Synthesis of chiral organotin reagents: synthesis of diphenyl-{(1*S*,2*R*,3*S*,4*R*)-3-(alkoxymethyl)bicyclo[2.2.1]heptan-2-yl}tin hydrides. X-Ray crystal structure of (*R*)-4,4-dimethyl-2-oxotetrahydrofuran-3-yl (1*S*,2*S*,3*R*,4*R*)-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate

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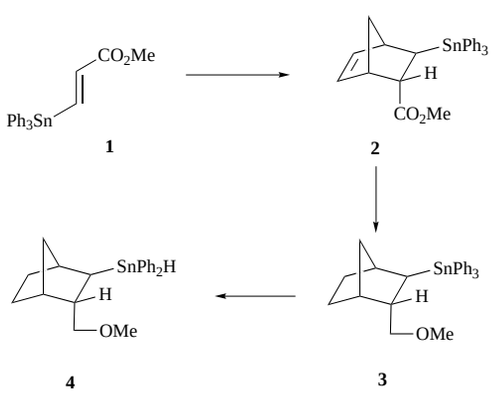
Conditions have been developed for the stereoselective Diels–Alder addition of cyclopentadiene to (*R*)-4,4-dimethyl-2-oxotetrahydrofuran-3-yl (*E*)-3-triphenylstannylprop-2-enoate 10 to give the *endo*-adduct 14 whose structure has been confirmed by X-ray crystallography. The adduct 14 is converted into (1*S*,2*R*,3*S*,4*R*)-3-hydroxymethylbicyclo[2.2.1]heptan-2-yl(triphenyl)stannane 22 which is shown to have an enantiomeric excess (ee) of 94%. This alcohol has been converted into its methyl ether (−)-3, trityl ether 25, *tert*-butyldimethylsilyl ether 26 and 1-naphthoate 27 which give the tin hydrides 4, 31–34 on treatment with iodine and sodium borohydride. Aspects of the chemistry of these enantiomerically enriched tin hydrides are briefly discussed.

In the preceding paper, a synthesis of the racemic bicyclo[2.2.1]heptan-2-yltin hydride **4** is reported.[1] The key step in this synthesis is the Diels–Alder reaction between methyl (*E*)-3-(triphenylstannyl)acrylate **1** and cyclopentadiene which gives the *endo*-adduct **2** with excellent stereoselectivity. This adduct is reduced, *O*-methylated and hydrogenated to give the 2-methoxymethylbicycloheptanyl(triphenyl)stannane **3** which is converted into the tin hydride **4** by treatment with iodine followed by reduction with sodium borohydride. The tin hydride **4** was found to reduce alkyl halides and to add to methyl propiolate under free-radical conditions.[1] We now report a synthesis of enantiomerically enriched tin hydrides including **4** using stereoselective Diels–Alder reactions of chiral 3-triphenylstannylacrylates.

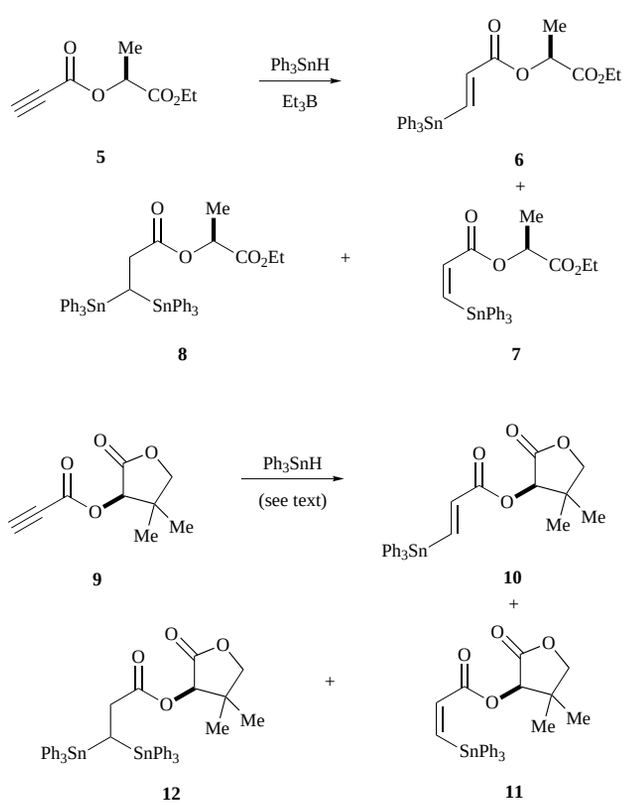


1 **2** **4** **3**

Results and discussion

Many procedures have been developed for the asymmetric synthesis of bicyclo[2.2.1]hept-5-enes by Diels–Alder reactions of cyclopentadiene and acrylates using both chiral auxiliaries and chiral, non-racemic Lewis acids as catalysts.[2,3] It was decided to investigate the use of chiral auxiliaries for the asymmetric synthesis of the ester **2** since it was not clear which Lewis acids would be compatible with the vinylstannane component of the dienophile. Since attempts to hydrolyse methyl (*E*)-3-(triphenylstannyl)propenoate **1** to the corresponding acid were unsuccessful, perhaps because the vinylstannane is incompatible with the carboxylic acid functionality, it was decided to prepare the chiral dienophiles by esterification of propiolic acid using chiral, non-racemic alcohols followed by conjugate addition of the triphenyltin moiety.[4,5]

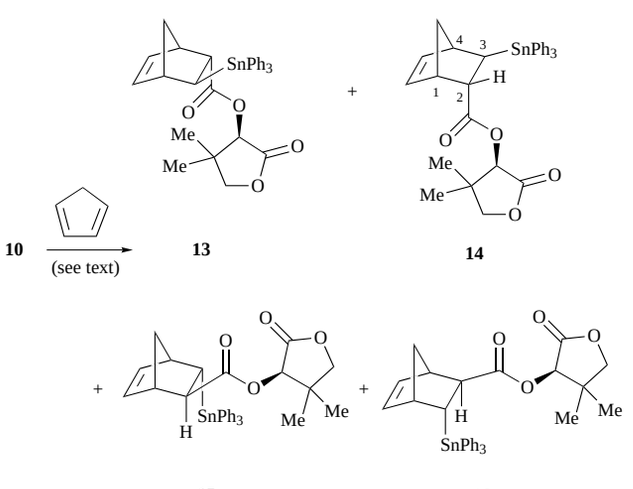
Propiolic acid was esterified using (*S*)-ethyl lactate and (*R*)-pantolactone to give the esters **5** and **9** using *N*,*N*-diisopropylcarbodiimide with a catalytic amount of 4-dimethylaminopyridine as the coupling reagent.[6] Hydrostannation of the ester **5** using triphenyltin hydride under free-radical conditions initiated by triethylborane[7] gave the (*E*)- and (*Z*)-3-(triphenylstannyl)acrylates **6** and **7** together with the 3,3-bis(triphenyl-



5 **6** **8** **7** **9** **10** **12** **11**

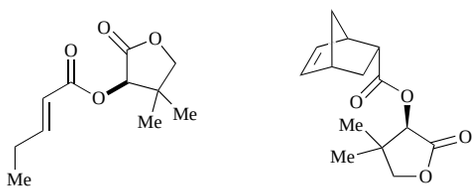
stannyl)propanoate **8** which were isolated in yields of 13, 30 and 25% using 1.2 mol equiv. of tin hydride. No attempt was made to improve this synthesis of the (*E*)-ester **6**. Hydrostannation of the pantolactone-derived ester **9** under free-radical conditions gave the (*E*)- and (*Z*)-vinylstannanes **10** and **11** in yields of 25 and 32%, respectively, using azoisobutyronitrile as the initiator in benzene heated under reflux,[8] and yields of 23 and 44% using triethylborane at room temperature.[7] The (*Z*)-isomer **11** is believed to be the predominant kinetic product in these reactions, partial isomerisation to the more stable (*E*)-isomer **10** taking place under the free-radical conditions.[9] The triphenyltin cuprate, $LiCuBr(Ph_3Sn)\cdot Me_2S$, which was prepared using either Ph_3SnCl–Li or Ph_3SnH–lithium diisopropylamide to generate the triphenyltin lithium, reacted with the propiolate **9** to give modest yields of the (*E*)- and (*Z*)-vinylstannanes **10** and **11**.[10–12] The cuprate reagents prepared from lithium bromide, copper(I) bromide, and either 1 or 2 mol equiv. of triphenyltin lithium, *i.e.* with no dimethyl sulfide present, gave similar results.[13] Better stereoselectivity, *ca*. 25:1, in favour of the (*E*)-vinylstannane **10** was obtained using 2 mol equiv. of the cuprate reagent prepared from lithium iodide, copper(I) iodide, and triphenyltin lithium [13] if the reaction was quenched by addition to a solution of glacial acetic acid in tetrahydrofuran at −78 °C. However, the yield was only modest being *ca*. 30% for larger scale reactions with 15% of the bis-adduct **12** also being obtained. The use of less than 2 mol equiv. of the reagent reduced the amount of bis-adduct **12** but gave a lower yield of the required (*E*)-vinylstannane **10**.

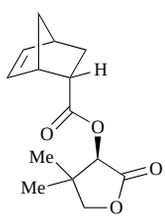
Diels–Alder reactions between cyclopentadiene and the lactate-derived (*E*)-vinylstannane **6** were carried out in benzene heated under reflux but gave mixtures of all four *endo*- and *exo*-products which could not be separated. From the ^{1}H NMR spectra of crude mixtures of products, the *endo*:*exo* selectivity was estimated to be 90:10, with a diastereoisomeric excess in the *endo*-manifold of 30%. The Diels–Alder reaction between the pantolactone-derived (*Z*)-vinylstannane **11** and cyclopentadiene in benzene heated under reflux similarly gave an inseparable mixture of all four stereoisomeric products with an *endo*:*exo* ratio of *ca*. 30:70. However, the *endo*-products **13**



and **14** from the Diels–Alder reactions between the (*E*)-vinylstannane **10** and cyclopentadiene could be separated and were isolated in yields of 56 and 19%, respectively, the *endo*–*exo* stereoselectivity being *ca*. 90:10 in favour of the *endo*-isomers **13** and **14** over the *exo*-isomers **15** and **16** which were never isolated in sufficient quantity to permit their characterisation.

