Synthesis of chiral organotin reagents: Diels–Alder reactions of methyl 3-(triphenylstannyl)acrylate: synthesis of diphenyl-(3-substituted bicyclo[2.2.1]heptan-2-yl)tin hydrides

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Cyclopentadiene undergoes Diels–Alder reactions with methyl (*E*)- and (*Z*)-3-(triphenylstannyl)acrylates 5 and 6 to give the *endo*-cycloadduct 9, and a mixture of the *exo*- and *endo*-isomers 10 and 11, respectively. The *endo*-product 9 is reduced to the alcohol 12 which is protected as its methyl ether 13. Attempts to remove one of the phenyl substituents from the tin using iodine are complicated by destannylation to the tricyclic iodide 14. However, after hydrogenation, treatment with 1 mol equivalent of iodine gives the tin iodide 17 which is reduced to the tin hydride 18. The hydroxyalkyltin hydride 21 is similarly prepared. The unsaturated tin hydrides 24 and 26 have been prepared by reduction of the Diels–Alder adducts 23 and 25 obtained from cyclopentadiene and methyl (*Z*)-3-(chlorodiphenylstannyl)acrylate. The tin hydrides 18 and 21 are found to undergo free-radical reactions as exemplified by addition to methyl propiolate and reductive dehalogenation of the iodo lactone 30.

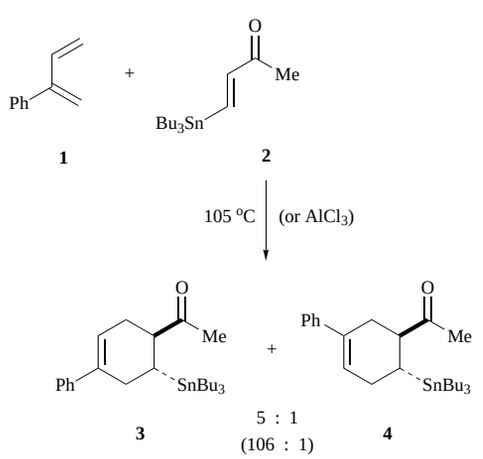
Tin reagents are becoming increasingly important in organic synthesis and useful procedures are being developed for their use in asymmetric synthesis.[1] For example, excellent enantiomeric excesses are obtained in reactions of allylstannanes with aldehydes in the presence of Lewis acids co-ordinated by chiral, non-racemic ligands[2] and tin(II) triflate in conjunction with chiral, non-racemic amines promotes effective asymmetric Mukaiyama aldol reactions of enol ethers with aldehydes.[3]

Because of the widespread use of trialkyltin hydrides for reduction and for the preparation of other organotin reagents, the development of chiral, non-racemic tin hydrides which exhibit reliably useful levels of asymmetric induction, *e.g.* in reactions with alkyl halides, would be a useful addition to organotin chemistry.

Considerable work has been carried out on the preparation and characterisation of organotin compounds with chiral, carbon-bound ligands on the tin, although these compounds have not yet been developed into generally useful reagents for organic synthesis. For example, several chiral, non-racemic organostannanes and organotin chlorides were prepared from monoterpenes, but the use of the tin chlorides as chiral Lewis acids was not developed.[4] Binaphthylstannanes have been synthesized and used to prepare lithium reagents by transmetallation.[5] However, the asymmetric reduction of alkyl halides using binaphthyltin hydrides gave products which had only modest enantiomeric excesses (ees).[6] (Alkyl and aminoalkyl)menthyltin halides and hydrides have been prepared and fully characterised, of interest being the extent of the co-ordination of the amino group to the tin in the tin halides and hydrides.[7–9] However, reduction of acetophenone using the (dialkyl)menthyltin hydrides under photochemical conditions which was found to be affected by the bulk of the alkyl substituents, gave 1-phenylethanol with ees only in the range 7–40%.[10] A chiral dialkyl(dipropenyl)stannane was prepared using optically active 2-phenylbutylmagnesium bromide, but was found to react with aldehydes to give homoallylic alcohols with only modest ees.[11] Several chiral, non-racemic stannanes have been prepared from monosaccharides, but they have not yet been converted into reagents for use in organic synthesis.[12]

Notwithstanding the very different carbon–tin and carbon–boron bond lengths, it was felt, by analogy with the extensive use of isopinocampheylboranes for asymmetric synthesis,[13] that trialkyltin hydrides in which the tin is directly attached to the 2-position of bicyclo[2.2.1]heptanes should be evaluated as reagents for asymmetric synthesis. *exo*- and *endo*-Bicyclo-[2.2.1]heptan-2-yl(trimethyl)stannanes have been prepared by stannylation of 2-norbornylmagnesium bromide.[4] However an alternative synthesis of bicycloheptanylstannanes based on Diels–Alder reactions between vinyl stannanes and cyclopentadiene would have the advantage of leading to adducts with additional functionality for further elaboration. We now describe the synthesis of racemic tin hydrides using this latter approach.

Vinylstannanes containing electron-withdrawing groups have been used in Diels–Alder reactions; for example, 2-phenylbutadiene **1** reacts with the ketone **2** to give a mixture of



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

the regioisomeric adducts **3** and **4** with the preference for regioisomer **3** being enhanced by aluminium trichloride.[14] For the synthesis of bicyclo[2.2.1]heptanyltin hydrides, it was decided to study Diels–Alder reactions of (triphenyl)vinylstannanes followed by removal of a phenyl group using either bromine or iodine since the rate of electrophilic cleavage of groups from tin is known to follow the order benzyl > aryl ~ vinyl > methyl > higher alkyl.[1] Reduction of the triorganotin halide so formed would then give the tin hydride. Although tetraalkylstannanes are configurationally stable at the tin, trialkyltin halides and analogues can racemise, *e.g. via* five-

co-ordinate tin species, and so compounds which are chiral at tin were not selected for study at this stage, although diastereoisomers with chiral tin and chiral ligands will be of interest later.[15]

