$]; *m*/*z* (EI) 300 (M^+, 16%), 285 (57), 135 (65) and 121 (100).

Diphenyl(methyl)[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]stannane 36

Following the general procedure, vinyl iodide **27** (1.50 g, 5.7 mmol) in dry THF (8 cm^3), butyllithium (1.6 M in hexanes; 3.7 cm^3, 6.3 mmol) and the tin iodide **30** (2.62 g, 6.3 mmol) dissolved in THF (5 cm^3) gave, after flash column chromatography of the residue using petrol–triethylamine (100 : 1) as eluent, the *title compound* **36** (1.64 g, 67%) as a colourless oil, $[\alpha]_D$ −28.8 (*c* 0.34 in $CHCl_3$) (Found: M^+, 424.1213. $C_{23}H_{28}Sn$ requires *M*, 424.1212); ν_{max}/cm^{-1} 3063, 2986, 2950, 2868, 1428 and 1075; δ_H (500 MHz) 7.58 (4 H, m, Ar–H), 7.41 (6 H, m Ar–H), 6.43 (1 H, d, *J* 2.9, $^3J_{HSn}$ 44.5, 3-H), 2.44 (1 H, t, *J* 3.2, 4-H), 1.90 (1 H, m), 1.60 (1 H, m), 1.10, 0.95 and 0.85 (each 3 H, s, 1-CH_3 and 2 × 7-CH_3), 1.04 (2 H, m) and 0.63 (3 H, s, $^2J_{HSn}$ 55.6/53.2, Sn–CH_3); δ_C (125 MHz) 149.8 (2-C), 148.7 ($^2J_{CSn}$ 23.5, 3-C), 140.3 and 140.2 (*ipso*-C), 136.6 ($^2J_{CSn}$ 34.9, *ortho*-C), 128.5 and 128.2 (*meta*-C and *para*-C), 57.5 ($^2J_{CSn}$ 39.0, 1-C), 56.6 (7-C), 53.9 ($^3J_{CSn}$ 54.4, 4-C), 31.4 (6-C), 24.3 (5-C), 19.9 (9-C and 10-C), 15.3 (8-C) and −10.1 ($^1J_{CSn}$ 371, Sn–CH_3); *m*/*z* (EI) 424 (M^+, 34%), 409 (100), 381 (27), 289 (49), 197 (45) and 91 (87).

Dimethyl(phenyl)[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]stannane 37

Following the general procedure, vinyl iodide **27** (1.31 g, 5.0 mmol) in dry THF (4 cm^3), butyllithium (1.6 M in hexanes; 3.42 cm^3, 5.5 mmol) and the tin iodide **33** (1.93 g, 5.5 mmol) in THF (2 cm^3) gave, after flash column chromatography of the residue using petrol–triethylamine (100 : 1) as eluent, the *title compound* **37** (1.29 g, 71%) as a pale yellow oil, $[\alpha]_D$ −26.4 (*c* 3.18 in $CHCl_3$) (Found: M^+, 362.1053. $C_{18}H_{26}Sn$ requires *M*, 362.1055); ν_{max}/cm^{-1} 2985, 2949, 2868 and 1428; δ_H 7.26 (2 H, m, Ar–H), 7.08 (3 H, m, Ar–H), 6.02 (1 H, d, *J* 3, 3-H), 2.09 (1 H, t, *J* 3.3, 4-H), 1.56 and 1.27 (each 1 H, m), 0.80 (3 H, s, 1-CH_3), 0.66 (2 H, m), 0.58 and 0.54 (each 3 H, s, 7-CH_3), 0.10 and 0.09 (each 3 H, s, $^2J_{HSn}$ 52.0, Sn–CH_3); δ_C (125 MHz) 150.6 (2-C), 146.4 (3-C, $^2J_{CSn}$ 25.9), 141.2 (*ipso*-C), 135.6 (*ortho*-C, $^2J_{CSn}$ 36.1), 127.7 and 127.5 (*meta* and *para*-C), 56.8 (1-C, $^3J_{CSn}$ 35.4), 55.8 (7-C, $^3J_{CSn}$ 17.4), 53.2 (4-C, $^3J_{CSn}$ 49.5), 30.8 (6-C), 23.9 (5-C), 19.3 (9-C and 10-C), 14.7 (8-C), −10.4 and −10.6 (2 × Sn–CH_3, $^1J_{CSn}$ 354); *m*/*z* (CI) 362 (M^+, 10%), 302 (27) and 244 (100).

tert-Butyl(diphenyl)[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]stannane 38

Following the general procedure, vinyl iodide **27** (555 mg, 2.11 mmol) in THF (2 cm^3), butyllithium (1.2 M in hexanes; 1.94 cm^3, 2.33 mmol) and the tin chloride **34** (850 mg, 2.33 mmol) in THF (7 cm^3) gave, after chromatography of the residue using petrol–triethylamine (100 : 1) as eluent, the *title compound* **38** (640 mg, 65%) as a colourless oil, $[\alpha]_D$ −27.3 (*c* 1.42 in $CHCl_3$) (Found: M^+ − $C(CH_3)_3$, 409.0980. $C_{22}H_{25}Sn$ requires *M*, 409.0977); ν_{max}/cm^{-1} 3063, 2986, 2951, 2869, 1466, 1428 and 1073; δ_H 7.35–7.68 (10 H, m, Ar–H), 6.52 (1 H, d, *J* 3, $^3J_{HSn}$ 40.7, 3-H), 2.44 (1 H, t, *J* 3.4, 4-H), 1.88 (1 H, m), 1.57