The effect of Lewis acid catalysts on the stereoselectivity of the Diels–Alder reaction between the vinylstannane **10** and cyclopentadiene was investigated.[5] No product was isolated from reactions catalysed by titanium(IV) chloride, boron trifluoride–diethyl ether or boron trichloride. It may be that the vinylstannane is unstable in the presence of these strong Lewis acids. With zinc(II) chloride or bromide or with tin(IV) chloride or bromide, only modest conversion into products was observed at temperatures in the range −20 to −55 °C. However, good conversion into products was found using aluminium trichloride or diethylaluminium chloride at temperatures in the range −20 to −78 °C.[5,14] Optimum results were obtained using 2 mol equiv. of diethylaluminium chloride at −50 °C for 19 h when the *endo*:*exo* selectivity was >98:2 and the ratio of the separable *endo*-adducts **13** and **14** was 10:90 leading to an isolated yield of the *endo*-adduct **14** of 63%. Reactions carried out at lower temperatures tended not to go to completion and the use of more than 2 mol equiv. of diethylaluminium chloride led to lower yields with the formation of a side-product identified as the pentenoate **17**. Note, that within the *endo*-manifold the diastereofacial selectivity of addition to the vinylstannane **10** under Lewis acid-promoted conditions is the reverse of that observed under thermal conditions.





The *endo*-structures **13** and **14** were assigned to the major Diels–Alder products from the reactions between the pantolactate **10** and cyclopentadiene by analogy with the reaction of the methyl ester **1** and cyclopentadiene and were consistent with spectroscopic data.[1] For example, in the ^{1}H NMR spectrum of the adduct **14**, the *endo*-3-hydrogen showed a 4-bond 'W'-coupling to the 7-hydrogen which is *syn* to the double bond (2 Hz) but was not coupled to the bridgehead 4-hydrogen whereas the *exo*-2-hydrogen was coupled to the bridgehead 1-hydrogen (3.5 Hz) but not to the *syn*-7-hydrogen. An NOE enhancement of the *exo*-2-hydrogen, but not of the *endo*-3-hydrogen, was also observed on irradiation of the 7-hydrogen *anti* to the double bond, and *vice versa*. The *exo*-orientation of the triphenylstannyl moiety in the adducts **13** and **14** was also supported by ^{13}C NMR data, specifically by comparison of the ^{13}C-$^{119/117}$-Sn coupling constants with those reported for *exo*- and *endo*-2-trimethylstannylbicyclo[2.2.1]heptanes.[15,16]

Full stereochemical assignments were made to the *endo*-products **13** and **14** by analogy with the diethylaluminium chloride-catalysed Diels–Alder reaction between cyclopentadiene and the acrylate ester of pantolactone which is known to give the adducts **18** and **19**, ratio 17:83, with an *endo*–*exo* stereoselectivity of 98:2.[5] A comparison of the ^{1}H NMR chemical shifts of the vinylic protons for the adducts **13** and **14** with those reported for **18** and **19** was consistent with this assignment. The structure **14** assigned to the major *endo*-Diels–Alder adduct obtained from the Lewis acid-catalysed reactions was also consistent with an X-ray crystal structure determination. Fig. 1 shows a projection of the major *endo*-adduct **14** from the diethylaluminium chloride-catalysed reaction as established by the X-ray crystal structure determination.

The *endo*-adduct **14** could, therefore, be conveniently prepared using the diethylaluminium chloride-catalysed reaction

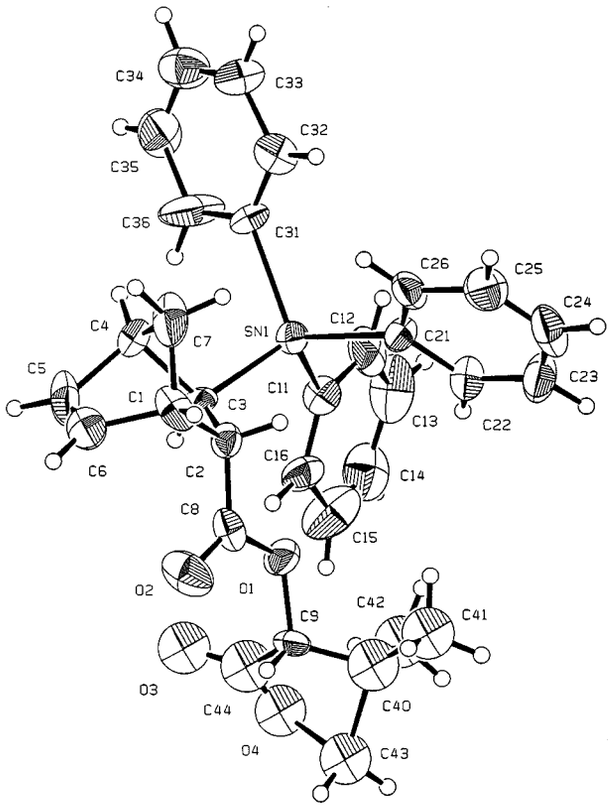
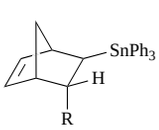


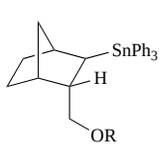
Fig. 1 A projection of a molecule of the Diels–Alder adduct **14** as established by X-ray diffraction

between the pantolactate **10** and cyclopentadiene. The adduct **14** is the predominant diastereoisomer from these reactions and can be isolated in yields in the range 60–65%.

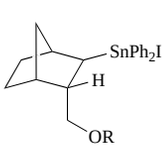
Several procedures were investigated for removing the chiral auxiliary from the adduct **14**. Reduction using diisobutylaluminium hydride gave the alcohol **20** and treatment with an excess of sodium methoxide effected efficient transesterification and gave the laevorotatory enantiomer of the methyl ester **2**.[1] However, saponification using lithium hydroxide in aqueous tetrahydrofuran gave only a low yield of the carboxylic acid **21**. Once again a triphenylstannyl group would appear to be incompatible with a carboxylic acid functionality in the same molecule.



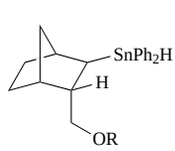
20 R = CH_2OH
(–)-2 R = CO_2Me
21 R = CO_2H



22 R = H
23 R = (*R*)-Ph(CF_3)C(OMe)CO
24 R = (*S*)-Ph(CF_3)C(OMe)CO
(–)-3 R = Me
25 R = CPh_3
26 R = $SiMe_2Bu^t$
27 R = 1-$C_{10}H_9CO$



28 R = H
29 R = CPh_3
30 R = 1-$C_{10}H_9CO$



31 R = H
32 R = CPh_3
33 R = 1-$C_{10}H_9CO$
4 R = Me
34 R = $SiMe_2Bu^t$

The alcohol **20** was hydrogenated to give the saturated alcohol **22** and the optical purity of this alcohol checked by comparison of the ^1H and ^{19}F NMR spectra of its (*R*)- and (*S*)-Mosher's derivatives **23** and **24** which were prepared in yields of ⩾98%.[17] The optical purity of the alcohol **22** was found to correspond to an enantiomeric excess of 94% since in the ^{19}F spectra of **23** and **24** signals were observed at δ −73.19 and −73.29, ratio 98:2, and at δ −73.21 and −73.31, ratio 4:96, respectively.

The alcohol **22** was now converted into several derivatives which had groups on oxygen with different steric and electronic requirements. These were to be taken through to provide a series of enantiomerically enriched tin hydrides for provisional evaluation as chiral reagents for asymmetric synthesis.

The alcohol **22** was converted into its methyl ether (−)-**3**, trityl ether **25**, *tert*-butyldimethylsilyl ether **26** and 1-naphthoate **27** using standard techniques. The hydroxyalkyl(triphenyl)stannane **22** and each of its derivatives (−)-**3** and **25**–**27** were then converted into tin hydrides using the procedures developed for the synthesis of the racemic tin hydride **4**, *i.e.* treatment with 1 mol equiv. of iodine to remove one of the phenyl groups from the tin to generate an alkyl(diphenyl)tin iodide which gave the tin hydride on reduction using sodium borohydride.[1] The tin iodides **28**, **29** and **30** from the alcohol **22**, trityl ether **25**, and naphthoate **27**, were isolated and characterised before reduction to the tin hydrides **31**–**33**. However, the iodides from the methyl and *tert*-butyldimethylsilyl ethers (−)-**3** and **26** were not purified being, instead, reduced directly to the corresponding tin hydrides **4** and **34**. All the tin hydrides were fully characterised.

The structures of the tin iodides and hydrides were consistent with their spectroscopic data. Of interest is the possibility of coordination of the tin atoms in these compounds by the heteroatom functionality, particularly for the tin iodides **28**–**30**.[18,19] The one-bond, Sn–C(2) coupling constants as measured in the ^{13}C NMR spectra of the trityl and naphthoyl tin iodides **29** and **30** were found to be similar to those of the parent triphenyltin compounds **25** and **27**, *i.e.* the one-bond coupling constants $^1J_{^{13}C(2)^{119/117}Sn}$ for **29** and **30** were 422/404 and 415/393 Hz *cf.* 424/406 and 418/399 Hz, respectively, for the triphenylstannanes **25** and **27**. These data suggest that the oxygen atoms of the heteroatom substituents in the tin iodides **29** and **30** are not coordinated to the tin atom since an increase in the coordination number at the tin from four to five would be expected to result in a significant increase in this one-bond coupling.[16,18] Moreover, the X-ray crystal structure of the Diels–Alder adduct **14**, see Fig. 1, shows that in the solid state the tin is tetrahedral and not coordinated by any of the oxygens.

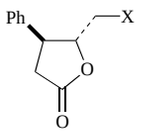
For the hydroxyalkyltin iodide **28** the one-bond tin–carbon coupling constants $^1J_{^{13}C(2)^{119/117}Sn}$ at 440/418 Hz are slightly larger than those of the parent triphenylstannane **22** at 421/403 Hz. However, this increase is very small and may be due to fast equilibration of the hydroxyalkyltin iodide **28** with a small amount of a dimeric, five-coordinated tin species in solution.

This lack of coordination of the tin by the oxygenated functional groups in the tin iodides **28**–**30** may be a consequence of the *trans*-disposition of the stannyl and alkoxymethyl substituents about the bicycloheptyl framework.[18,19] A comparison with their *cis*-substituted stereoisomers would be of interest.

Coordination of the tin by the ester and alkoxy groups is less likely for the tin hydrides.[18,19] The one-bond, tin–carbon coupling constants $^1J_{^{13}C(2)^{119/117}Sn}$ measured for the 3-(hydroxymethyl)- and 3-(methoxymethyl)-bicycloheptyltin hydrides **31** and **4** at 430/410 and 427/408 Hz are indeed consistent with four-coordinated tin in these compounds. In their IR spectra, the C=O stretching frequencies of the naphthoate esters **27**, **30** and **33** were all in the range 1713–1714 cm^{-1} consistent with no significant coordination of the tin by the carbonyl oxygen in these compounds.