Results and discussion

Triphenyltin hydride added to methyl propiolate when heated in benzene containing a trace of azoisobutyronitrile to give the (*E*)- and (*Z*)-vinylstannanes **5** and **6**.[16] The ratio of these products was dependent on the reaction temperature, reaction time and the molar ratio of the reactants and varied from 70:30 in favour of the (*Z*)-stannane **6** for reactions carried out at 55 °C for 4 h to 50:50 for reactions carried out under reflux.[17] The stannanes **5** and **6** were separated by chromatography and their double-bond geometries assigned on the basis of their vinylic coupling constants of 19 and 13 Hz, respectively. Similar stereoselectivity, 2:1 in favour of the (*Z*)-isomer **6**, was observed for the triethylborane-induced hydrostannation of methyl propiolate using triphenyltin hydride at room temperature.[18] Palladium-catalysed hydrostannation[19] gave exclusively the 2-triphenylstannylacrylate **7** using tetrakis(triphenylphosphine)-palladium as the catalyst and a mixture of all three vinyl stannanes **5**, **6** and **7** using bis(triphenylphosphine)palladium(II) chloride. However, the (*E*)-isomer **5** was the only product isolated from reaction of the triphenylstannylcopper(I) reagent **8** with methyl propiolate at −78 °C (45%).[20]

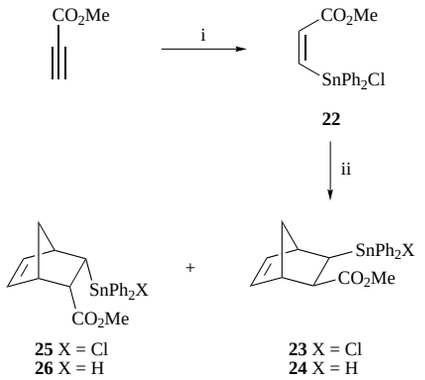
The Diels–Alder reaction between the (*E*)-vinylstannane **5** and cyclopentadiene was carried out in benzene under reflux and gave an excellent yield of the adduct **9** in which the methoxycarbonyl group is in the *endo*-position. No *exo*-isomer was isolated from this reaction. In contrast, the (*Z*)-vinylstannane **6** gave a mixture of the *exo*- and *endo*-adducts **10** and **11**, ratio *ca.* 2:1. Configurations were assigned to these products on the basis of NOE experiments and ^{1}H NMR chemical shifts. For example, for adducts **9** and **11** significant enhancements of the *syn*-7-H were observed on irradiation of 2-H (12.7%), and 2-H (7.5%) and 3-H (8%), respectively, whereas for adduct **10**, enhancements of 3-H (28%), 1-H (7.2%), and 6-H (5%), rather than the *syn*-7-H, were observed on irradiation of 2-H. The relative chemical shifts of the *exo*- and *endo*-hydrogens at C(2) and C(3) were also used to assign stereochemistry. For example, the *endo*-3-H hydrogens in isomers **9** and **10** were observed at δ 1.87 and 1.82, respectively, whereas the *exo*-3-H for the *endo*-isomer **11** was at δ 2.47.[21]

Reduction of the Diels–Alder adduct **9** using diisobutylaluminium hydride gave the alcohol **12** which was converted into its methyl ether **13** on reaction with sodium hydride and methyl iodide. At this point it was intended to cleave one of the phenyl substituents from the tin to generate a tin halide which would be reduced to the corresponding tin hydride. However, treatment with iodine gave a product which had lost both the triphenyltin substituent and the double bond and was identified as the tricyclic iodide **14** (79%). It would appear that destannylation of the *exo*-iodonium ion, see **15**, was taking place rather than the required electrophilic aromatic substitution. The formation of cyclopropanes by elimination from 3-substituted stannanes is indeed a well known reaction.[22] To avoid the destannylation, the alkene **13** was hydrogenated to give the saturated bicyclic alkyl stannane **16** which on treatment with iodine[23] followed by reduction with sodium borohydride[24] was converted into the tin hydride **18** *via* the iodostannane **17**.

Scheme 1 *Reagents*: i, diisobutylaluminium hydride (93%); ii, sodium hydride, methyl iodide (65%); iii, iodine, $CHCl_3$ (**14**, 79%; **17**, 73%); iv, hydrogen, 10% Pd–C, methanol (81%); v, sodium borohydride, ethanol (96%)

The structure of the tin hydride **18** was established on the basis of spectroscopic evidence. In particular, the ^{1}H NMR results indicated the loss of one phenyl group and a signal at δ 6.62 (1 H) which was assigned to the tin hydride proton. In its ^{119}Sn NMR spectrum, the ^{119}Sn signal was observed at δ −118.1. The alcohol **12** was similarly taken through to the tin hydride **21** by hydrogenation followed by treatment of the saturated hydroxyalkylstannane **19** with iodine and sodium borohydride.

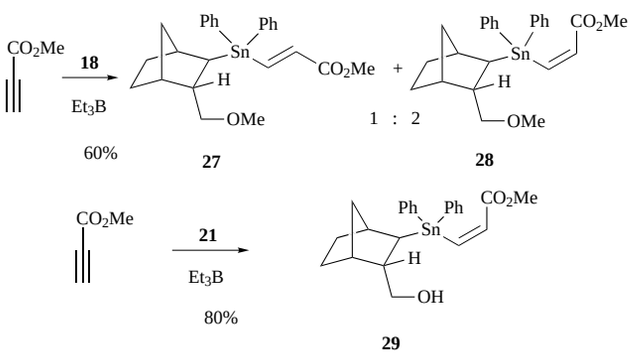
As a second route to bicycloalkyltin hydrides, the Diels–Alder reaction between the (*Z*)-vinyltin chloride **22** and cyclopentadiene was investigated. The vinyltin chloride was prepared by adding diphenylhydridotin chloride to methyl propiolate, the hydridotin chloride being prepared from equimolar amounts of diphenyltin dihydride and diphenyltin dichloride.[25] The *Z*-geometry of the vinyltin chloride **22**, which was not purified, was established by the vinylic coupling of 9 Hz observed in its ^{1}H NMR spectrum, and may well be due to co-ordination of the electron-deficient tin by the carbonyl oxygen of the ester.[26] The Diels–Alder reaction between the tin chloride **22** and cyclopentadiene gave a mixture of adducts **23** and **25** which were immediately reduced using sodium borohydride in