(1 H, m), 1.36 [9 H, s, $^3J_{HSn}$ 72.1/68.8, Sn–C(CH$_3$)$_3$], 1.07 (1 H, m), 0.98 and 0.97 (each 3 H, s, 2 × 7-CH$_3$), 0.91 (1 H, m) and 0.82 (3 H, s, 1-CH$_3$); δ_C (125 MHz) 149.7 (3-C), 149.6 (2-C), 140.3 and 140.4 (*ipso*-C), 137.4 and 137.5 (*ortho*-C), 128.2 and 128.3 (*meta*-C and *para*-C), 57.5 (1-C), 56.5 (7-C), 53.9 (4-C, $^3J_{CSn}$ 50.0), 31.3 (6-C), 31.0 [–C(*C*H$_3$)$_3$], 27.9 [–*C*(CH$_3$)$_3$], 24.3 (5-C), 20.1 and 19.9 (9-C and 10-C) and 15.6 (8-C); *m*/*z* (EI) 466 (M$^+$, 10%), 409 (100), 381 (10), 275 (12) and 197 (34).

Preparation of 1,7,7-trimethylbicyclo[2.2.1]hept-2-ylstannanes general procedure: (trimethyl)[(1*R*,4*R*)-1,7,7-trimethylbicyclo-[2.2.1]hept-2-yl]stannanes 18 and 39

Vinylstannane **35** (2.25 g, 7.52 mmol) was dissolved in 1,2-dimethoxyethane (35 cm^3) containing 4-methylbenzenesulfonyl hydrazide (17.4 g, 93.3 mmol). The mixture was heated under reflux and sodium acetate (15.4 g, 0.19 mol) in water (20 cm^3) was added over a period of 4 h. On completion of the addition the mixture was heated under reflux for a further 1 h before being cooled and concentrated under reduced pressure. The residue was taken up in saturated aqueous ammonium chloride (50 cm^3) and was extracted using dichloromethane (3 × 30 cm^3). The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was dissolved in petrol (10 cm^3) and passed through a plug of silica gel using petrol as eluent. The organic phase was concentrated. Preparative HPLC of the resulting mixture using hexane as eluent afforded an inseparable mixture of the stannanes **18** and **39** (15 : 85) (1.81 g, 80%) as a colourless oil, $[\alpha]_D$ +2.1 (*c* 0.76, in CHCl$_3$) (Found: M$^+$, 302.1059. $C_{13}H_{26}Sn$ requires *M*, 302.1055); ν_{max}/cm^{-1} 2949, 1459, 1386 and 763; δ_H (500 MHz) 2.03 (1 H, m, 4-H), 1.75 and 1.69 (each 1 H, m), 1.55 (2 H, m), 1.24 (2 H, m), 1.12 (1 H, m), 0.91 (0.45 H, s, 1-CH$_3$), 0.88 (5.10 H, s, 2 × 7-CH$_3$), 0.86 (0.90 H, s, 2 × 7-CH$_3$), 0.84 (2.55 H, s, 1-CH$_3$), 0.09 [7.65 H, s, $^2J_{HSn}$ 50.4/48.2, Sn–(CH$_3$)$_3$] and 0.05 [1.35 H, s, Sn–(CH$_3$)$_3$]; δ_C (125 MHz) **39** 49.0 (1-C), 48.0 (7-C, $^3J_{CSn}$ 48.8), 45.7 (4-C, $^3J_{CSn}$ 18.2), 36.8 (6-C, $^3J_{CSn}$ 41.9), 35.1 (2-C, $^1J_{CSn}$ 426/408), 32.9 (3-C), 28.5 (5-C), 19.5 and 18.8 (9-C and 10-C), 16.2 (8-C) and −9.4 (Sn–CH$_3$, $^1J_{CSn}$ 305/289); δ_C (125 MHz) **18** 48.8 (1-C), 47.1 (7-C), 45.8 (4-C), 41.8 (6-C), 37.9 (2-C), 34.0 (3-C), 27.8 (5-C), 20.6 and 19.8 (9-C and 10-C), 17.5 (8-C) and −8.3 (Sn–CH$_3$); *m*/*z* (EI) 287 (M$^+$ − 15, 6%), 163 (12), 136 (16), 84 (80) and 49 (100).

Methyllithium (1.0 M in THF–cumene; 0.93 cm^3, 0.93 mmol) was added to a solution of the *endo*-tin chloride **46** (100 mg, 0.31 mmol) in THF–diethyl ether (1 : 1) (2 cm^3) at 0 °C. The mixture was warmed to ambient temperature and stirred for 2.5 h before being cooled to 0 °C and quenched by the addition of water (1 cm^3). The mixture was extracted using diethyl ether (3 × 5 cm^3) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford the stannane **39** (79 mg, 84%) as a colourless oil, $[\alpha]_D$ +13.4 (*c* 1.58 in CHCl$_3$) [lit.[14] $[\alpha]_D$ +20.6 (*c* 2.54 in CHCl$_3$)]; δ_C (125 MHz) 49.0 (1-C), 48.0 (7-C, $^3J_{CSn}$ 48.8), 45.7 (4-C, $^3J_{CSn}$ 18.2), 36.8 (6-C, $^3J_{CSn}$ 41.9), 35.1 (2-C, $^1J_{CSn}$ 426/408), 32.9 (3-C), 28.5 (5-C), 19.5 and 18.8 (9-C and 10-C), 16.2 (8-C) and −9.4 [Sn–(CH$_3$)$_3$, $^1J_{CSn}$ 305/289]. All other data were consistent with the material provided by the previous synthetic route.