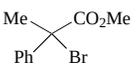
The phenyl groups attached to the tin in the iodides **28**–**30**

and the hydrides **4**, **31**–**34** are diastereotopic. However, triorganotin halides are known to be configurationally unstable on the NMR timescale,[20] and only one set of peaks was observed for the aromatic carbons in the ^{13}C NMR spectra of the iodides **28**–**30**. In contrast, the two phenyl rings in the tin hydrides **31**, **34** and **4**, for which ^{13}C NMR data are available, did give rise to different resonances for the *ipso* carbons of the phenyl substituents at δ 138.7/138.8, 138.6/138.65 and 138.8/138.9, respectively. It would appear that the chiral tin atoms of these tin hydrides are configurationally stable on the NMR timescale.[20,21] The one-bond, tin–hydrogen coupling constants, $^{1}J_{H^{119/117}Sn}$, were measured for the tin hydrides **4**, **31**–**33** using the tin satellites in the ^{1}H NMR spectra, and were in the range 1763–1791/1681–1711 Hz as expected.[22]



35 X = I

36 X = H



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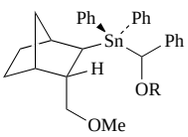
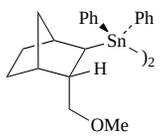


38 R = H

39 R = Ac



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Preliminary investigations were carried out into the chemistry of the tin hydrides **4**, **31**–**34**. The 5-iodomethylbutyrolactone **35** was reduced to the 5-methylbutyrolactone **36** using catalytic quantities (20 mol%) of the hydroxy- and methoxy-alkyltin hydrides **31** and **4** with triethylborane initiation[23] in the presence of sodium borohydride[24] as the stoicheiometric reducing agent (60–70%). However, triethylborane-initiated reduction of methyl 2-bromo-2-phenylpropanoate **37** using catalytic amounts (20 mol%) of the bicycloheptanyl(diphenyl)tin iodides **28**–**30** with sodium borohydride as the stoicheiometric reducing agent gave only racemic methyl 2-phenylpropanoate (41–65%). Reduction of the bromo ester **37** using catalytic quantities of the tin hydrides **4** and **34** gave only racemic 2-phenylpropanol after reduction of the ester using lithium aluminium hydride. The addition of the lithiated stannane formed by deprotonation of the methoxyalkyltin hydride **4** by lithium diisopropylamide to benzaldehyde was not stereoselective and gave a 60% yield of a 1:1 mixture of the adducts **38**, characterised as their acetates **39**, together with a small amount of the distananne **40**.

Conclusions

This work has resulted in an asymmetric synthesis of bicyclo[2.2.1]heptan-2-yltin hydrides using Diels–Alder chemistry and confirms that the selective cleavage of a (triphenyl)-stannane by iodine followed by reduction of the tin iodide so obtained using sodium borohydride provides a reliable route to structurally complex tin hydrides. The most difficult step in this synthesis is the conjugate addition of the triphenylstannyl moiety to the propiolate **9**, and this, at present, restricts the amount of material which can be prepared. The bicycloalkyltin hydrides reported in this paper would appear to act as reducing agents for alkyl halides with only catalytic quantities of the tin hydrides being required. However the products obtained to date from the chiral bromide **37** were found to be racemic, although it may be that racemisation of the initially formed product under the free-radical conditions of the reactions is at least partially responsible for this. Nevertheless, the development of an effective tin hydride for the stereoselective transfer of a hydrogen atom to a prochiral radical may well require a tin hydride with more bulky substituents than those reported here since steric factors will have to be instrumental in controlling the stereoselectivity. For the catalytic asymmetric reduction of ketones, tin hydrides in which the tin is trigonal bipyramidal, at least in the transition structure for hydride transfer, due to coordination of a heteroatom, may be preferred since the direction of hydride transfer will be predictable.[25] Approaches to the synthesis of enantiomerically enriched tin hydrides containing suitably positioned functional groups based on the bicyclo[2.2.1]heptane framework are reported in the following paper.[26]

Experimental

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

(*S*)-1-(Ethoxycarbonyl)ethyl propiolate 5

A solution of dicyclohexylcarbodiimide (5.60 g, 27.1 mmol) and 4-dimethylaminopyridine (220 mg, 1.8 mmol) in dichloromethane (15 cm^3) was added to a solution of propiolic acid (1.85 g, 26.4 mmol) and ethyl (*S*)-lactate (2.84 g, 24 mmol) in dichloromethane (15 cm^3) at −25 °C. The mixture was stirred at −25 °C for 1 h and then at room temperature for 17 h, after which it was filtered. The filter was washed with dichloromethane (4 × 15 cm^3) and filtrate concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:3) as eluent gave the *title compound* **5** (1.97 g, 48%) as an oil, $[a]_D$ −23.9 (*c* 0.8, CH_2Cl_2) (Found: M + NH_4^+, 188.0925. $C_8H_{14}NO_4$ requires *M*, 188.0923); ν_{max}/cm^{-1} 3262, 2121, 1723, 1451, 1096 and 760; δ_H 1.26 (3 H, t, *J* 7, OCH_2CH_3), 1.50 (3 H, d, *J* 7, 2′-H_3), 2.96 (1 H, s, 3-H), 4.20 (2 H, q, *J* 7, OCH_2CH_3) and 5.14 (1 H, q, *J* 7, 1′-H); δ_C 61.7, 61.8, 70.2, 70.3, 74.1, 75.1, 151.7 and 169.3; *m*/*z* 188 (M^+ + 18, 100%).

(*R*)-4,4-Dimethyl-2-oxotetrahydrofuran-3-yl propiolate 9

A solution of diisopropylcarbodiimide (15.58 g, 123.5 mmol) and 4-dimethylaminopyridine (1.01 g, 8.27 mmol) in dichloromethane (270 cm^3) was added to a solution of propiolic acid (8.46 g, 120.7 mmol) and (*R*)-pantolactone (14.29 g, 109.8 mmol) in dichloromethane (52 cm^3) at −25 °C over a period of 1.5 h. The mixture was stirred at −25 °C for 2 h and at ambient temperature for 16 h, after which it was filtered and the filter washed with dichloromethane–hexane (4:1; 4 × 30 cm^3). The filtrate was concentrated under reduced pressure. Chromatography of the residue using dichloromethane–hexane (4:1) as eluent gave the *title compound* **9** (17.39 g, 87%) as an oil which crystallised slowly with time, mp 49–51 °C; $[a]_D$ +11.2 (*c* 2.15 in CH_2Cl_2) (Found: M + NH_4^+, 200.0920. $C_9H_{14}NO_4$ requires *M*, 200.0923); ν_{max}/cm^{-1} 3269, 2125, 1795, 1727, 1591, 1225, 1162, 1074 and 999; δ_H 1.19 and 1.28 (each 3 H, s, CH_3), 3.10 (1 H, s, 3-H), 4.05 and 4.13 (each 1 H, d, *J* 8, 5′-H) and 5.45 (1 H, s, 3′-H); δ_C 19.9, 23.0, 40.3, 73.4, 76.2, 76.5, 77.5, 151.4 and 171.1; *m*/*z* (CI) 200 (M^+ + 18, 100%).

Addition of triphenyltin hydride to (*S*)-1-(ethoxycarbonyl)ethyl propiolate 5

Triethylborane (1.0 M in hexane; 0.02 mmol) was added to a solution of triphenyltin hydride (84 mg, 0.24 mmol) and the propiolate **5** (34 mg, 0.20 mmol) in toluene. The mixture was stirred at 20 °C for 1.5 h and then concentrated under reduced pressure. Chromatography of the residue using dichloromethane–light petroleum (1:1) as eluent gave (S)-(*ethoxycarbonyl*)-*ethyl* (Z)-3-*triphenylstannylpropenoate* **7** (30 mg, 30%) as an oil (Found: $M^+ - C_6H_5$, 445.0467. $C_{20}H_{21}O_4Sn$ requires *M*, 445.0461); ν_{max}/cm^{-1} 3064, 1752, 1709, 1430, 1356, 1201, 1096, 1075, 823, 729 and 699; δ_H 1.17 (3 H, t, *J* 7, CH_3CH_2O), 1.96 (3 H, d, *J* 7, 2′-H_3), 4.10 (2 H, m, OCH_2CH_3), 5.12 (1 H, q, *J* 7, 1′-H), 7.13 (1 H, d, *J* 12, 2-H), 7.40–7.70 (15 H, m, ArH) and 7.60

(1 H, d, *J* 12, 3-H); δ_C 14.0, 16.9, 53.5, 61.4, 69.5, 77.2, 128.3, 136.2, 140.0, 154.4, 167.1 and 170.4; *m/z* 540 (M^+ + 18, 63%) and 445 (80). Further elution gave (S)-(*ethoxycarbonyl*)*ethyl* 3,3-*bis*(*triphenylstannyl*)*propanoate* **8** (43 mg, 25%) as an oil, $[\alpha]_D$ −18.0 (*c* 1.4, CH_2Cl_2) (Found: $M^+ - C_6H_5$, 797.0729. $C_{38}H_{37}O_4Sn$ requires *M*, 797.0736); ν_{max}/cm^{-1} 3064, 1750, 1736, 1481, 1429, 1191, 1097, 1074, 727 and 699; δ_H 1.14 (3 H, d, *J* 7.5, 2′-H_3), 1.24 (3 H, t, *J* 7.5, CH_3CH_2O), 2.28 (1 H, dd, *J* 7.5, 5.5, 3-H), 3.26 (2 H, m, 2-H_2), 4.15 (2 H, m, CH_3CH_2O), 4.50 (1 H, q, *J* 7.5, 1′-H) and 7.32 (30 H, m, ArH); δ_C 2.7, 14.1, 15.3, 16.7, 61.2, 65.9, 68.8, 128.4, 137.4, 139.3, 170.6 and 174.6; δ_{Sn} −83.7 and −84.9; *m/z* 795 (M^+ − 77, 5%). Further elution gave (S)-(*ethoxycarbonyl*)*ethyl* (E)-3-*triphenylstannylpropenoate* **6** (13 mg, 13%) as an oil (Found: $M^+ - C_6H_5$, 445.0462. $C_{20}H_{21}O_4Sn$ requires *M*, 445.0461); ν_{max}/cm^{-1} 3065, 1750, 1728, 1430, 1202, 1154, 1098, 998, 730 and 699; δ_H 1.28 (3 H, t, *J* 7.5, CH_3CH_2O), 1.52 (3 H, d, *J* 7.5, 2′-H_3), 4.20 (2 H, q, *J* 7.5, OCH_2CH_3), 5.15 (1 H, q, *J* 7.5, 1′-H), 6.56 (1 H, d, *J* 19, 2-H), 7.30–7.70 (15 H, m, ArH) and 8.05 (1 H, d, *J* 19, 3-H); δ_C 14.2, 17.1, 61.5, 69.0, 128.8, 129.4, 136.9, 138.1, 148.9, 168.6 and 170.6; *m/z* (EI) 521 (M^+ − 1, 4%), 445 (88) and 351 (42).