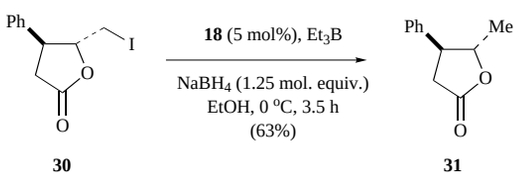
Scheme 2 *Reagents*: i, Ph_2SnHCl, AIBN (trace), benzene, 55 °C (95%); ii, cyclopentadiene, then sodium borohydride, ethanol (**24**:**26** = 50:50; combined yield 56%)

ethanol to give the *exo*- and *endo*-tin hydrides **24** and **26** which were separated by chromatography. Structures were assigned to these tin hydrides on the basis of spectroscopic evidence. Characteristic Sn–H stretching absorptions were observed in the IR spectra of the compounds at 1844 and 1843 cm^{-1}, and *endo*–*exo*-assignments were made on the basis of the relative chemical shifts of 2-H and 3-H, *cf*. those observed for the *exo*- and *endo*-isomers **10** and **11**.[21]

Having prepared functionalised tin hydrides, preliminary studies were carried out into their chemistry. Hydrostannation of methyl propiolate by the tin hydrides **18** and **21** gave the (*E*)- and (*Z*)-adducts **27** and **28** and the (*Z*)-adduct **29**, respectively.



Reduction of the iodo lactone **30**[27] to the lactone **31** was achieved using the tin hydride **18** in the presence of triethylborane[28] using both stoicheiometric and catalytic amounts of the tin hydride, the latter using sodium borohydride as the stoicheiometric reducing agent.[29]



Conclusions

This work has established a synthetic route to racemic, functionalised bicycloheptanyltin hydrides and has shown that these tin hydrides reduce alkyl halides under free-radical conditions with only catalytic quantities of the tin hydride being required. The next stage of this programme was to prepare enantiomerically enriched tin hydrides and evaluate their use for asymmetric reduction. Aspects of this work are outlined in the accompanying paper.[30]

Experimental

Melting points were determined on a Buchi 510 apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer 297 and 1710 spectrometers as liquid films unless otherwise stated. Low- and high-resolution mass spectra were taken on a Kratos Concept mass spectrometer using the chemical ionisation mode (CI) unless otherwise stated. Characteristic isotope peaks were observed for the organostannanes; those quoted correspond to ^{120}Sn. ^1H NMR spectra were recorded on a Varian Unity 500 (500 MHz) and on a Bruker AC-300 or Varian INOVA 300 (300 MHz) spectrometer in [^2H]chloroform unless otherwise stated. ^{13}C NMR were recorded on a Bruker AC 300 or Varian INOVA 300 spectrometer. Flash chromatography was carried out using Merck silica gel 60 (40–60 μm, 230–400 mesh) or May and Baker Sorbsil C60 silica gel (40–60 μm). All solvents were dried and distilled before use. Light petroleum refers to the fraction boiling in the range 40–60 °C. Ether refers to diethyl ether.

Hydrostannation of methyl propiolate

Triphenyltin hydride (4.5 g, 12.8 mmol) and azoisobutyronitrile (AIBN) (5 mg, 0.03 mmol) in benzene (6 cm^3) were added dropwise to a degassed solution of methyl propiolate (803 mg, 9.55 mmol) in benzene (40 cm^3). The mixture was cautiously[16] heated to 80 °C for 24 h and then cooled to room temperature and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:10) as eluent gave *methyl* (Z)-*triphenylstannylacrylate* **6** (2.41 g, 58%) as a white solid, mp 58–60 °C (Found: C, 60.4; H, 4.7. $C_{22}H_{20}O_2Sn$ requires C, 60.7; H, 4.6%: Found: $M^+ - Ph$, 359.0094. $C_{16}H_{15}O_2Sn$ requires *M*, 359.0094); ν_{max}/cm^{-1} 3063, 1711, 1429, 1341, 1221, 728 and 698; δ_H 3.68 (3 H, s, OMe), 7.10 (1 H, d, *J* 13, 2-H), 7.20–7.80 (15 H, m, ArH) and 7.53 (1 H, d, *J* 13, 3-H); *m*/*z* 359 ($M^+ - 77$, 100%). Further elution gave *methyl* (E)-*triphenylstannylacrylate* **5** (1.70 g, 41%) as a white solid, mp 67–69 °C; ν_{max}/cm^{-1} 3064, 1726, 1430, 1216, 729 and 699; δ_H 3.84 (3 H, s, OMe), 6.57 (1 H, d, *J* 19, 2-H), 7.20–7.75 (15 H, m, ArH) and 8.05 (1 H, d, *J* 19, 3-H); *m*/*z* (EI) 359 ($M^+ - 77$, 40%).

Alternative procedures for the preparation of vinylstannanes **5** and **6** included the following: triethylborane (1.0 M in hexane; 0.1 cm^3, 0.1 mmol) was added to a solution of triphenyltin hydride (421 mg, 1.2 mmol) and methyl propiolate (84 mg, 1.0 mmol) in toluene (5 cm^3). The mixture was stirred at 20 °C for 1.5 h and then concentrated under reduced pressure to give the vinylstannanes **5** and **6** (392 mg, 90%), as an oil, ratio 1:2.

Tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol) was added to methyl propiolate (84 mg, 1.0 mmol) and triphenyltin hydride (432 mg, 1.2 mmol) in dry benzene (7 cm^3). The mixture was stirred at 20 °C for 1 h after which solvent removal under reduced pressure gave the vinylstannane **7** (418 mg, 96%) as an oil: δ_H 3.74 (3 H, s, OMe), 6.18 (1 H, d, *J* 1, 3-H), 7.21 (1 H, d, *J* 1, 3-H′) and 7.3–7.75 (15 H, m, ArH).