Methyl(diphenyl)[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]stannanes 40 and 43

Vinylstannane **36** (1.32 g, 3.12 mmol) was subjected twice to the conditions outlined in the general procedure to afford an inseparable mixture of the *title compounds* **40** and **43** (78 : 22) after preparative HPLC using hexane as the eluent (1.18 g, 89%) as a white oil, $[\alpha]_D$ +10.7 (*c* 1.54 in CHCl$_3$) (Found: M$^+$ − CH$_3$, 411.1142. $C_{22}H_{27}Sn$ requires *M*, 411.1134); ν_{max}/cm^{-1} 3063, 2948, 1480, 1428 and 1074; δ_H (500 MHz) 7.45 (4 H, m, Ar–H), 7.26 (6 H, m, Ar–H), 2.2 and 2.1 (each 1 H, m), 1.69 (2 H, m), 1.6, 1.46, 1.34 and 0.98 (each 1 H, m), 0.83, 0.78 and 0.75 (each 3 H, s, 1-CH$_3$ and 2 × 7-CH$_3$), 0.49 (2.34 H, s, $^2J_{HSn}$ 51.2/49.0, Sn–CH$_3$) and 0.43 (0.66 H, s, $^2J_{HSn}$ 46.4/44.0, Sn–CH$_3$); δ_C (125 MHz) **40** 141.5 (*ipso*-C), 141.3 (*ipso*-C), 136.7 (*ortho*-C), 128.1 and 128.3 (*meta*-C and *para*-C), 49.1 (1-C), 48.1 (7-C, $^3J_{CSn}$ 57.8), 45.5 (4-C, $^3J_{CSn}$ 20.0), 37.7 (6-C, $^3J_{CSn}$ 42.5), 36.9 (2-C, $^1J_{CSn}$ 449/428), 33.1 (3-C), 28.2 (5-C), 19.5 and 18.9 (9-C and 10-C), 16.3 (8-C) and −9.6 (Sn–CH$_3$, $^1J_{CSn}$ 314); δ_C (125 MHz) **43** 141.5 (*ipso*-C), 141.3 (*ipso*-C), 136.7 (*ortho*-C), 128.1 and 128.3 (*meta*-C and *para*-C), 48.9 (1-C), 47.4 (7-C), 46.8 (4-C), 41.5 (6-C), 38.2 (2-C), 34.2 (3-C), 27.7 (5-C), 20.8 and 19.5 (9-C and 10-C), 18.2 (8-C) and −8.1 (Sn–CH$_3$); *m*/*z* (EI) 411 (M$^+$ − 15, 3%), 349 (10), 289 (81), 197 (47), 136 (19) and 81 (100).

Dimethyl(phenyl)[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]stannanes 41 and 44

Following the above procedure, vinylstannane **37** (2.35 g, 6.51 mmol) gave, after preparative HPLC using hexane as the eluent, an inseparable mixture of the *title compounds* **41** and **44** (78 : 22) (2.27 g, 97%) as a colourless oil, $[\alpha]_D$ +6.2 (*c* 0.92 in CHCl$_3$) (Found: M$^+$ − CH$_3$, 349.0969. $C_{17}H_{25}Sn$ requires *M*, 349.0977); ν_{max}/cm^{-1} 3062, 2983, 2949, 2926, 2873, 1480, 1459, 1428, 1386, 1075 and 745; δ_H (500 MHz) 7.24 (2 H, m, Ar–H), 7.06 (3 H, m, Ar–H), 1.83 (1 H, m, 4-H), 1.49, 1.32 and 1.04 (each 2 H, m), 0.80 (1 H, m), 0.62 (6 H, s, 2 × 7-CH$_3$), 0.57 (3 H, s, 1-CH$_3$), 0.08 (3 H, s, $^2J_{HSn}$ 51.4/48.4, Sn–CH$_3$) and 0.05 (3 H, s, $^2J_{HSn}$ 50.8/48.6, Sn–CH$_3$); δ_C (125 MHz) **41** 142.5 (*ipso*-C), 135.6 (*ortho*-C, $^2J_{CSn}$ 28.1), 127.5 (*meta*-C and *para*-C), 48.5 (1-C), 47.4 (7-C, $^3J_{CSn}$ 52), 45.2 (4-C), 36.8 (6-C, $^3J_{CSn}$ 46.6), 35.5 (2-C, $^1J_{CSn}$ 437, 412), 32.4 (3-C), 27.8 (5-C), 19.0 and 18.4 (9-C and 10-C), 15.6 (8-C) and −9.8 (Sn–CH$_3$, $^1J_{CSn}$ 300, 310) and −10.3 (Sn–CH$_3$, $^1J_{CSn}$ 318, 305); δ_C (125 MHz) **44** 142.5 (*ipso*-C), 135.6 (*ortho*-C, $^2J_{CSn}$ 28.1), 127.5 (*meta*-C and *para*-C), 48.3 (1-C), 46.8 (7-C), 46.4 (4-C), 41.0 (6-C), 37.6 (2-C), 33.6 (3-C), 27.3 (5-C), 20.2 and 19.1 (9-C and 10-C), 17.3 (8-C) and −8.1 and −9.6 (2 × Sn–CH$_3$); *m*/*z* (EI) 349 (M$^+$ − 15, 9%), 227 (88), 197 (22), 136 (66) and 81 (100).

tert-Butyl(diphenyl)[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]stannanes 42 and 45