Addition of triphenyltin hydride to (*R*)-4,4-dimethyl-2-oxotetrahydrofuran-3-yl propiolate 9

Cuprate addition. A solution of triphenyltin chloride (56.3 g, 146 mmol) in tetrahydrofuran (THF) (120 cm^3) was added to a suspension of lithium shavings (10.1 g, 1.46 mol) in THF (120 cm^3) at ambient temperature over 30 min. The mixture was stirred for 20 h before being added over a period of 30 min to a solution of copper(I) iodide (27.80 g, 146 mmol) and lithium iodide (19.54 g, 146 mmol) in THF (290 cm^3) at −60 °C. The mixture was stirred for 30 min before the dropwise addition of the propiolate **9** (13.3 g, 73 mmol) in THF (70 cm^3). The mixture was stirred at −65 °C for 1.5 h before being added to a cold (−78 °C) solution of glacial acetic acid (17 cm^3) in tetrahydrofuran (50 cm^3); the mixture was then warmed to ambient temperature. The mixture was washed with saturated aqueous ammonium chloride containing ammonium hydroxide (pH 8; 5 × 100 cm^3), water (5 × 100 cm^3) and then brine (2 × 100 cm^3). The aqueous extracts were washed with dichloromethane (2 × 100 cm^3) and the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure. Repeated chromatography of the residue using chloroform then dichloromethane–hexane (3:2) as eluent gave (R)-4,4-*dimethyl*-2-*oxotetrahydrofuran*-3-*yl* (E)-3-*triphenylstannylpropenoate* **10** (11.48 g, 29%) which crystallised slowly on standing, mp 118–120 °C; $[\alpha]_D$ +7.43 (*c* 1.36 in CH_2Cl_2) (Found: $M^+ - C_6H_5$, 457.0458. $C_{21}H_{21}O_4Sn$ requires *M*, 457.0462); ν_{max}/cm^{-1} 3065, 1800, 1733, 1430, 1200, 1148, 1076, 998, 730 and 699; δ_H 1.17 and 1.27 (each 3 H, s, CH_3), 4.09 and 4.1 (each 1 H, d, *J* 9, 5′-H), 5.49 (1 H, s, 3′-H), 6.62 (1 H, d, *J* 19, $^3J_{H^{119/117}Sn}$ 65.5/63, 2-H), 7.4–7.7 (15 H, m, ArH) and 8.15 (1 H, d, *J* 19, $^2J_{H^{119/117}Sn}$ 73/70, 3-H); δ_C 20.0, 23.1, 40.5, 75.4, 76.3, 129.0, 129.6, 136.4, 137.1, 138.5, 150.9, 163.2 and 172.4; *m/z* (EI) 457 (M^+ − 77, 50%) and 351 (70). Further elution gave (R)-4,4-*dimethyl*-2-*oxotetrahydrofuran*-3-*yl* 3,3-*bis*(*triphenylstannyl*)*propanoate* **12** (9.5 g, 15%) which crystallised slowly on standing, mp 125–127 °C; $[\alpha]_D$ +1.53 (*c* 3.67 in CH_2Cl_2) (Found: C, 60.9; H, 4.8. $C_{45}H_{42}O_4Sn_2$ requires C, 61.1; H, 4.8%); ν_{max}/cm^{-1} 3064, 1795, 1743, 1428, 1146, 1074, 998, 910, 728 and 699; δ_H 0.82 and 0.84 (each 3 H, s, CH_3), 2.26 (1 H, dd, *J* 7.5, 5.0, 3-H), 3.32 (1 H, dd, *J* 19, 7.5, 2-H), 3.50 (1 H, dd, *J* 19, 5, 2-H′), 3.90 and 3.95 (each 1 H, d, *J* 9, 5′-H), 5.03 (1 H, s, 3′-H) and 7.23–7.50 (30 H, m, ArH); δ_C 2.4 ($^1J_{CSn}$ 310/296), 19.6, 22.8, 34.4 ($^2J_{CSn}$ 23.0), 40.0, 75.4, 75.8, 128.4, 128.8, 137.3 ($^2J_{CSn}$ 36.5), 137.4 ($^2J_{CSn}$ 36.0), 138.9 ($^1J_{CSn}$ 507/494) and 171.7, 174.5 ($^3J_{CSn}$ 44, 22); *m/z* 809 (M^+ − 77, 50%). Mixed fractions containing the (*E*)-vinylstannane **10** (0.26 g) and *ca.* 4% of the (*Z*)-vinylstannane **11** and 4% of the bis-stannane **12** were also obtained.

By free-radical addition. Triphenyltin hydride (2.04 g, 5.8 mmol) and azoisobutyronitrile (5 mg, 0.03 mmol) in benzene (6 cm^3) were added dropwise to a degassed solution of the propiolate **9** (1.0 g, 5.49 mmol) in benzene (20 cm^3). The mixture was heated cautiously to 80 °C for 17 h, cooled to room temperature and concentrated under reduced pressure. Chromatography of the residue using chloroform as the eluent gave the (R)-4,4-*dimethyl*-2-*oxotetrahydrofuran*-3-*yl* (Z)-3-*triphenylstannylpropenoate* **11** (936 mg, 32%) as a white solid, mp 112–114 °C; $[\alpha]_D$ −13.7 (*c* 2.03 in CH_2Cl_2) (Found: C, 60.85; H, 5.2. $C_{27}H_{26}O_4Sn$ requires C, 60.8; H, 4.9%; Found: $M^+ - C_6H_5$, 457.0458. $C_{21}H_{21}O_4Sn$ requires *M*, 457.0462); ν_{max}/cm^{-1} 3065, 1796, 1718, 1430, 1260, 1075, 998, 911, 821, 730 and 700; δ_H 1.01 and 1.09 (each 3 H, s, CH_3), 3.99 and 4.06 (each 1 H, d, *J* 9, 5′-CH), 5.44 (1 H, s, 3′-H), 7.22 (1 H, d, *J* 12.5, $^3J_{HSn}$ 144/138, 2-H), 7.64 (1 H, d, *J* 12.5, $^2J_{HSn}$ 72.0/68.0, 3-H) and 7.35–7.75 (15 H, m, ArH); δ_C 19.9, 22.8, 40.5, 75.8, 76.2, 128.5, 128.9, 135.6 ($^2J_{CSn}$ 12.5), 137.0 ($^2J_{CSn}$ 39.0), 139.5 ($^1J_{CSn}$ 575/549), 156.4 ($^1J_{CSn}$ 461/441), 166.89 ($^3J_{CSn}$ 34.5) and 172.2; *m/z* 552 (M^+ + 18, 20%) and 457 (35). Further elution gave the (*E*)-isomer **10** (726 mg, 25%).

(*R*)-4,4-Dimethyl-2-oxotetrahydrofuran-3-yl (1*R*,2*R*,3*S*,4*S*)- and (1*S*,2*S*,3*R*,4*R*)-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylates 13 and 14

Lewis acid-catalysed Diels–Alder reaction. Diethylaluminium chloride (1 mol dm^{-3} in hexanes; 43.54 cm^3) was added dropwise to a cooled (−50 °C) solution of the (*E*)-vinylstannane **10** (11.61 g, 21.77 mmol) in dichloromethane–hexane (1:1; 120 cm^3). After 1 h, freshly distilled cyclopentadiene (17.9 cm^3, 217.7 mmol) was added dropwise the pale green colour of the solution being gradually discharged on addition of the diene. After stirring for 16 h, powdered hydrated sodium carbonate (62.0 g, 217.7 mmol) was added and the mixture warmed to ambient temperature and filtered. The filter was washed with dichloromethane (4 × 50 cm^3) and the filtrate concentrated under reduced pressure. Chromatography of the residue using dichloromethane–light petroleum (2:1) as eluent gave the (1S,2S,3R,4R)-*isomer of the title compound* **14** (8.16 g, 63%), mp 112–114 °C; $[\alpha]_D$ −51.1 (*c* 2.3 in $CHCl_3$) (Found: C, 64.15; H, 5.5. $C_{32}H_{32}O_4Sn$ requires C, 64.1; H, 5.4%; Found: $M^+ + NH_4$, 618.1667. $C_{32}H_{36}NO_4Sn$ requires *M*, 618.1666); ν_{max}/cm^{-1} 1788, 1743, 1429, 1152, 1111, 1075, 1014, 997, 729 and 699; δ_H 0.97 and 1.12 (each 3 H, s, CH_3), 1.27 (1 H, d, *J* 9, 7-H), 1.32 (1 H, dd, *J* 9, 2, 7-H′), 1.90 (1 H, dd, *J* 5.5, 2, 3-H), 3.15 (1 H, m, 4-H), 3.31 (1 H, m, 1-H), 3.47 (1 H, dd, *J* 5.5, 3.5, 2-H), 3.98 (2 H, s, 5′-H_2), 5.31 (1 H, s, 3′-H), 5.85 (1 H, dd, *J* 5.5, 3, vinylic-H), 6.32 (1 H, dd, *J* 5.5, 3, vinylic-H), 7.32–7.42 (9 H, m, ArH) and 7.42–7.65 (6 H, m, ArH); δ_C 19.9, 23.1, 26.8 ($^1J_{CSn}$ 394/376), 40.1, 46.1, 46.7, 47.4, 49.4, 74.8, 76.0, 128.7 ($^3J_{CSn}$ 48.6), 129.0, 129.9, 137.2 ($^2J_{CSn}$ 35.0), 138.0 ($^1J_{CSn}$ 485/464), 139.5, 172.1 and 173.5; *m/z* 618 (M^+ + 18, 23%), 540 (10) and 523 (48). Further elution gave mixtures of (1*S*,2*S*,3*R*,4*R*)-stannane **14** and the (1*R*,2*R*,3*S*,4*S*)-stannane **13** (5:1; 1.21 g, 9%) and (1:1; 2.27 g, 17%) (combined yield of the Diels–Alder products; 11.64 g, 90%).