Bis(triphenylphosphine)palladium(II) chloride (7 mg, 0.01 mmol) was added to methyl propiolate (42 mg, 0.5 mmol) and triphenyltin hydride (216 mg, 0.6 mmol) in tetrahydrofuran (THF) (5 cm^3). The mixture was stirred at 20 °C for 1 h after which concentration under reduced pressure gave the vinylstannanes **5**, **6** and **7** (205 mg, 94%), as an oil.

Butyllithium (1.60 M in hexane; 1.63 cm^3, 2.6 mmol) was added dropwise to diisopropylamine (3.12 mmol) in THF (10 cm^3). The solution was stirred for 15 min at 0 °C after which it was treated with triphenyltin hydride (913 mg, 2.60 mmol) in THF (5 cm^3) and further stirred at 0 °C for 15 min. The solution was cooled to −78 °C and stirred for 15 min, after which copper(I) bromide–dimethyl sulfide (536 mg, 2.60 mmol) were added portionwise, over 45 min. The mixture was then stirred for a further 20 min, after which methyl propiolate (178

mg, 2.0 mmol) in THF (1 cm^3) was added *via* a cannula and stirring continued at −78 °C for 4 h. The mixture was then diluted with methanol (5 cm^3) and allowed to warm to room temperature. It was then diluted with ether (40 cm^3), filtered through Celite and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:10) as eluent gave the (*E*)-vinylstannane **5** (392 mg, 45%) as an oil.

Methyl (1*RS*,2*RS*,3*SR*,4*SR*)-3-triphenylstannylbicyclo[2.2.1]-hept-5-ene-2-carboxylate 9

Freshly distilled cyclopentadiene (1.50 g, 22.68 mmol) was added dropwise to a solution of the (*E*)-vinylstannane **5** (820 mg, 1.89 mmol) in benzene (20 cm^3) and the resultant mixture was heated under reflux for 5 h. It was then allowed to cool to room temperature when solvent was removed under reduced pressure. Flash chromatography of the residue using ether–light petroleum (1:10) as eluent gave the *title compound* **9** (940 mg, 99%), as a white solid, mp 98–99 °C (Found: C, 64.5; H, 5.3. $C_{27}H_{26}O_2Sn$ requires C, 64.7; H, 5.25%); ν_{max}/cm^{-1} 3064, 1732, 1429, 1197, 1112, 1074, 1053, 1022, 998, 728 and 700; δ_H 1.29 (2 H, m, 7-H_2), 1.87 (1 H, dd, *J* 5, 2.5, 3-H), 3.15 (1 H, br s, 4-H), 3.26 (2 H, m, 1-H and 2-H), 3.61 (3 H, s, OMe), 5.87 (1 H, dd, *J* 5.5, 3, vinylic H), 6.31 (1 H, dd, *J* 5.5, 3, vinylic H) and 7.35–7.75 (15 H, m, ArH); δ_C 27.5, 46.1, 46.8, 47.1, 49.4, 51.5, 128.6, 129.0, 130.5, 137.3, 138.4, 139.0 and 175.1; δ_{Sn} −97.1; *m*/*z* (EI) 502 (M^+, 3%), 425 (19) and 351 (100).

Methyl (1*RS*,2*SR*,3*SR*,4*SR*)- and (1*RS*,2*RS*,3*RS*,4*SR*)-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylates 10 and 11

Freshly distilled cyclopentadiene (1 g, 15 mmol) was added to a solution of the (*Z*)-vinylstannane **6** (0.27 g, 0.62 mmol) in benzene (5 cm^3). The mixture was heated under reflux for 4 h and then cooled to room temperature and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:30) as eluent gave the *title compound* **10** (160 mg, 51%) as an oil (Found: M^+, 502.0945. $C_{27}H_{26}O_2Sn$ requires *M*, 502.0946); ν_{max}/cm^{-1} 3061, 1718, 1578, 1568, 1481, 1429, 1349, 1201, 1074, 908, 873, 727 and 699; δ_H 1.25 and 1.53 (each 1 H, d, *J* 8, 7-H), 1.82 (1 H, dd, *J* 8, 2, 3-H), 2.65 (1 H, d, *J* 8, 2-H), 3.18 (1 H, m, 4-H), 3.30 (1 H, m, 1-H), 3.50 (3 H, s, OMe), 6.15 and 6.37 (each 1 H, m, vinylic H) and 7.30–7.75 (15 H, m, ArH); *m*/*z* (EI) 502 (M^+, 6%), 425 (12) and 351 (100). Further elution gave the *title compound* **11** (80 mg, 26%) as an oil (Found: $M^+ - C_6H_5$, 425.0573. $C_{21}H_{21}O_2Sn$ requires *M*, 425.0564); ν_{max}/cm^{-1} 3061, 1718, 1428, 1216, 1202, 1072, 727 and 699; δ_H 1.45 and 1.66 (each 1 H, d, *J* 8, 7-H), 2.47 (1 H, dd, *J* 8, 2, 3-H), 3.33 (1 H, m, 4-H), 3.46 (3 H, s, OMe), 3.47 (2 H, m, 1-H and 2-H), 6.02 and 6.2 (each 1 H, m, vinylic H) and 7.20–7.75 (15 H, m, ArH); *m*/*z* (EI) 425 ($M^+ - 77$, 30%), 351 (89) and 197 (100).