Following the above procedure, which was repeated seven times, vinylstannane **38** (600 mg, 1.3 mmol) afforded an inseparable mixture of the *title compounds* **42** and **45** (82 : 18) after preparative HPLC using hexane as eluent (402 mg, 67%) as a colourless oil, $[\alpha]_D$ +4.5 (*c* 1.72 in CHCl$_3$) (Found: M$^+$ − C(CH$_3$)$_3$, 411.1138. $C_{22}H_{27}Sn$ requires *M*, 411.1134); ν_{max}/cm^{-1} 3063, 2950, 2928, 2872, 2844, 1480, 1464, 1427, 1365 and 1071; δ_H (500 MHz) 7.33–7.64 (10 H, m, Ar–H), 2.24 (1 H, m, 4-H), 1.28–1.74 (6 H, m), 1.31 [7.4 H, s, $^3J_{HSn}$ 66.9/63.9, Sn–C(CH$_3$)$_3$], 1.26 [1.6 H, s, $^3J_{HSn}$ 65.5/62.6, Sn–C(CH$_3$)$_3$], 0.88 (1H, m) and 0.95, 0.875 and 0.865 (each 3 H, s); δ_C (125 MHz) **42** 141.3 (*ipso*-C, $^1J_{CSn}$ 375/360), 137.7 (*ortho*-C), 128.0 (*meta*-C and *para*-C), 49.0 (1-C), 48.0 (7-C, $^3J_{CSn}$ 53.4), 45.4 (4-C, $^3J_{CSn}$ 16.2), 38.04 (6-C, $^3J_{CSn}$ 31.0), 38.0 (2-C, $^1J_{CSn}$ 368/361), 33.5 (3-C), 31.0 [Sn–C(*C*H$_3$)$_3$], 28.2 (5-C), 19.7 [Sn–*C*(CH$_3$)$_3$], 19.7 and 18.9 (9-C and 10-C) and 16.7 (8-C); *m*/*z* (EI) 411 (M$^+$ − 57, 10%), 197 (25), 137 (27), 95 (32) and 81 (100).

(Dimethyl)[(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]-tin chloride 46

Tin(IV) chloride (1.0 M in dichloromethane; 6.0 cm^3, 6.0 mmol) was added to a solution of stannanes **39**–**18** (1.80 g, 6.0 mmol; **39**–**18** = 85 : 15) in dichloromethane (6 cm^3) at 0 °C. The mixture was stirred at 0 °C for 45 min before being concentrated under reduced pressure. Methyltin trichloride was then removed by sublimation by heating the residue to 60 °C under reduced pressure (1 mmHg). The remaining brown solid was crystallised

from hot hexane to afford the tin chloride **46** and its *exo*-isomer (85 : 15) (1.47 g, 76%) as a cream solid, mp 54–57 °C; $[\alpha]_D$ +3.6 (*c* 0.74 in $CHCl_3$). This mixture was repeatedly recrystallised from hexane to yield the tin chloride **46** (786 mg, 54%) as a white solid, mp 68–70 °C (lit.[14] mp 70–71 °C); $[\alpha]_D$ +19.2 (*c* 1.32 in $CHCl_3$) [lit.[14] $[\alpha]_D$ +20.5 (*c* 3.61 in $CHCl_3$)] (Found: $M^+ - CH_3$, 307.0275. $C_{11}H_{20}Sn$ requires *M*, 307.0275); ν_{max}/cm^{-1} 2976, 2952, 2929, 2874, 1459, 1450, 1387, 1095, 779 and 759; δ_H 2.22 and 2.04 (each 1 H, m), 1.83 (2 H, m), 1.71, 1.55, 1.28 and 1.1 (each 1 H, m), 0.98 (3 H, s, 1-CH_3), 0.93 and 0.92 (each 3 H, s, 2 × 7-CH_3) and 0.70 [6 H, s, $^2J_{HSn}$ 49.7, Sn–$(CH_3)_2$]; δ_C (125 MHz) 49.1 (1-C), 48.3 (7-C), 45.5 (4-C, $^3J_{CSn}$ 23.2), 44.1 (2-C), 37.9 (6-C, $^3J_{CSn}$ 57.4), 32.0 (3-C), 28.2 (5-C), 19.4 and 18.7 (9-C and 10-C), 16.2 (8-C) and −0.36 and −1.26 (2 × Sn–CH_3); *m*/*z* (EI) 307 (M^+, 10%), 287 (36), 253 (19), 185 (10), 137 (30) and 81 (100).

(Methyl)[(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]tin dichloride 47

A solution of tin chloride **46** (100 mg, 0.31 mmol) in dichloromethane (0.31 cm^3) was heated under reflux with tin(IV) chloride (1.0 M in dichloromethane; 0.31 cm^3, 0.31 mmol) for 24 h. The mixture was concentrated under reduced pressure and the methyltin trichloride removed by sublimation on heating to 60 °C under reduced pressure (1 mmHg). The residue was taken up in dichloromethane–carbon tetrachloride (2 cm^3) (1 : 1) before being treated with decolourising charcoal (20 mg). The mixture was filtered, the filtrate was concentrated and the residue was recrystallised from hexane to afford the tin dichloride **47** (92 mg, 87%) as a white solid, mp 84–86 °C (lit.[14] mp 85–86 °C); $[\alpha]_D$ +11.4 (*c* 1.30 in $CHCl_3$) [lit.[14] $[\alpha]_D$ +13.8 (*c* 5.81 in $CHCl_3$)] (Found: $M^+ + NH_4$, 360.0312. $C_{11}H_{24}Cl_2NSn$ requires *M*, 360.0307); ν_{max}/cm^{-1} 2956, 2880, 1460, 1388, 1105 and 770; δ_H 2.49–0.99 (8 H, overlapping m, 2-H, 3-H_2, 4-H, 5-H_2 and 6-H_2), 1.12 (3 H, s, $^2J_{HSn}$ 56.2/53.7, Sn–CH_3), 0.96 (3 H, s, 1-CH_3) and 0.84 (6 H, s, 2 × 7-CH_3); δ_C (125 MHz) 54.2 (2-C, $^1J_{CSn}$ 545/521), 49.5 (1-C), 48.6 (7-C, $^3J_{CSn}$ 93.9), 45.2 (4-C, $^3J_{CSn}$ 29.1), 38.9 (6-C, $^3J_{CSn}$ 72.9), 31.2 (3-C, $^2J_{CSn}$ 13.2), 27.8 (5-C), 19.4 and 18.7 (9-C and 10-C), 16.2 (8-C) and 7.5 (Sn–CH_3, $^1J_{CSn}$ 360/344); *m*/*z* (CI) 360 (M^+ + 18, 75%), 326 (25), 154 (27), 137 (62) and 102 (100).