Following this procedure, the dienophile **10** (57 mg, 0.11 mmol) and cyclopentadiene (0.09 cm^3, 1.07 mmol) in the presence of diethylaluminium chloride (1 mol dm^{-3} in hexanes; 0.27 cm^3) gave the adducts **13** and **14** (41%, 62% de) after chromatography using dichloromethane as eluent. Further elution gave (R)-4,4-*dimethyl*-2-*oxotetrahydrofuran*-3-*yl* (E)-*pent*-2-*enoate* **17** (5 mg, 22%) as an oil; ν_{max}/cm^{-1} 1789, 1730, 1653, 1289, 1250, 1157, 1124, 1092, 1014 and 997; δ_H 1.09 (3 H, t, *J* 7, 5-H_3), 1.12 and 1.21 (each 3 H, s, CH_3), 2.25 (2 H, m, 4-H_2), 4.02 and 4.06 (each 1 H, d, *J* 9, 5′-H), 5.40 (1 H, s, 3′-H), 5.90 (1 H, d, *J* 15, 2-H) and 7.15 (1 H, dt, *J* 15, 7, 3-H); *m/z* 230 (M^+ + 18, 100%).

Thermal Diels–Alder reaction. Cyclopentadiene (60 mg, 1.0 mmol) was added dropwise to a solution of the vinylstannane **10** (48 mg, 0.09 mmol) in dry benzene (1.5 cm^3). The mixture

was heated under reflux for 20 h, cooled to room temperature and concentrated under reduced pressure. Chromatography of the residue using dichloromethane–light petroleum (7:3) as eluent gave the (1*S*,2*S*,3*R*,4*R*)-isomer of the title compound **14** (10 mg, 19%). Further elution gave the (1R,2R,3S,4S)-isomer of the *title compound* **13** (30 mg, 56%) as an oil (Found: $M^+ - C_6H_5$, 523.0920. $C_{26}H_{27}O_4Sn$ requires *M*, 523.0931); ν_{max}/cm^{-1} 3064, 1790, 1745, 1429, 1152, 1112, 1075, 1014, 997, 730 and 700; δ_H 0.95 and 1.15 (each 3 H, s, CH_3), 1.3 (2 H, m, 7-H_2), 1.94 (1 H, dd, *J* 5.5, 2.5, 3-H), 3.22 (1 H, m, 4-H), 3.42 (2 H, m, 1-H and 2-H), 4.01 (2 H, s, 5′-H_2), 5.32 (1 H, s, 3′-H), 6.04 (1 H, dd, *J* 5.5, 2.5, vinylic-H), 6.38 (1 H, dd, *J* 5.5, 3, vinylic-H), 7.38–7.47 (9 H, m, ArH) and 7.47–7.75 (6 H, m, ArH); δ_C 19.8, 23.0, 27.3, 40.1, 46.3, 46.6, 47.8, 49.4, 74.9, 76.2, 128.7, 129.1, 130.5, 137.3, 138.1, 138.9, 172.2 and 173.7; *m*/*z* (EI) 600 (M^+, 1%), 523 (1) and 351 (11).

(1*R*,2*R*,3*S*,4*S*)-3-Hydroxymethyl-2-triphenylstannylbicyclo-[2.2.1]hept-5-ene 20

Diisobutylaluminium hydride (1 mol dm^{-3} in dichloromethane; 78.09 cm^3) was added dropwise over 1.5 h, to a solution of the adduct **14** (9.36 g, 15.62 mmol) in dry dichloromethane (150 cm^3) at −78 °C. The solution was allowed to warm to 0 °C and stirred for 19 h before methanol (100 cm^3) was added and the mixture allowed to warm to ambient temperature. Saturated aqueous Rochelle's salt (200 cm^3) was added and the mixture extracted with dichloromethane (4 × 200 cm^3). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give the (1*R*,2*R*,3*S*,4*S*)-enantiomer of the *title compound* **20** (7.40 g, 100%) as an oil, $[\alpha]_D$ +19.7 (*c* 1.2 in $CHCl_3$), with spectroscopic data identical with those of the racemic compound.[1]

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

A solution of the adduct **14** (8.15 g, 13.60 mmol) in carbon tetrachloride (40 cm^3) was added dropwise to sodium methoxide (2.72 mol dm^{-3}) in methanol (250 cm^3) at ambient temperature. The mixture was stirred for 30 min then saturated aqueous ammonium chloride (100 cm^3) was added. After concentration under reduced pressure, the aqueous residue was extracted with ether (4 × 40 cm^3). The organic phase was separated, dried ($MgSO_4$), and concentrated under reduced pressure, to give the (1*S*,2*S*,3*R*,4*R*)-enantiomer of the *title compound* (−)-**2** (6.54 g, 96%), as an oil, $[\alpha]_D$ −45.7 (*c* 1.7 in $CHCl_3$) (Found: $M^+ - C_6H_5$, 425.0575. $C_{21}H_{21}O_2Sn$ requires *M*, 425.0564); δ_C 27.4 ($^1J_{CSn}$ 398/381), 46.1, 46.8, 47.1, 49.4, 51.6, 128.5 ($^3J_{CSn}$ 47), 128.9, 130.3, 137.2 ($^2J_{CSn}$ 34), 138.2 ($^1J_{CSn}$ 481/458), 138.8 ($^3J_{CSn}$ 54.5) and 174.9; *m*/*z* 442 (100%) and 425 (60); other spectroscopic data were identical with those of the racemic compound.[1]

(1*S*,2*S*,3*R*,4*R*)-3-Triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid 21

A solution of the Diels–Alder adduct **14** (0.10 g, 0.165 mmol) in tetrahydrofuran (0.5 cm^3) was added to a solution of lithium hydroxide monohydrate (0.86 mol dm^{-3}) in tetrahydrofuran–water (1:1; 1.7 cm^3) at ambient temperature and the mixture was stirred for 17 h. Solvent was removed under reduced pressure and the residue was suspended in water (2 cm^3) which was then acidified to pH 3 with concentrated aqueous hydrogen chloride (0.25 cm^3) and extracted with hexane–dichloromethane (50:1; 3 × 10 cm^3). The organic phase was separated, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether–acetic acid (50:1) as eluent gave the *title compound* **21** (17 mg, 20%) as a solid; ν_{max}/cm^{-1} 3500–2500, 3063, 1699, 1428, 1260, 1074, 1022, 728 and 699; δ_H 1.10–1.40 (2 H, m, 7-H_2), 1.88 (1 H, dd, *J* 5, 2, 3-H), 3.16 (1 H, m, 4-H), 3.31 (2 H, m, 1-H and 2-H), 5.92 (1 H, dd, *J* 5.5, 2, vinylic-H), 6.32 (1 H, dd, *J* 5.5, 3, vinylic-H), 7.4 (9 H, m, ArH), 7.50–7.72 (6 H, m, ArH) and 11.7 (1 H, br s, CO_2H); *m*/*z* 428 (100%) and 411 (30).

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

Palladium (10% on charcoal; 2.0 g, 1.88 mmol Pd) was added to a solution of the alkene **20** (7.40 g, 15.64 mmol) in ethanol (195 cm^3) and the suspension stirred vigorously for 22 h under an atmosphere of hydrogen, filtered through Celite, and the retained solids washed with ether (5 × 20 cm^3). The filtrate was concentrated under reduced pressure to give the (1*S*,2*R*,3*S*,4*R*)-enantiomer of the *title compound* **22** (6.15 g, 83%) as an oil, which slowly crystallised on standing, mp 85–87 °C; $[\alpha]_D$ +7.7 (*c* 0.7 in $CHCl_3$) (Found: C, 65.5; H, 5.8. $C_{26}H_{28}OSn$ requires C, 65.7; H, 5.95%); δ_C 22.4, 33.9 ($^1J_{CSn}$ 421/403), 34.0 ($^3J_{CSn}$ 68.5), 39.1 ($^3J_{CSn}$ 18.5), 40.3, 40.8 ($^2J_{CSn}$ 8), 48.0 ($^2J_{CSn}$ 22.5), 64.9 ($^3J_{CSn}$ 21.0), 128.7 ($^3J_{CSn}$ 46), 128.9 ($^4J_{CSn}$ 9.5), 137.5 ($^2J_{CSn}$ 33) and 139.0 ($^1J_{CSn}$ 465/444); δ_{Sn} −106.54; other spectroscopic data were identical with those of the racemic compound.[1]

Oxalyl chloride (0.1 cm^3, 1.11 mmol) followed by dimethylformamide (0.01 cm^3, 0.13 mmol) was added to a solution of (*R*)-2-methoxy-2-trifluoromethylphenylacetic acid (52 mg, 0.22 mmol) in hexane (1.5 cm^3). The solution was stirred for 1 h then the supernatant was decanted and concentrated under reduced pressure. A solution of the alcohol **22** (42 mg, 0.09 mmol), triethylamine (0.05 cm^3, 0.36 mmol) and 4-dimethylaminopyridine (2.0 mg, 0.015 mmol) in dichloromethane (1 cm^3) was added. The solution was stirred for 18 h and then washed with saturated aqueous sodium hydrogen carbonate (3 × 10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to yield the (R)-*Mosher's ester* **23** (60 mg, ⩾98%) as an oil, $[\alpha]_D$ +13.2 (*c* 0.95 in $CHCl_3$) (Found: $M^+ - C_6H_5$, 615.1174. $C_{30}H_{30}F_3O_3Sn$ requires *M*, 615.1169); ν_{max}/cm^{-1} 3064, 1747, 1599, 1569, 1429, 1270, 1170, 1123, 1075, 1021, 998, 728 and 699; δ_H 1.20 (1 H, dd, *J* 7, 2, 2-H), 1.23–1.80 (6 H, overlapping m, 5-H_2, 6-H_2 and 7-H_2), 2.23 (1 H, m, 4-H), 2.56 (1 H, m, 1-H), 2.68 (1 H, m, 3-H), 3.54 (3 H, s, OMe), 4.21 (1 H, t, *J* 11, 3-CH), 4.38 (1 H, dd, *J* 11, 5, 3-CH′) and 7.33 (20 H, m, ArH); δ_C 22.1, 32.5, 33.8, 39.3, 40.0, 40.7, 43.8, 55.4, 66.8, 77.2, 127.3, 128.4, 128.6, 129.0, 129.5, 132.4, 137.3, 138.3, 166.3; δ_F −73.19 (s, major-CF_3) and −73.29 (s, minor-CF_3); *m*/*z* (EI) 692 (M^+, 0.5%), 615 (3.5) and 351 (100).