(1*RS*,2*RS*,3*SR*,4*SR*)-3-Hydroxymethyl-2-triphenylstannylbicyclo[2.2.1]hept-5-ene 12

Diisobutylaluminium hydride (1.0 M in hexane; 7.40 cm^3, 7.40 mmol) was added dropwise to a solution of the ester **9** (1.48 g, 2.96 mmol) in dichloromethane (16 cm^3) at −78 °C. The solution was warmed to 0 °C and stirred for 17 h, methanol (18 cm^3) was added and the mixture warmed to room temperature. The mixture was washed with saturated aqueous Rochelle's salt (3 × 30 cm^3) and the combined aqueous phases were back-extracted with dichloromethane (4 × 30 cm^3). The combined organic phases were then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using dichloromethane as eluent gave the *title compound* **12** (1.30 g, 93%) as an oil (Found: $M^+ - C_6H_5$, 397.0608. $C_{20}H_{21}OSn$ requires *M*, 397.0614); ν_{max}/cm^{-1} 3333, 3062, 1480, 1429, 1074, 1022, 727 and 699; δ_H 1.03 (1 H, dd, *J* 5.5, 2.5, 2-H), 1.30 (1 H, br s, OH), 1.36 and 1.43 (each 1 H, m, 7-H), 2.75 (1 H, m, 3-H), 3.10 (1 H, m, 4-H), 3.19 (1 H, m, 1-H), 3.28 (1 H, t, *J* 10, 3-CH), 3.48 (1 H, dd, *J* 10, 7, 3-CH′), 5.95 and 6.3 (each 1 H, m, vinylic H) and 7.30–7.25 (15 H, m, ArH); δ_{Sn} −101.9; δ_C 27.5, 44.8, 45.6, 45.7, 49.2, 66.4, 128.6, 128.9, 130.2, 137.4, 138.4 and 138.7; *m*/*z* 414 (100%) and 397 (77).

(1*RS*,2*RS*,3*SR*,4*SR*)-3-Methoxymethyl-2-triphenylstannylbicyclo[2.2.1]hept-5-ene 13

A solution of the alcohol **12** (100 mg, 0.21 mmol) in THF (0.5 cm^3) was added dropwise to a stirred suspension of sodium hydride (60% in mineral oil; 8.5 mg, 0.21 mmol) in THF (1.5 cm^3) at 0 °C. The mixture was stirred for 1 h at 20 °C and then cooled to 0 °C and methyl iodide (150 mg, 1.06 mmol) was added. The mixture was then stirred for 12 h at 20 °C, filtered through Celite, and the solids triturated with dichloromethane (2 × 5 cm^3). The filtrate and washings were washed with brine (8 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:4) as eluent gave the *title compound* **13** (69 mg, 67%) as a colourless oil (Found: $M^+ - C_6H_5$, 411.0770. $C_{21}H_{23}OSn$ requires *M*, 411.0771); ν_{max}/cm^{-1} 3063, 1429, 1109, 1074, 728 and 700; δ_H 0.93 (1 H, dd, *J* 5.5, 2.5, 2-H), 1.29 and 1.35 (each 1 H, m, 7-H), 2.79 (1 H, m, 3-H), 2.99 (1 H, t, *J* 9, 3-CH), 3.01 (1 H, br s, 4-H), 3.08 (1 H, br s, 1-H), 3.12 (1 H, dd, *J* 9, 6, 3-CH′), 3.22 (3 H, s, OMe), 5.90 and 6.23 (each 1 H, dd, *J* 5.5, 3, 5-H and 6-H) and 7.35–7.75 (15 H, m, ArH); δ_C 27.8, 42.5, 45.1, 45.6, 49.1, 58.7, 76.3, 128.5, 128.9, 130.6, 137.4, 137.6 and 139.0; δ_{Sn} −102.1; *m*/*z* 428 (47%) and 411 (100).

5-Iodo-3-methoxymethyltricyclo[2.2.1.$0^{2,6}$]heptane 14

Iodine (26 mg, 0.205 mmol) was added to a solution of the triphenylstannane **13** (60 mg, 0.123 mmol) in chloroform (1 cm^3). The mixture was stirred for 15 min at 20 °C and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:6) as the eluent gave the *title compound* **14** (26 mg, 79%) as an oil; ν_{max}/cm^{-1} 3065, 1453, 1195, 1119, 1094, 802 and 705; $\delta_H(C_6D_6)$ 0.75 (1 H, t, *J* 5, 1-H), 1.11 (1 H, dt, *J* 5, 1, 2-H), 1.17 (1 H, d, *J* 11, 7-H), 1.39 (1 H, t, *J* 5, 6-H), 1.70 (1 H, t, *J* 7.5, 3-H), 2.03 (1 H, br s, 4-H), 2.18 (1 H, d, *J* 11, 7-H′), 2.85 (2 H, m, 3-CH_2), 3.07 (3 H, s, OMe) and 3.98 (1 H, s, 5-H); $\delta_C(C_6D_6)$ 13.4, 16.2, 19.9, 32.0, 34.4, 40.2, 44.3, 58.6 and 72.3; *m*/*z* 137 (100%).

(1*SR*,2*RS*,3*SR*,4*RS*)-3-Methoxymethyl-2-triphenylstannylbicyclo[2.2.1]heptane 16

Palladium (10% on charcoal; 220 mg, 0.211 mmol) was added to a solution of the unsaturated stannane **13** (870 mg, 1.79 mmol) in ethanol (33 cm^3), the mixture stirred vigorously for 22 h under an atmosphere of hydrogen, then filtered through Celite, the absorbent being subsequently washed with ethanol (5 × 10 cm^3). The combined filtrate and washings were concentrated under reduced pressure to give the *title compound* **16** (830 mg, 96%) as an oil (Found: $M^+ - C_6H_5$, 413.0931. $C_{21}H_{25}OSn$ requires *M*, 413.0927); ν_{max}/cm^{-1} 3063, 1481, 1429, 1111, 1074, 727 and 699; δ_H 1.25 (1 H, dd, *J* 5.5, 2.5, 2-H), 1.29–1.77 (6 H, m, 5-H_2, 6-H_2 and 7-H_2), 2.35 (1 H, m, 4-H), 2.54 (1 H, m, 1-H), 2.63 (1 H, m, 3-H), 3.26 (3 H, s, OMe), 3.40 (2 H, m, 3-CH_2) and 7.35–7.75 (15 H, m, ArH); δ_C 22.5, 33.9, 34.1, 39.5, 40.2, 40.7, 45.0, 58.7, 74.8, 128.4, 128.7, 137.3 and 139.1; *m*/*z* (EI) 413 ($M^+ - 77$, 63%) and 351 (100).