Diphenylbis[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]stannane 48

Butyllithium (1.9 M in hexanes; 1.04 cm^3, 1.97 mmol) was added to a solution of vinyl iodide **27** (505 mg, 1.93 mmol) in THF (2 cm^3) at −78 °C. The mixture was stirred for 1 h before the addition of dichloro(diphenyl)stannane **31** (331 mg, 0.96 mmol) in THF–diethyl ether (1 : 1) (4 cm^3) *via* cannula. The solution was stirred for 1 h before the addition of methanol (3 cm^3). The solution was washed with water (3 × 5 cm^3) and the organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. Chromatography of the residue using petrol–triethylamine (100 : 1) as eluent afforded the *title compound* **48** (220 mg, 42%) as a cream coloured oil, $[\alpha]_D$ −46.5 (*c* 0.92 in $CHCl_3$) (Found: M^+, 544.2158. $C_{32}H_{40}Sn$ requires *M*, 544.2151); ν_{max}/cm^{-1} 3063, 2948, 2868, 1471, 1428, 1384, 1289 and 1074; δ_H 7.50 (10 H, m, Ar–H), 6.46 (2 H, d, *J* 3.2, $^3J_{HSn}$ 46, 2 × 3-H), 2.42 (2 H, t, *J* 3.3, 2 × 4-H), 1.89 and 1.57 (each 2 H, m), 1.15–0.96 (4 H, overlapping m) and 1.05, 0.94 and 0.82 (each 6 H, s, 2 × 1-CH_3 and 4 × 7-CH_3); δ_C 149.6, 149.5, 140.1, 137.1, 128.2, 128.1, 57.5, 56.6, 53.8, 31.3, 24.2, 19.9, 19.8 and 15.3; *m*/*z* (EI) 544 (M^+, 10%), 467 (25), 408 (44), 211 (33), 197 (25), 84 (65) and 49 (100).

(Methyl)(phenyl)[(1*R*,2*SR*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl]tin iodide 49

Iodine (120 mg, 0.47 mmol) was added to a solution of stannanes **40** and **43** (201 mg, 0.47 mmol) in dichloromethane (3 cm^3) and the mixture was stirred at ambient temperature for 20 min. The solution was concentrated under reduced pressure. The residue was distilled under reduced pressure to remove iodobenzene (bp 23–25 °C, 1 mmHg) leaving the *title compound* **49** (223 mg, >99%) as a pale yellow oil, used without further purification; ν_{max}/cm^{-1} 2981, 2950, 2873, 1479, 1458, 1428, 1388, 1072 and 751; δ_H 7.52 (2 H, m, Ar–H), 7.30 (3 H, m, Ar–H), 2.17 (1 H, m, 4-H), 1.83–1.04 (7 H, m, 2-H, 3-H_2, 5-H_2 and 6-H_2), 1.01 (3 H, s, Sn–CH_3) and 0.81 (9 H, m, 2 × 7-CH_3 and 1-CH_3); δ_C 135.6, 129.4, 128.6, 45.3, 37.6, 33.2, 27.9, 19.4, 18.6, 16.2 and −2.0; *m*/*z* (CI) 416 (M^+ + 18 − 77, 100%), 366 (35) and 137 (65).

Methyl(phenyl)[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl][(1*R*,2*RS*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]-stannane 50

Butyllithium (1.6 M in hexanes; 3.2 cm^3, 5.09 mmol) was added to a solution of vinyl iodide **27** (1.21 g, 4.63 mmol) in THF (5 cm^3) at −78 °C and the mixture was stirred for 1 h. The tin iodide **49** (2.20 g, 4.63 mmol) dissolved in THF (5 cm^3) was added *via* cannula and the solution was stirred at −78 °C for 1 h before the addition of methanol (5 cm^3). The mixture was warmed to ambient temperature and was concentrated under reduced pressure. Chromatography of the residue using petrol–triethylamine (100 : 1) as eluent afforded the *title compound* **50** (1.33 g, 60%) as a mixture of four diastereoisomers, $[\alpha]_D$ −15.9 (*c* 0.54 in $CHCl_3$) (Found: $M^+ - C_{10}H_{17}$, 347.0822. $C_{17}H_{23}Sn$ requires *M*, 347.0821); ν_{max}/cm^{-1} 3062, 3046, 2984, 2949, 2871, 1459, 1428, 1384, 1290 and 1073; δ_H 7.16–7.52 (5 H, m, Ar–H), 6.21 (1 H, d, *J* 2.9, 3′-H), 2.25 (1 H, t, *J* 3.3, 4′-H), 0.60–2.12 (12 H, m), 0.95, 0.81, 0.78, 0.76, 0.69 and 0.67 (each 3 H, s) and 0.34 (3 H, s, $^2J_{HSn}$ 49.6, Sn–CH_3); δ_C 147.4, 147.3, 142.7, 136.4, 127.9, 127.8, 57.3, 56.3, 53.7, 49.0, 48.0, 45.5, 37.1, 36.3, 33.4, 31.3, 28.4, 24.3, 19.8, 19.5, 18.8, 16.2, 15.3 and −9.3; *m*/*z* (EI) 467 (M^+ − 17, 65%), 347 (M^+ − 137, 80) and 197 (29).