Following this procedure, the alcohol **22** (14 mg, 0.03 mmol) gave the (S)-*Mosher's ester* **24** (24 mg, ⩾98%) as an oil, $[\alpha]_D$ −29.1 (*c* 1.25 in $CHCl_3$) (Found: $M^+ - C_6H_5$, 615.1147. $C_{30}H_{30}F_3O_3Sn$ requires *M*, 615.1169); ν_{max}/cm^{-1} 3064, 1747, 1428, 1270, 1170, 1123, 1075, 1021, 998, 910, 728 and 699; δ_H 1.20 (1 H, dd, *J* 7, 2, 2-H), 1.22–1.76 (6 H, overlapping m, 5-H_2, 6-H_2 and 7-H_2), 2.15 (1 H, m, 4-H), 2.55 (1 H, m, 1-H), 2.67 (1 H, m, 3-H), 3.47 (3 H, s, OMe), 4.26 (2 H, m, 3-CH_2) and 7.35–7.70 (20 H, m, ArH); δ_C 22.2, 32.7, 33.8, 39.2, 40.0, 40.8, 43.9, 55.4, 66.9, 77.2, 127.3, 128.4, 128.6, 129.0, 129.6, 132.4, 137.3, 138.3 and 166.4; δ_F −73.21 (s, minor-CF_3) and −73.31 (s, major-CF_3); *m*/*z* 615 (M^+ − 77, 15%) and 368 (50).

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

A solution of the alcohol **22** (0.94 g, 1.98 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a stirred suspension of sodium hydride (60% in mineral oil; 0.15 g, 3.75 mmol) in tetrahydrofuran (6 cm^3) at ambient temperature. The solution was stirred for 1.5 h before the addition of methyl iodide (1 cm^3, 15.8 mmol) then stirred at ambient temperature for 18 h. After concentration under reduced pressure, the residue was partitioned between dichloromethane (20 cm^3) and brine (20 cm^3). The organic phase was separated, dried ($MgSO_4$) and concentrated under reduced pressure to give the (1*S*,2*R*,3*S*,4*R*)-enantiomer of the title compound (−)-**3** (0.895 g, 93%) as an oil, used without further purification (Found: $M^+ - C_6H_5$, 413.0934. $C_{21}H_{25}OSn$ requires *M*, 413.0927); $[\alpha]_D$ −20.5 (*c* 0.8

in $CHCl_3$); the spectroscopic data were identical with those of the racemic compound.[1]

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

A solution of the alcohol **22** (0.133 g, 0.28 mmol) and triethylamine (0.07 cm^3, 0.50 mmol) in dichloromethane (1.5 cm^3) was added to a solution of trityl chloride (86 mg, 0.305 mmol) and 4-dimethylaminopyridine (1.0 mg, 0.008 mmol) in dichloromethane (1.5 cm^3) at ambient temperature. After 19 h, more trityl chloride (32 mg, 0.115 mmol) and 4-dimethylaminopyridine (3.0 mg, 0.025 mmol) were added. After 20 h the solution was washed with saturated aqueous ammonium chloride (3 × 5 cm^3) and water (5 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using dichloromethane–hexane (1:1) as eluent gave the *title compound* **25** (0.184 g, 92%) as an oil (Found: M^+, 718.2264. $C_{45}H_{42}OSn$ requires *M*, 718.2258); ν_{max}/cm^{-1} 3062, 1428, 1217, 1073, 760, 728 and 699; δ_H 1.04 (1 H, dd, *J* 7.5, 2, 2-H), 1.18–1.38 (4 H, overlapping m), 1.5 (2 H, m), 2.40 (1 H, d, *J* 4, 1-H), 2.50 (1 H, m, 4-H), 2.71 (1 H, m, 3-H), 2.86 (1 H, t, *J* 8.5, 3-CH), 3.25 (1 H, dd, *J* 8.5, 5, 3-CH′), 7.15–7.39 (24 H, m, ArH) and 7.45 (6 H, m, ArH); δ_C 22.3, 33.5 ($^1J_{CSn}$ 424/406), 33.7, 39.7 ($^3J_{CSn}$ 18.5), 40.0, 40.9, 45.5 ($^2J_{CSn}$ 21), 64.9 ($^3J_{CSn}$ 22), 86.2, 126.7, 127.6, 128.4, 128.7, 137.3, 138.9 ($^1J_{CSn}$ 462/441) and 144.3; *m/z* (EI) 718 (M^+, 0.2%), 475 (4) and 351 (60).

(1*S*,2*R*,3*S*,4*R*)-3-(*tert*-Butyldimethylsilyloxymethyl)-2-triphenylstannylbicyclo[2.2.1]heptane 26

tert-Butyldimethylsilyl chloride (19 mg, 0.125 mmol), triethylamine (0.03 cm^3, 0.215 mmol) and 4-dimethylaminopyridine (1 mg, 0.008 mmol) were added to a solution of the alcohol **22** (50 mg, 0.105 mmol) in dimethylformamide (1 cm^3). The mixture was stirred at 0 °C for 5 min then warmed to ambient temperature and stirred for a further 21 h before the addition of more *tert*-butyldimethylsilyl chloride (32 mg, 0.21 mmol) and triethylamine (0.06 cm^3, 0.43 mmol). After stirring for 3 h, the solution was washed with brine (4 × 10 cm^3) and the organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to yield the *title compound* **26** (62 mg, 100%), an oil, used without further purification (Found: $M^+ - C_6H_5$, 513.1650. $C_{26}H_{37}OSiSn$ requires *M*, 513.1636); $[\alpha]_D$ −16.6 (*c* 0.7 in $CHCl_3$); ν_{max}/cm^{-1} 3063, 1428, 1253, 1096, 1075, 836, 776, 727 and 699; δ_H −0.08 and −0.06 (each 3 H, s, $SiCH_3$), 0.83 [9 H, s, $Si(CH_3)_3$], 1.25–1.75 (7 H, overlapping m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.40 (1 H, m, 4-H), 2.57 (2 H, m, 1-H and 3-H), 3.57 (1 H, t, *J* 10, 3-CH), 3.69 (1 H, dd, *J* 10, 6.5, 3-CH′), 7.46 (9 H, m, ArH) and 7.51–7.72 (6 H, m, ArH); δ_C −5.45, −5.35, −5.4, 18.4, 22.4, 26.0, 33.3, 33.9, 39.4, 40.2, 41.0, 47.8, 64.8, 128.5, 128.8, 137.5 and 139.1; *m/z* 513 ($M^+ - 77$, 100%) and 368 (60).

(1*R*,2*S*,3*R*,4*S*)-3-Triphenylstannylbicyclo[2.2.1]heptan-2-ylmethyl 1-naphthoate 27

A solution of the alcohol **22** (0.238 g, 0.50 mmol) and triethylamine (0.08 cm^3, 0.60 mmol) in chloroform (3 cm^3) was added to 1-naphthoyl chloride (0.118 g, 0.62 mmol) in chloroform (2 cm^3) at ambient temperature. After 19 h, more 1-naphthoyl chloride (19 mg, 0.10 mmol) and triethylamine (0.015 cm^3, 0.10 mmol) were added. After 23 h, the solution was washed with saturated aqueous sodium hydrogen carbonate (4 × 10 cm^3) and the organic phase dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using chloroform–hexane (1:1) as eluent gave *title compound* **27** (0.254 g, 81%) as an oil (Found: $M^+ - C_6H_5$, 553.1196. $C_{25}H_{24}O_2Sn$ requires *M*, 553.1190); ν_{max}/cm^{-1} 3062, 1713, 1428, 1241, 1195, 1133, 1073, 1009, 782, 728 and 699; δ_H 1.36 (2 H, m), 1.42 (1 H, dd, *J* 6.5, 2.5, 3′-H), 1.5 (2 H, m), 1.71 (2 H, m), 2.44 (1 H, m, 1′-H), 2.56 (1 H, d, *J* 3, 4′-H), 2.83 (1 H, m, 2′-H), 4.4 (2 H, m, 2′-CH_2), 7.32 (10 H, m, ArH), 7.42–7.63 (8 H, m, ArH), 7.86 (1 H, d, *J* 8, ArH), 7.92 (1 H, dd, *J* 7.5, 1.5, ArH), 7.95 (1 H, d, *J* 8.5) and 8.83 (1 H, d, *J* 8.5); δ_C 22.6, 33.6, 33.9 ($^1J_{CSn}$ 418/399), 39.9 ($^3J_{CSn}$ 17.5), 40.2, 41.0 ($^2J_{CSn}$ 8), 43.9 ($^2J_{CSn}$ 21), 67.2 ($^3J_{CSn}$ 22), 124.4, 125.3, 125.7, 125.8, 126.1, 127.2, 127.6, 128.5 ($^3J_{CSn}$ 47.5), 128.8 ($^4J_{CSn}$ 11), 131.2, 133.7, 137.3 ($^2J_{CSn}$ 33), 138.5 ($^1J_{CSn}$ 469/448) and 167.5; *m/z* (FAB) 553 ($M^+ - 77$, 40%), 445 (40), 351 (95) and 155 (100).

Preparation of tin iodides

General procedure: preparation of diphenyl{(1*S*,2*R*,3*S*,4*R*)-3-hydroxymethylbicyclo[2.2.1]heptan-2-yl}tin iodide 28. Iodine (61 mg, 0.24 mmol) was added to a solution of the triphenylstannane **22** (0.12 g, 0.25 mmol) in dichloromethane (4 cm^3) and the mixture stirred for 1.5 h at ambient temperature. Concentration of the mixture under reduced pressure gave the *title compound* **28** (0.11 g, 83%), as an oil, used without further purification, $[\alpha]_D$ −6.0 (*c* 1.8 in $CHCl_3$) (Found: $M^+ - C_6H_5$, 448.9430. $C_{14}H_{18}IOSn$ requires *M*, 448.9424); ν_{max}/cm^{-1} 3397, 3063, 1429, 1070, 1021, 999, 728 and 697; δ_H 1.2–1.9 (8 H, overlapping m, 2-H, 5-H_2, 6-H_2, 7-H_2 and OH), 2.43 (1 H, m, 4-H), 2.55 (1 H, m, 3-H), 2.62 (1 H, m, 1-H), 3.71 (2 H, d, *J* 7.5, 3-CH_2), 7.46 (6 H, m, ArH) and 7.54–7.80 (4 H, m, ArH); δ_C 22.5, 33.5 ($^3J_{CSn}$ 89/85), 39.0 ($^1J_{CSn}$ 440/418), 39.2, 40.1, 41.4, 48.4 ($^2J_{CSn}$ 29.5), 65.0 ($^3J_{CSn}$ 25.5), 128.9 ($^3J_{CSn}$ 54.5), 129.9 ($^4J_{CSn}$ 12), 136.5 ($^2J_{CSn}$ 43.5) and 137.7; $\delta_{Sn}(CDCl_3)$ −38.8; *m/z* 466 (50%), 449 (60) and 399 (70).