Diphenyl {(1*SR*,2*RS*,3*SR*,4*RS*)-3-methoxymethylbicyclo-[2.2.1]heptan-2-yl}tin iodide 17

Iodine (11 mg, 0.086 mmol) was added to a solution of the triphenylstannane **16** (35 mg, 0.072 mmol) in chloroform (1 cm^3). The reaction mixture was stirred for 15 min at 20 °C and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:6) as eluent

gave the *title compound* **17** as a colourless oil (28 mg, 73%) (Found: $M^+ - C_6H_5$, 462.9581. $C_{15}H_{20}IOSn$ requires *M*, 462.9581); ν_{max}/cm^{-1} 3064, 1430, 1108, 1072, 728 and 696; δ_H 1.25–1.71 (7 H, m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.32 (1 H, br s, 4-H), 2.52 (1 H, m, 3-H), 2.61 (1 H, m, 1-H), 3.26 (3 H, s, OMe), 3.40 (2 H, m, 3-CH_2) and 7.35–7.75 (10 H, m, ArH); *m*/*z* 480 (4%) and 463 (36).

Diphenyl{(1*SR*,2*RS*,3*SR*,4*RS*)-3-methoxymethylbicyclo-[2.2.1]heptan-2-yl}tin hydride 18

Sodium borohydride (6.4 mg, 0.17 mmol) was added portionwise to a solution of the tin iodide **17** (26 mg, 0.048 mmol) in ethanol (1 cm^3). After 1 h at 20 °C, the solvent was removed under reduced pressure and the residue was partitioned between ether and water (5 cm^3). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give the *title compound* **18** (19 mg, 96%) as a colourless oil which was chromatographed using ether–light petroleum (1:30) as eluent (Found: $M^+ - H$, 413.0924. $C_{21}H_{25}OSn$ requires *M*, 413.0927); ν_{max}/cm^{-1} 3063, 1822, 1429, 1111, 729 and 699; δ_H 1.28–1.75 (7 H, m, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.32 (1 H, m, 4-H), 2.60 (1 H, m, 3-H), 2.68 (1 H, m, 1-H), 3.27 (3 H, s, OMe), 3.37 (1 H, t, *J* 8.5, 3-CH), 3.49 (1 H, dd, *J* 8.5, 7.5, 3-CH′), 5.30 (1 H, s, SnH) and 7.35–7.75 (10 H, m, ArH); *m*/*z* (EI) 413 ($M^+ - 1$, 53%) and 371 (82).

(1*SR*,2*RS*,3*SR*,4*RS*)-3-Hydroxymethyl-2-triphenylstannylbicyclo[2.2.1]heptane 19

The hydroxy alkene **12** (1.40 g, 2.96 mmol) was hydrogenated following the procedure outlined for the synthesis of the bicycloheptane **16** to give, after chromatography using dichloromethane as eluent, the *title compound* **19** (740 mg, 52%) as a white solid, mp 85–87 °C (Found: C, 65.5; H, 5.85. $C_{26}H_{28}OSn$ requires C, 65.7; H, 5.95%; Found: $M^+ - C_6H_5$, 399.0779. $C_{20}H_{23}OSn$ requires *M*, 399.0771); ν_{max}/cm^{-1} 3377, 3063, 1578, 1481, 1429, 1074, 1023, 998, 727 and 699; δ_H 1.11 (1 H, br s, OH), 1.20–1.75 (7 H, m, 2-H, 5-H_2, 6-H_2, 7-H_2), 2.38 (1 H, m, 4-H), 2.55 (2 H, m, 1-H and 3-H), 3.65 (2 H, m, 3-CH_2) and 7.35–7.70 (15 H, m, ArH); *m*/*z* (EI) 399 ($M^+ - 77$, 35%) and 351 (100).

Diphenyl{(1*SR*,2*RS*,3*SR*,4*RS*)-3-hydroxymethylbicyclo[2.2.1]-heptan-2-yl}tin hydride 21

Iodine (30 mg, 0.12 mmol) was added to a solution of the stannane **19** (56 mg, 0.12 mmol) in dichloromethane (1.5 cm^3) and the mixture was stirred for 5 min at room temperature. The solvent was removed under reduced pressure and the residue dissolved in ethanol (2 cm^3). After cooling to −78 °C, sodium borohydride (4.5 mg, 0.12 mmol) was added portionwise. After 10 min, saturated aqueous ammonium chloride (5 cm^3) was added and the solution warmed to room temperature. The resulting two-phase mixture was extracted with ether (8 × 15 cm^3) and the organic phase separated, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue gave the *title compound* **21** (3 mg, 7%)† as an oil; ν_{max}/cm^{-1} 3352, 1821, 1428, 1071, 1023, 729 and 698; $\delta_H(C_6D_6)$ 0.89–1.52 (8 H, m, OH, 2-H, 5-H_2, 6-H_2 and 7-H_2), 2.15 (1 H, m, 4-H), 2.36 (2 H, m, 3-H and 1-H), 3.35 (2 H, m, 3-CH_2), 6.53 (1 H, s, Sn-H) and 7.10–7.60 (6 H, m, ArH).

Diphenyl{(1*RS*,2*RS*,3*RS*,4*SR*)- and -(1*RS*,2*SR*,3*SR*,4*SR*)-3-methoxycarbonylbicyclo[2.2.1]heptan-2-yl}tin hydrides 24 and 26

Methyl propiolate (1.3 g, 15 mmol) was added to a stirred solution of chlorodiphenyltin hydride (3.95 g, 12.8 mmol) containing a trace of AIBN in benzene (5 cm^3) under argon and the reaction mixture was heated cautiously to 55 °C over 2 h. A white suspension formed and the mixture was stirred at 55 °C for 2 h and then at room temperature for a further 15 h. Concentration under reduced pressure gave the vinyltin chloride **22** (5.0 g, 95%) as a white gum which was used immediately; δ_H 3.92 (3 H, s, OMe), 6.99 (1 H, d, *J* 9, 2-H), 7.1–7.9 (10 H, m, ArH) and 7.76 (1 H, d, *J* 9, 3-H).