Methyl(phenyl)bis[(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl]stannane 51

The stannane **50** (1.33 g, 2.75 mmol) was dissolved in 1,2-dimethoxyethane (45 cm^3) containing 4-methylbenzenesulfonyl hydrazide (6.35 g, 34.4 mmol) and the mixture was heated under reflux. Anhydrous sodium acetate (5.64 g, 68.8 mmol) dissolved in water (20 cm^3) was added dropwise over a period of 4 h. On completion of addition the mixture was heated under reflux for a further 1 h before being cooled and poured into saturated aqueous ammonium chloride (50 cm^3). The mixture was extracted using dichloromethane (3 × 75 cm^3) and the organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Chromatography of the residue through a small silica plug using petrol as eluent, followed by preparative HPLC using hexane as eluent, afforded the product **51** together with minor *exo*-diastereoisomers (1.24 g, 93%). Repeated recrystallisation using acetone yielded the *title compound* **51** (534 mg, 63%) as white crystals, mp 99–100 °C; $[\alpha]_D$ +23.6 (*c* 1.07 in $CHCl_3$) (Found: $M^+ - CH_3$, 471.2064. $C_{26}H_{39}Sn$ requires *M*, 471.2073); ν_{max}/cm^{-1} 2982, 2948, 2928, 2872, 1459 and 1386; δ_H 7.28–7.64 (5 H, m, Ar–H), 2.18 (1 H, tt, *J* 11.5, 5.7, 4-H_a), 2.04 (1 H, tt, *J* 12.4, 3.7, 4-H_b), 1.90–1.10 (14 H, m), 0.93 and 0.89 (each 6 H, s, 2 × 7-CH_3), 0.91 and 0.77 (each 3 H, s, 1-CH_3) and 0.50 (3 H, s, $^2J_{HSn}$ 47/45, Sn–CH_3); δ_C (125 MHz) 143.4 (*ipso*-C), 136.7 (*ortho*-C), 127.8 and 127.7 (*meta*-C and *para*-C), 49.3 and 49.1 (2 × 1-C), 48.2 and 48.0 (2 × 7-C), 45.6 (2 × 4-C), 37.2 and 37.1 (2 × 6-C), 33.6 and 33.3 (2 × 2-C), 28.6 (2 × 3-C), 28.1 (2 × 5-C), 19.5, 19.4 and 18.8 (2 × 9-C and 2 × 10-C), 16.2 and 16.1 (2 × 8-C) and −9.0 (Sn–CH_3); *m*/*z* (EI) 471 (M^+, 13%), 409 (4), 349 (10), 197 (42), 137 (53) and 81 (100).

(1*R*,4*R*)-1-[(Dimethylamino)methyl]-7,7-dimethylbicyclo[2.2.1]-heptan-2-one hydrazone 53

Keto-amide **52**[22] (1.01 g, 5.1 mmol) was dissolved in di(ethyleneglycol)–ethanol (5 : 1) (6 cm^3). Hydrazine hydrate (0.69 cm^3, 22.1 mmol) was added and the mixture was heated under reflux for 18 h. After cooling to ambient temperature the mixture was extracted using hexane–benzene (1 : 1) (3 × 10 cm^3). The combined organic layers were extracted using cold hydrochloric acid (3.5 M, 3 × 10 cm^3) and the combined aqueous layers were immediately added to a mixture of 10% aqueous sodium bicarbonate (10 cm^3) and hexane–benzene (1 : 1) (8 cm^3). The pH of the mixture was adjusted to pH ≈ 14 before extraction using hexane–benzene (1 : 1) (2 × 10 cm^3). The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to yield the *title compound* **53** (535 mg, 50%) as a brown oil, used without further purification, $[\alpha]_D$ +5.5 (*c* 1.38 in $CHCl_3$) (Found: M^+, 209.1893. $C_{12}H_{23}N_3$ requires *M*, 209.1892); ν_{max}/cm^{-1} 3360, 2963, 2882, 2816, 2763, 1664, 1452, 1386, 1370, 1296, 1263, 1096, 1039, 1027, 842 and 797; δ_H 4.75 (2 H, br s, NH_2), 2.64 [1 H, d, *J* 14.0, C*H*HN(CH_3)$_2$], 2.31 (6 H, s, 2 × NCH_3), 2.29 (2 H, m), 2.08 (1 H, m), 1.9 (2 H, m), 1.74 [1 H, d, *J* 16.5, CH*H*N(CH_3)$_2$], 1.5 and 1.21 (each 1 H, m) and 1.01 and 0.79 (each 3 H, s, 7-CH_3); δ_C 163.7, 57.1, 55.2, 48.6, 48.3, 44.0, 32.2, 28.1, 27.3, 19.8 and 19.6; *m*/*z* (CI) 210 (M^+ + 1, 100%) and 193 (13).

***N,N*-Dimethyl-[(1*R*,4*R*)-2-iodo-7,7-dimethylbicyclo[2.2.1]hept-2-en-1-yl]methylamine 54**

Hydrazone **53** (1.68 g, 8.0 mmol) was dissolved in diethyl ether (10 cm^3) containing tetramethylguanidine (3.50 cm^3, 28.0 mmol). A solution of iodine (4.27 g, 16.8 mmol) in diethyl ether (80 cm^3) was added dropwise over 15 min. On completion of addition the mixture was stirred for a further 15 min before being washed with dilute hydrochloric acid (3.5 M, 3 × 50 cm^3), saturated aqueous sodium thiosulfate (3 × 50 cm^3) and saturated aqueous sodium bicarbonate (3 × 50 cm^3). The pH of the solution was adjusted to pH 14 using aqueous sodium carbonate solution, and the organic phase was dried over magnesium sulfate, filtered and concentrated under reduced pressure. Chromatography of the residue, using petrol–diethyl ether (8 : 1) as eluent, afforded the *title compound* **54** (472 mg, 19%) as a pale yellow oil, $[\alpha]_D$ +1.3 (*c* 0.92 in $CHCl_3$) (Found: M^+, 305.0643. $C_{12}H_{20}IN$ requires *M*, 305.0642); ν_{max}/cm^{-1} 2950, 2875, 2817, 2764, 1453, 1285, 1035 and 812; δ_H 6.47 (1 H, d, *J* 3.4, 3-H), 2.59 and 2.44 [each 1 H, d, *J* 14.2, C*H*HN(CH_3)$_2$], 2.37 [6 H, s, N(CH_3)$_2$], 2.34 (1 H, m, 4-H), 1.88 and 1.07 (each 2 H, m) and 0.98 and 0.97 (each 3 H, s, 2 × 7-CH_3); δ_C 144.4, 104.0, 60.3, 59.9, 56.4, 55.3, 48.4, 26.9, 24.9, 20.4 and 19.9; *m*/*z* (CI) 306 (M^+ + 1, 100%).