Diphenyl{(1*S*,2*R*,3*S*,4*R*)-3-(triphenylmethoxymethyl)bicyclo-[2.2.1]heptan-2-yl}tin iodide 29. Following the above procedure, iodine (62 mg, 0.245 mmol) and the triphenylstannane **25** (0.18 g, 0.26 mmol) gave, after 30 min at ambient temperature, the *title compound* **29** (0.19 g, 96%), as an oil, used without further purification; ν_{max}/cm^{-1} 3062, 1448, 1429, 1072, 762, 728 and 697; δ_H 1.00 (1 H, m, 2-H), 1.20–1.55 (6 H, overlapping m, 5-H_2, 6-H_2 and 7-H_2), 2.48 (1 H, m, 1-H), 2.55 (1 H, m, 4-H), 2.72 (1 H, m, 3-H), 2.92 (1 H, t, *J* 9, 3-CH), 3.24 (1 H, dd, *J* 8.5, 6, 3-CH′) and 7.20–7.58 (25 H, overlapping m, ArH); δ_C 22.3, 33.1 ($^3J_{CSn}$ 87), 38.4 ($^1J_{CSn}$ 422/404), 39.7, 39.8, 41.5, 45.9 ($^3J_{CSn}$ 27.5), 64.8 ($^3J_{CSn}$ 27.5), 86.4, 126.8, 127.7, 128.7, 128.8, 129.7 ($^4J_{CSn}$ 13), 136.4 ($^3J_{CSn}$ 44), 137.5 ($^1J_{CSn}$ 465/443) and 144.1.

Diphenyl{(1*S*,2*R*,3*S*,4*R*)-3-(1-naphthoyloxymethyl)bicyclo-[2.2.1]heptan-2-yl}tin iodide 30. Following the above procedure, iodine (59 mg, 0.23 mmol) and the triphenylstannane **27** (0.155 g, 0.245 mmol) after 2 h at ambient temperature gave the *title compound* **30** (0.167 g, 100%), as an oil, used without further purification (Found: $M^+ - C_6H_5$, 602.9828. $C_{25}H_{24}IO_2Sn$ requires *M*, 602.9843); ν_{max}/cm^{-1} 3063, 3048, 1713, 1429, 1276, 1241, 1195, 1133, 1072, 1010, 782, 728 and 696; δ_H 1.30–1.76 (7 H, overlapping m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.51 (1 H, m, 4-H), 2.61 (1 H, d, *J* 3, 1-H), 2.85 (1 H, m, 3-H), 4.44 (2 H, m, 3-CH_2), 7.20–7.36 (7 H, m, ArH), 7.48–7.64 (6 H, m, ArH), 7.86 (1 H, d, *J* 8, ArH), 7.95 (1 H, d, *J* 8, ArH), 7.98 (1 H, dd, *J* 7.5, 1, ArH) and 8.83 (1 H, d, *J* 8.5, ArH); δ_C 22.7, 33.2 ($^3J_{CSn}$ 86.5), 38.4 ($^1J_{CSn}$ 415/393), 39.96, 40.02, 41.7, 44.5 (J_{CSn} 25.0), 67.14 ($^3J_{CSn}$ 25), 124.4, 125.73, 126.1, 126.9, 127.7, 128.5, 128.8 ($^3J_{CSn}$ 56), 129.8 ($^4J_{CSn}$ 12), 131.2, 133.7, 136.3 ($^2J_{CSn}$ 44) and 167.5; *m/z* 698 ($M^+ + 18$, 12%), 603 (60) and 553 (30).

Preparation of tin hydrides from tin iodides

General procedure: preparation of diphenyl{(1*S*,2*R*,3*S*,4*R*)-3-hydroxymethylbicyclo[2.2.1]heptan-2-yl}tin hydride 31. A solution of sodium borohydride (5.5 mg, 0.145 mmol) in dry ethanol (1 cm^3) was added to a solution of the tin iodide **28** (70 mg, 0.135 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 organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to afford the *title compound* **31**[1] (54 mg, 100%) as an oil, used without further purification (Found: $M^+ - C_6H_5$,

323.0467. $C_{14}H_{19}OSn$ requires *M*, 323.0458); ν_{max}/cm^{-1} 3380, 3063, 1825, 1428, 1330, 1074, 1022, 728 and 699; $\delta_H(C_6D_6)$ 0.85 (1 H, br, OH), 0.95–1.65 (7 H, overlapping m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.25 (1 H, m, 4-H), 2.45 (2 H, m, 1-H and 3-H), 3.42 (2 H, m, 3-CH_2), 6.51 (1 H, d, *J* 2, $^1J_{HSn}$ 1771/1688, SnH), 7.17–7.32 (6 H, m, ArH) and 7.55–7.76 (4 H, m, ArH); δ_C 22.6, 33.3 ($^1J_{CSn}$ 430/410), 33.9 ($^3J_{CSn}$ 70.5), 39.61 ($^2J_{CSn}$ 18.5), 40.2, 41.7 ($^2J_{CSn}$ 8), 48.9 ($^3J_{CSn}$ 23.5), 64.8 ($^3J_{CSn}$ 21), 128.9 ($^3J_{CSn}$ 47), 129.1 ($^4J_{CSn}$ 11), 137.8 ($^2J_{CSn}$ 34.5), 137.9 ($^2J_{CSn}$ 35), 138.7 ($^1J_{CSn}$ 449) and 138.8 ($^1J_{CSn}$ 449); $\delta_{Sn}(C_6D_6)$ −119 (d, $^1J_{SnH}$ 1769); *m*/*z* 399 ($M^+ - 1$, 10%) and 323 (20).

Diphenyl{(1*S*,2*R*,3*S*,4*R*)-3-triphenylmethoxymethylbicyclo-[2.2.1]heptan-2-yl}tin hydride 32. Following the above procedure, sodium borohydride (12 mg, 0.315 mmol) and the tin iodide **29** (0.19 g) gave, after chromatography using hexane–ether (50:1) as eluent, the *title compound* **32** (64 mg, 40%) as an oil; ν_{max}/cm^{-1} 3060, 1820, 1447, 1072 and 701; $\delta_H(C_6D_6)$ 0.85 (2 H, m), 1.40 (4 H, m), 1.56 (1 H, d, *J* 9), 2.32 (1 H, d, *J* 4, 1-H), 2.45 (1 H, m, 4-H), 2.75 (1 H, m, 3-H), 3.08 (1 H, t, *J* 8.5, 3-CH), 3.35 (1 H, dd, *J* 8.5, 5, 3-CH′), 6.49 (1 H, d, *J* 2, $^1J_{HSn}$ 1781/1701, SnH), 7.00–7.27 (14 H, m, ArH) and 7.38–7.65 (11 H, m, ArH); *m*/*z* (EI) 399 (4.5%) and 243 (100).

Diphenyl{(1*S*,2*R*,3S,4*R*)-3-(1-naphthoyloxymethyl)bicyclo-[2.2.1]heptan-2-yl}tin hydride 33. Following the above procedure, sodium borohydride (9 mg, 0.24 mmol) and the tin iodide **30** (0.145 g, 0.215 mmol) in ethanol (5 cm^3) gave the *title compound* **33** (0.115 g, 97%), as an oil; ν_{max}/cm^{-1} 3060, 1821, 1714, 1243, 1195, 1134, 1010, 784 and 700; $\delta_H(C_6D_6)$ 1.05–1.58 (7 H, overlapping m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.21 (1 H, m, 4-H), 2.37 (1 H, d, *J* 4, 1-H), 2.75 (1 H, m, 3-H), 4.32 (1 H, dd, *J* 11, 8, 3-CH), 4.41 (1 H, dd, *J* 11, 7, 3-CH′), 6.50 (1 H, d, *J* 1.5, $^1J_{HSn}$ 1791/1711, SnH), 7.06–7.16 (7 H, m, ArH), 7.23 (1 H, ddd, *J* 8, 7, 1, ArH), 7.40 (1 H, ddd, *J* 8.5, 7, 1.5, ArH), 7.55 (5 H, m, ArH), 7.61 (1 H, d, *J* 8, ArH), 8.13 (1 H, dd, *J* 7.5, 1.5, ArH) and 9.38 (1 H, dd, *J* 8.5, 1, ArH); *m*/*z* 553 ($M^+ - 1$, 90%), 172 (80) and 155 (100).

Preparation of tin hydrides from triphenylstannanes without isolation of the tin iodides

General procedure: diphenyl{(1*S*,2*R*,3*S*,4*R*)-3-methoxymethylbicyclo[2.2.1]heptan-2-yl}tin hydride 4. Iodine (0.44 g, 1.74 mmol) was added to a solution of the triphenylstannane (−)-**3** (0.89 g, 1.83 mmol) in dichloromethane (20 cm^3) and the mixture stirred for 1 h at ambient temperature then concentrated under reduced pressure. Sodium borohydride (90 mg, 2.38 mmol) in ethanol (5 cm^3) was added to a solution of the residue in ethanol (20 cm^3). After 1 h, the mixture was concentrated under reduced pressure and the residue partitioned between saturated aqueous ammonium chloride (20 cm^3) and ether (30 cm^3). The aqueous phase was extracted with ether (3 × 30 cm^3) and the organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to afford the *title compound* **4**[1] (0.78 g, 100%) as an oil, used without further purification (Found: $M^+ - H$, 413.0930. $C_{21}H_{25}OSn$ requires *M*, 413.0927); ν_{max}/cm^{-1} 3063, 1819, 1428, 1111, 1075, 728 and 699; $\delta_H(C_6D_6)$ 1.10–1.65 (7 H, overlapping m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.32 (1 H, m, 4-H), 2.45 (1 H, m, 1-H), 2.69 (1 H, m, 3-H), 3.11 (3 H, s, OMe), 3.36 (2 H, d, *J* 7.5, 3-CH_2), 6.62 (1 H, d, *J* 1.5, $^1J_{HSn}$ 1763/1681, SnH), 7.26 (6 H, m, ArH) and 7.7 (4 H, m, ArH); δ_C(50 MHz, C_6D_6) 22.8, 33.8 ($^1J_{CSn}$ 427/408), 34.0 ($^3J_{CSn}$ 71), 40.1, 40.3, 41.8 (J_{CSn} 8), 46.3 (J_{CSn} 22), 58.5, 75.4 ($^3J_{CSn}$ 20.5), 128.8, 129.0, 137.8 ($^2J_{CSn}$ 40), 138.8 and 138.9; δ_{Sn}(111 MHz; C_6D_6) −118.1 ($^1J_{SnH}$ 1762); *m*/*z* 413 ($M^+ - 1$, 40%) and 337 (100).