Cyclopentadiene (2.0 g, 30 mmol) was added to a suspension of the vinyltin chloride **22** (1.5 g, 3.0 mmol) in THF (10 cm^3), under argon and the reaction mixture was heated under reflux for 6 h and then concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:10) as eluent gave the tin chlorides **23** and **24** (1.4 g, 79%). Sodium borohydride (0.14 g, 3.7 mmol) was added portionwise to a stirred suspension of the adducts **23** and **25** (0.5 g, 1.11 mmol) in ethanol (20 cm^3) under argon and the reaction mixture was stirred at room temperature for 1 h and then concentrated under reduced pressure. The residue was partitioned between dichloromethane (50 cm^3) and water (50 cm^3) and the organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:30) as the eluent gave the *title compound* **24** (158 mg, 28%) as a colourless oil (Found: $M^+ - H$, 425.0568. $C_{21}H_{21}O_2Sn$ requires *M*, 425.0563); ν_{max}/cm^{-1} 3062, 1843, 1715, 1430, 1231, 1203, 1049, 973 and 938; δ_H 1.14 and 1.36 (each 1 H, d, *J* 8, 7-H), 1.92 (1 H, dd, *J* 2, 7, 2-H), 2.78 (1 H, d, *J* 7, 3-H), 3.32 (1 H, br s, 1-H), 3.67 (1 H, br s, 4-H), 3.96 (3 H, s, OMe), 5.30 (1 H, s, Sn-H), 6.2 (1 H, m, 5-H), 6.42 (1 H, m, 6-H) and 7.30–8.02 (10 H, m, ArH); *m*/*z* (EI) 425 ($M^+ - 1$, 76%) and 359 (20). Further elution gave the *title compound* **26** (158 mg, 28%) as a colourless oil; ν_{max}/cm^{-1} 3062, 1844, 1717, 1429, 1251, 1015, 729 and 700; δ_H 1.48 and 1.72 (each 1 H, d, *J* 8, 7-H_2), 2.55 (1 H, dd, *J* 2, 7, 2-H), 3.45 (2 H, m, 1-H and 3-H), 3.66 (1 H, br s, 4-H), 3.88 (3 H, s, OMe), 5.29 (1 H, s, Sn-H), 5.85 and 6.16 (each 1 H, dd, *J* 2, 5, 5-H and 6-H) and 7.30–7.90 (10 H, m, ArH); *m*/*z* (EI) 425 ($M^+ - 1$, 60%).

Methyl (*E*)- and (*Z*)-3-{(1*SR*,2*RS*,3*SR*,4*RS*)-3-methoxymethylbicyclo[2.2.1]heptan-2-yl(diphenyl)stannyl}prop-2-enoates 27 and 28

Triethylborane (1 M in hexane; 0.024 cm^3, 0.0024 mmol) was added to a solution of the tin hydride **18** (10 mg, 0.024 mmol) and methyl propiolate (1.7 mg, 0.02 mmol) in benzene (1 cm^3). The mixture was stirred at 20 °C for 1.5 h and then concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:20) as eluent gave the (*Z*)-isomer of the *title compound* **28** (4 mg, 40%) as an oil (Found: $M^+ - C_6H_5$, 421.0824. $C_{19}H_{25}O_3Sn$ requires *M*, 421.0826); ν_{max}/cm^{-1} 1713, 1341, 1216, 1111, 1074, 824, 728 and 699; δ_H 1.20–1.70 (7 H, m, 2′-H, 5′-H_2, 6′-H_2, 7′-H_2), 2.30 (1 H, m, 4′-H), 2.40 (1 H, m, 1′-H), 2.49 (1 H, m, 3′-H), 3.28 (3 H, s, OCH_3), 3.37 (2 H, m, 3′-CH_2), 3.70 (3 H, s, CO_2CH_3), 6.99 (1 H, d, *J* 13, 2-H), 7.45 (1 H, d, *J* 13, 3-H) and 7.35–7.70 (10 H, m, ArH); *m*/*z* (EI) 421 ($M^+ - C_6H_5$, 20%) and 359 (100). Further elution gave the (*E*)-isomer of the *title compound* **27** (2 mg, 20%) as an oil; ν_{max}/cm^{-1} 1724, 1430, 1215, 1075, 728 and 699; δ_H 1.20–1.70 (7 H, m, 2′-H, 5′-H_2, 6′-H_2, 7′-H_2), 2.30 (1 H, m, 4′-H), 2.40 (1 H, m, 1′-H), 2.48 (1 H, m, 3′-H), 3.26 (3 H, s, OCH_3), 3.36 (2 H, m, 3′-CH_2), 3.80 (3 H, s, CO_2CH_3), 6.45 (1 H, d, *J* 18, 2-H), 7.35–7.75 (10 H, m, ArH) and 7.91 (1 H, d, *J* 18, 3-H); *m*/*z* (EI) 421 ($M^+ - 77$, 100%) and 359 (80%).

Methyl (*Z*)-3-{(1*SR*,2*RS*,3*SR*,4*RS*)-3-hydroxymethylbicyclo-[2.2.1]heptan-2-yl(diphenyl)stannyl}prop-2-enoate 29

Following the procedure outlined for the synthesis of the acrylates **27** and **28**, the tin hydride **21** (3 mg, 0.008 mmol) and methyl propiolate (0.44 mg, 0.005 mmol) gave, after chromatography using ether–light petroleum (1:3) as eluent, the *title compound* **29** (2 mg, 80%) as an oil; ν_{max}/cm^{-1} 3420, 1646, 1430, 1342, 1075, 998, 729 and 698; δ_H 1.25–1.75 (8 H,

† The yield of this hydroxyalkyltin hydride was low, but was significantly improved when the enantiomerically enriched material was prepared.[30]

m, OH, 2′-H, 5′-H_2, 6′-H_2 and 7′-H_2), 2.30 (1 H, m, 4′-H), 2.5 (2 H, m, 1′-H and 3′-H), 3.5–3.80 (5 H, m, CO_2CH_3 and 3′-CH_2), 6.99 (1 H, d, *J* 13, 2-H) and 7.35–7.70 (11 H, m, ArH and 3-H).