***N,N*-Dimethyl-{(1*R*,4*R*)-2-[dimethyl(phenyl)stannyl]-7,7-dimethylbicyclo[2.2.1]hept-2-en-1-yl} methylamine 56**

Butyllithium (1.6 M in hexanes; 0.50 cm^3, 0.79 mmol) was added to a solution of vinyl iodide **54** (220 mg, 0.72 mmol) in THF (2 cm^3) at −78 °C. The mixture was stirred for 1.5 h before a solution of the phenyl(dimethyl)tin iodide **33** (280 mg, 0.79 mmol) in THF (2 cm^3) was added *via* cannula. The reaction mixture was stirred at −78 °C for 1 h before being quenched by addition of methanol (2 cm^3). The mixture was washed with water (3 × 3 cm^3) and the organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. Chromatography of the residue using petrol–diethyl ether–triethylamine (80 : 20 : 1) gave the *title compound* **56** (179 mg, 66%) as a yellow oil, $[\alpha]_D$ −48.9 (*c* 0.92 in $CHCl_3$) (Found: M^+ − CH_3, 390.1246. $C_{19}H_{28}NSn$ requires *M*, 390.1243); ν_{max}/cm^{-1} 3061, 2984, 2949, 2871, 1454, 1428, 1029, 1010 and 747; δ_H 6.98–7.24 (5 H, m, Ar–H), 5.94 (1 H, d, *J* 3.0, $^3J_{HSn}$ 47, 3-H), 2.28 [1 H, d, *J* 12.6, CHHN(CH_3)$_2$], 2.02 (1 H, t, *J* 3.3, 4-H), 1.77 [6 H, s, N(CH_3)$_2$], 1.69 [1 H, d, *J* 12.4, CH*H*N(CH_3)$_2$], 1.55, 1.33, 0.93 and 0.67 (each 1 H, m), 0.61 and 0.52 (each 3 H, s), 0.03 (3 H, s, $^2J_{HSn}$ 56.4/54.0, Sn–CH_3) and 0.00 (3 H, s, $^2J_{HSn}$ 55.9/53.4, Sn–CH_3'); δ_C 149.2, 147.2, 144.7, 135.9, 127.6, 127.4, 65.8, 60.3, 60.0, 57.3, 53.6, 48.2, 30.9, 24.3, 20.4, 20.3, −8.9 and −9.0; *m*/*z* (EI) 390 (M^+ − 15, 26%), 328 (14), 135 (18), 84 (43), 58 (49) and 49 (100).

***N,N*-Dimethyl-{(1*R*,4*R*)-2-[dimethyl(phenyl)stannyl]-7,7-dimethylbicyclo[2.2.1]hept-2-yl}methylamine 57**

The vinyl stannane **56** (173 mg, 0.5 mmol) was dissolved in 1,2-dimethoxyethane (8 cm^3) containing 4-methylbenzenesulfonyl hydrazide (1.07 g, 5.7 mmol) and the mixture was heated under reflux. Anhydrous sodium acetate (0.95 g, 11.6 mmol) dissolved in water (2 cm^3) was added over a period of 4 h. On completion of addition the mixture was heated under reflux for a further 1 h before being cooled and poured into saturated aqueous ammonium chloride (5 cm^3). The mixture was extracted using dichloromethane (3 × 10 cm^3) and the organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Chromatography of the residue through a small silica plug using petrol as eluent afforded the *title compound* **57** (15 mg, 9%) as a colourless oil (Found: M^+ + H, 408.1711. $C_{20}H_{34}NSn$ requires *M*, 408.1712); ν_{max}/cm^{-1} 3062, 2955, 2923, 2871, 2853, 1428 and 1075; *m*/*z* (CI) 408 (M^+ + H, 6%), 306 (13), 244 (88), 224 (100) and 207 (78).

(Dimethyl)[(1*R*,2*SR*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]tin iodide 58

A mixture of the *endo*- and *exo*-stannanes **41**–**44** (78 : 22) (257 mg, 0.71 mmol) was dissolved in dichloromethane (2 cm^3). Iodine (180 mg, 0.71 mmol) was added and the mixture was stirred at ambient temperature for 3 h before being concentrated under reduced pressure. Iodobenzene (bp 23–25 °C, 1 mmHg) was removed by distillation under reduced pressure to afford the *title compound* **58** (275 mg, 94%) (*endo*–*exo* 78 : 22) as a white solid, mp 61–63 °C; $[\alpha]_D$ +7.4 (*c* 0.9 in $CHCl_3$); (Found: M^+, 413.9867. $C_{12}H_{13}ISn$ requires *M*, 413.9867); ν_{max}/cm^{-1} 2973, 2948, 2926, 2872, 1458 and 752; δ_H 2.2–1.10 (7 H, m), 1.0 (3 H, s) and 0.94 (13 H, m); δ_C 49.5, 48.7, 45.3, 43.2, 37.2, 33.0, 28.1, 19.4, 18.6, 16.2 and −1.3; *m*/*z* (EI) 414 (3%), 399 (M^+ − 15, 6), 287 (35), 247 (21), 137 (48) and 81 (100).