Diphenyl{(1*R*,2*S*,3*R*,4*S*)-3-(*tert*-butyldimethylsilyloxymethyl)-bicyclo[2.2.1]heptan-2-yl}tin hydride 34. Following the above procedure, iodine (29 mg, 0.115 mmol) and the triphenylstannane **26** (67 mg, 0.115 mmol) in dry dichloromethane (1 cm^3) followed by reduction using sodium borohydride (5 mg, 0.13 mmol) in dry ethanol (1 cm^3) gave, after chromatography using light petroleum–ether (100:1) as eluent, the *title compound* **34** (24 mg, 42%) (Found: $M^+ - C_6H_5$, 437.1327. $C_{20}H_{33}OSiSn$ requires *M*, 437.1323); ν_{max}/cm^{-1} 3050, 1822, 1428, 1405, 1254, 1096, 835, 727 and 699; $\delta_H(C_6D_6)$ −0.05 and −0.07 (each 3 H, s, $SiCH_3$), 1.00 [9 H, s, $Si(CH_3)_3$], 1.05–1.75 (7 H, overlapping m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.45 (2 H, m, 1-H and 4-H), 2.61 (1 H, m, 3-H), 3.59 (1 H, dd, *J* 9.5, 9, 3-CH), 3.70 (1 H, dd, *J* 10, 6.5, 3-CH′), 6.58 (1 H, d, *J* 2, SnH), 7.20–7.34 (6 H, m, ArH) and 7.65 (4 H, m, ArH); $\delta_C(C_6D_6)$ −5.3, −5.2, 18.5, 22.7, 26.2, 32.8, 33.9, 39.9, 40.1, 41.7, 49.0, 65.2, 128.8, 129.0, 137.8, 138.6 and 138.65; *m*/*z* 513 ($M^+ - 1$, 3%) and 437 (5).

Reduction of (4*RS*,5*SR*)-4,5-dihydro-5-iodomethyl-4-phenylfuran-2(3*H*)-one 35

The tin hydride **4** (8 mg, 0.02 mmol) in ethanol (0.5 cm^3) was added to a solution of the iodo lactone **35**[1] (29 mg, 0.096 mmol) in ethanol (0.5 cm^3) at −20 °C. Triethylborane (1 mol dm^{-3} in hexanes; 0.01 cm^3) was added, followed rapidly by a cooled (−20 °C) solution of sodium borohydride (5 mg, 0.13 mmol) in ethanol (1 cm^3) and the mixture stirred at −20 °C for 4 h then concentrated under reduced pressure. The residue was partitioned between ether (10 cm^3) and saturated aqueous ammonium chloride (10 cm^3) and the aqueous phase extracted with ether (4 × 10 cm^3). The ethereal extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane–ether (3:1) as eluent gave the 5-methylfuranone **36**[1] (12 mg, 71%). Further elution gave recovered tin hydride **4** (5 mg, 63% recovery).

Reduction of methyl 2-bromo-2-phenylpropanoate 37

The tin iodide **28** (39 mg, 0.075 mmol) in ethanol (1 cm^3) was added to a solution of the bromo ester **37** (90 mg, 0.37 mmol) in ethanol (2 cm^3) at ambient temperature. Triethylborane (1 mol dm^{-3} in hexanes; 0.01 cm^3) was added, followed rapidly by a solution of sodium borohydride (22 mg, 0.58 mmol) in ethanol (1 cm^3). The mixture was stirred for 19 h and then concentrated under reduced pressure and the residue partitioned between ether (10 cm^3) and saturated aqueous ammonium chloride (10 cm^3). Following extraction with ether (4 × 10 cm^3), the organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography, of the residue using hexane–ether (30:1) as eluent gave methyl 2-phenylpropanoate (33 mg, 54%).

{[(1*S*,2*R*,3*S*,4*R*)-3-Methoxymethylbicyclo[2.2.1]heptan-2-yl]-(diphenyl)stannyl}phenylmethanol 38

Butyllithium (1.5 mol dm^{-3} in hexanes; 0.49 cm^3) was added dropwise to a solution of diisopropylamine (0.10 cm^3, 0.73 mmol) in tetrahydrofuran (4 cm^3) at 0 °C. The solution was stirred for 20 min then cooled to −78 °C. The tin hydride **4** (0.15 g, 0.365 mmol) was added and the solution stirred for 5 min. Benzaldehyde (0.04 cm^3, 0.40 mmol) was then added dropwise and after stirring at −78 °C for 20 min, saturated aqueous ammonium chloride (2 cm^3) was added and the mixture then allowed to warm to room temperature. The mixture was extracted with ether (4 × 15 cm^3) and the organic phase dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane–ether (9:1) as eluent gave the *distannane* **40** (38 mg, 25%) as an oil (Found: $M^+ - C_9H_{15}O$, 687.0740. $C_{33}H_{35}OSn_2$ requires *M*, 687.0732); δ_H 1.09–1.60 (14 H, m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.16 (2 H, m, 4-H), 2.30 (2 H, d, *J* 3, 1-H), 2.42 (2 H, m, 3-H), 3.03 (6 H, s, 2 × OMe), 3.14 (4 H, m, 3-CH_2), 7.29 (12 H, m, ArH) and 7.45 (8 H, m, ArH); *m*/*z* 747 ($M^+ - 77$, 4%). Further elution gave the *title compounds* **38** (0.112 g, 60%) in a 50:50 ratio; ν_{max}/cm^{-1} 3401, 3062, 1428, 1108, 1073, 727 and 698; δ_H 1.00–1.70 (7 H, overlapping m, 2-H, 5-H_2, 6-H_2, 7-H_2), 2.25 (1 H, m), 2.35 and 2.4 (each 0.5 H, m), 2.62 (1 H, m, 3-H), 3.35–3.50 (4 H, m, 3-CH and OMe), 3.61 (1 H, m, 3-CH′), 4.28, 4.46, 5.57 and 5.61 (each 0.5 H, d, *J* 5) and 6.95–7.70 (15 H, m, ArH); *m*/*z* 503 (10%), 443 (3) and 413 (60).

A solution of the alcohols **38** (82 mg, 0.16 mmol), acetic anhydride (0.03 cm^3, 0.32 mmol), triethylamine (0.09 cm^3, 0.63 mmol) and 4-dimethylaminopyridine (1.0 mg, 0.008 mmol) in dichloromethane (2 cm^3) was stirred at ambient temperature for 20 h. The mixture was partitioned between water (10 cm^3) and ether (10 cm^3) and the aqueous phase 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–hexane (4:1) as eluent gave the *esters* **39** (38 mg, 44%) in a 50:50 ratio (Found: $M^+ - C_6H_5$, 485.1147. $C_{24}H_{29}O_3Sn$ requires *M*, 485.1139); ν_{max}/cm^{-1} 3063, 1743, 1719, 1428, 1370, 1244, 1110, 1072, 1020, 728 and 698; δ_H 1.05–1.70 (7 H, m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 1.97 and 2.0 (each 1.5 H, s, CH_3), 2.30 (1 H, m), 2.35 and 2.44 (each 0.5 H, d, *J* 3), 2.54 (1 H, m, 3-H), 3.18–3.37 (2 H, m, 3-CH_2), 3.22 and 3.27 (each 1.5 H, s, OMe), 6.25 and 6.28 (each 0.5 H, s, CHOAc) and 7.10–7.48 (15 H, m, ArH); *m/z* 503 ($M^+ - 59$, 10%) and 485 (100).†

X-Ray crystal structure for the Diels–Alder adduct 14

A number of attempts at this crystal structure were made since the structure tends to be disordered. The results of the crystal structure reported here are from the best crystal that could be obtained although some disorder was apparent around the oxofuranyl moiety as indicated by the relatively high *R* values, generally high displacement parameters and some poor bond lengths for this part of the molecule. Nevertheless the results are sufficient to support the chemical discussion in particular the stereochemical assignments made around the bicyclic core.

Crystal data. $C_{32}H_{32}O_4Sn$, $M = 599.29$, orthorhombic, space group $P2_12_12_1$, $a = 10.442(3)$, $b = 29.031(9)$, $c = 9.480(2)$ Å, $U = 2874(1)$ $Å^3$ (by least-squares refinement on diffractometer angles of 25 automatically centred reflections in the 2θ range 29.5–35.0°), $\lambda = 1.54178$ Å, $Z = 4$, $D_c = 1.385$ g cm^{-3}, $\mu = 74.89$ cm^{-1}, $F(000) = 1224$, colourless prism, crystal dimensions 0.20 × 0.25 × 0.25 mm.

Data were collected at 297 K using a Rigaku AFC-5R diffractometer with graphite monochromated Cu-Kα radiation and a rotating anode generator. A total of 2482 independent reflections were measured in the ω–2θ scan mode to a $2\theta_{max}$ of 120.1°. An empirical absorption correction was applied, using the program DIFABS (transmission factors: 0.92–1.19).[27] A decay correction (based on the intensities of three standard reflections, measured every 150 reflections) was also applied (2.82% decline). The data were corrected for Lorentz and polarisation effects. 2047 Reflections had $I > 3\sigma(I)$.

The structure was solved by direct methods using SHELXS-86[28] and refined using full-matrix least-squares refinement using TEXSAN.[29] The non-hydrogen atoms were refined anisotropically except for the atoms of the oxofuranyl ring. For these atoms it was possible to refine the positions, whilst maintaining a fixed isotropic thermal parameter for all atoms of this part of the molecule. The hydrogen atoms were included in calculated positions, with isotropic thermal parameters which were 20% greater than the B_{eq} of the atom to which they were bonded. Refinement of the 272 variables converged (maximum shift/error <0.01) with $R = 0.070$, $R_w = 0.093$ using the 2047 observed reflections (weighting scheme $w = 1/[\sigma^2F_o + 0.00022\,|F_o|^2]$). Max./min. peaks in the final difference map 1.17/–2.02 e $Å^{-3}$. Maximum peak at 0.5908, 0.5030, 0.0541 close to O4. Minimum trough at 0.6839, 0.5061, 0.1347 close to O4.

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/173.

Acknowledgements

We thank the EPSRC and Zeneca Pharmaceuticals for a CASE Award (to R. M. P.), Dr A. Thomas of Zeneca for helpful discussions, and Dr M. Helliwell for help in preparing the X-ray data for publication.

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Paper 7/06293A
Received 28*th August* 1997
Accepted 5*th November* 1997