Dimethyl[(1*R*,2*SR*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]-tin hydride 59

The tin iodide **58** (1.14 g, 2.8 mmol) was taken up in ethanol (7 cm^3) and the solution cooled to 0 °C. Sodium borohydride (240 mg, 5.6 mmol) was added portionwise, and the mixture was stirred for 10 min before the addition of water (3 cm^3). The mixture was extracted using diethyl ether (3 × 10 cm^3) and the combined organic extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Chromatography of the residue using petrol–triethylamine (100 : 1) afforded the *title compound* **59** (621 mg, 78%) (*endo*–*exo* 78 : 22) as a colourless oil, $[\alpha]_D$ −7.5 (*c* 0.98 in hexane) (Found: M^+ − H, 287.0813. $C_{12}H_{23}Sn$ requires *M*, 287.0821); ν_{max}/cm^{-1} 2983, 2948, 2928, 2874, 1816, 1479, 1459, 1386, 1372, 1097, 761 and 707; δ_H (C_6D_6) 5.02 (0.2 H, br, Sn–H), 4.89 (0.8 H, br, Sn–H), 1.96–0.96 (7 H, 3-H_2, 4-H, 5-H_2 and 6-H_2), 0.77 (1 H, m, 2-H), 0.73 (6 H, s, 2 × 7-CH_3), 0.72 (3 H, s, 1-CH_3) and 0.06 (6 H, m, 2 × –$SnCH_3$); δ_C (C_6D_6) 48.6, 47.5, 45.8, 36.4, 34.2, 33.4, 28.4, 19.4, 18.5, 15.8, −12.0 and −12.5; *m*/*z* (EI) 287 (M^+ − 1, 49%), 273 (84), 205 (44), 136 (51) and 81 (100).

(Methyl)bis[(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]-tin hydride 61

Iodine (100 mg, 0.63 mmol) was added to a solution of stannane

51 (305 mg, 0.63 mmol) in dichloromethane (2 cm^3) at ambient temperature. The solution was stirred for 20 min before being concentrated under reduced pressure. The residue was taken up in ethanol–diethyl ether (2 : 1) (6 cm^3) and the solution cooled to 0 °C. Sodium borohydride (100 mg) was added over 10 min and the solution was stirred at 0 °C for 10 min then water (2 cm^3) was added. The mixture was allowed to warm to ambient temperature and was extracted using diethyl ether (3 × 5 cm^3). The organic extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Column chromatography of the residue using petrol as the eluent afforded the *title compound* **61** (246 mg, 96%) as a colourless oil, $[\alpha]_D$ +39.3 (*c* 1.4 in hexane) (Found: $M^+ - H$, 409.1917. $C_{21}H_{37}Sn$ requires *M*, 409.1916); ν_{max}/cm^{-1} 2982, 2948, 2928, 2873, 1801, 1478, 1459, 1386, 1371 and 738; δ_H (C_6D_6) (500 MHz) 5.26 (1 H, m, $^1J_{HSn}$ 1566/1500, Sn–H), 2.14–0.72 (16 H, m, 2 × 2-H, 2 × 3-H_2, 2 × 4-H, 2 × 5-H_2 and 2 × 6-H_2), 0.94, 0.870, 0.867, 0.85, 0.84 and 0.83 (each 3 H, 2 × CH_3 and 4 × 7-CH_3) and 0.29 (3 H, d, *J* 2.4, Sn–CH_3); δ_C (C_6D_6) (125 MHz) 8.8 and 48.7 (2 × 1-C), 47.6 and 47.5 (2 × 7-C), 45.9 and 45.8 (2 × 4-C), 36.8 and 36.7 (2 × 6-C), 34.5 and 33.4 (2 × 2-C), 29.8 (2 × 3-C), 28.6 and 28.4 (2 × 5-C), 19.5, 19.4, 18.6 and 18.5 (2 × 9-C and 2 × 10-C), 15.9 and 15.7 (2 × 8-C) and −11.9 (Sn–CH_3); *m*/*z* (CI) 427 ($M^+ - 1$, + 18, 100%), 409 (12) and 137 (23).

Crystal data § for (dimethyl)[(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo-[2.2.1]hept-2-yl]tin chloride 46

$C_{12}H_{23}ClSn$, *M* = 321.46, monoclinic, *a* = 6.696(7), *b* = 10.816(8), *c* = 9.659(7) Å, *U* = 698(1) $Å^3$, *T* = 296(1) K, space group $P2_1$ (#4), *Z* = 2, $\mu_{Mo\text{-}K\alpha}$ = 2.00 mm^{-1}; 1406 reflections measured, 1291 unique (R_{int} = 0.095); Flack parameter = 0.12 (6). The final R_ω on *F* = 0.042 [based on 971 reflections with $I > 2.00\sigma(I)$].

Crystal data § for methyl(phenyl)bis[(1*R*,2*S*,4*R*)-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-yl]stannane 51

$C_{27}H_{42}Sn$, *M* = 485.32, orthorhombic, *a* = 10.072(2), *b* = 25.978(3), *c* = 9.617(2) Å, *U* = 2516.2(6)$Å^3$, *T* = 296(1) K, space group $P2_12_12_1$ (#19), *Z* = 4, $\mu_{Cu\text{-}K\alpha}$ radiation = 8.30 mm^{-1}, Flack parameter = 0.019(5), 2769 reflections measured, final R_ω on *F* = 0.028 [based on 2438 reflections with $I > 2.00\sigma(I)$].

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