(4*RS*,5*SR*)-5-Methyl-4-phenyldihydrofuran-2(3*H*)-one 31

A solution of triphenyltin hydride (677 mg, 1.93 mmol) in toluene (8 cm^3) was added to a solution of the iodo lactone **30** (583 mg, 1.93 mmol) in toluene (8 cm^3) at −78 °C, followed rapidly by triethylborane (1.0 M in hexane; 0.20 cm^3, 0.20 mmol). The mixture was stirred at −78 °C for 1.5 h and then diluted with ethyl acetate (30 cm^3). Saturated aqueous potassium fluoride (4.0 cm^3) and potassium fluoride (2 g, 34.5 mmol) were added to the mixture which was warmed to room temperature. The precipitated tin fluoride was filtered off and the combined filtrates were washed with brine (2 × 20 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:3) as eluent gave the *title compound* **31** (239 mg, 70%) as an oil (Found: M^+, 176.0837. $C_{11}H_{12}O_2$ requires *M*, 176.0837); ν_{max}/cm^{-1} 1784, 1499, 1204, 1072, 940, 758 and 702; δ_H 1.40 (3 H, d, *J* 6.5, 5-Me), 2.85 (1 H, dd, *J* 10, 17, 3-H), 2.99 (1 H, dd, *J* 7, 17, 3-H′), 3.25 (1 H, dt, *J* 11.5, 8.5, 4-H), 4.55 (1 H, dq, *J* 8.5, 6.5, 5-H) and 7.30 (5 H, m, ArH); δ_C 19.1, 37.4, 49.6, 83.1, 127.5, 128.4, 129.4, 138.4 and 175.6; *m*/*z* (EI) 176 (M^+, 7%).

A solution of the tin hydride **18** (16 mg, 0.04 mmol) in toluene (0.5 cm^3) was added to a solution of the iodo lactone **30** (12 mg, 0.04 mmol) in toluene (0.5 cm^3) at −78 °C followed rapidly by triethylborane (1.0 M in hexane; 0.05 cm^3, 0.005 mmol). The mixture was stirred at −78 °C for 1.5 h and then diluted with ethyl acetate (2 cm^3). Saturated aqueous potassium fluoride (0.2 cm^3) and potassium fluoride (100 mg, 1.72 mmol) were added and the mixture warmed to room temperature. The precipitated tin fluoride was filtered off and the combined filtrates were washed with brine (2 × 5 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:3) as eluent gave the title compound **31** (4 mg, 60%) as an oil.

A solution of the tin hydride **18** (15 mg, 0.04 mmol) in degassed absolute ethanol (2 cm^3) was added to a solution of the iodo lactone **30** (55 mg, 0.18 mmol) in ethanol (2 cm^3) at 0 °C. Triethylborane (1.0 M in hexane; 0.01 cm^3, 0.01 mmol) was added followed rapidly by a pre-cooled solution of sodium borohydride (9 mg, 0.24 mmol) in ethanol (1 cm^3). The reaction mixture was stirred at 0 °C for 3.5 h and then partitioned between saturated aqueous sodium hydrogen carbonate (10 cm^3) and ether (10 cm^3). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether–light petroleum (1:2) as eluent gave the *title compound* **31** (20 mg, 63%) as an oil together with the recovered tin hydride **18** (11 mg, 73%).

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References

1 M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987.
2 A. L. Costa, M. G. Piazza, E. Tagliavini, C. Trombini and A. Umani-Ronchi, *J. Am. Chem. Soc.*, 1993, **115**, 7001; G. E. Keck, K. H. Tarbet and L. S. Geraci, *J. Am. Chem. Soc.*, 1993, **115**, 8467; S. Aoki, K. Mikami, M. Terada and T. Nakai, *Tetrahedron*, 1993, **49**, 1783; G. E. Keck, D. Krishnamurthy and M. C. Grier, *J. Org. Chem.*, 1993, **58**, 6543; G. E. Keck and L. S. Geraci, *Tetrahedron Lett.*, 1993, **34**, 7827; G. E. Keck, D. Krishnamurthy and X. Chen, *Tetrahedron Lett.*, 1994, **35**, 8323; A. Yanagisawa, H. Nakashima, A. Ishiba and H. Yamamoto, *J. Am. Chem. Soc.*, 1996, **118**, 4723; J. W. Faller, D. W. Sams and X. Liu, *J. Am. Chem. Soc.*, 1996, **118**, 1217; C.-M. Yu, H.-S. Choi, W.-H. Jung, H.-J. Kim and J. Shin, *Chem. Commun.*, 1997, 761; A. Yanagisawa, A. Ishiba, H. Nakashima and H. Yamamoto, *Synlett*, 1997, 88; P. G. Cozzi, P. Orioli, E. Tagliavini and A. Umani-Ronchi, *Tetrahedron Lett.*, 1997, **38**, 145; J. A. Marshall and Y. Tang, *Synlett*, 1992, 653.
3 S. Kobayashi and T. Mukaiyama, *Chem. Lett.*, 1989, 297; T. Mukaiyama, H. Uchiro and S. Kobayashi, *Chem. Lett.*, 1989, 1001; T. Mukaiyama, H. Uchiro and S. Kobayashi, *Chem. Lett.*, 1989, 1757; T. Mukaiyama, S. Kobayashi and T. Sano, *Tetrahedron*, 1990, **46**, 4653; S. Kobayashi, H. Uchiro, Y. Fujishita, I. Shiina and T. Mukaiyama, *J. Am. Chem. Soc.*, 1991, **113**, 4247; T. Mukaiyama, H. Uchiro, I. Shiina and S. Kobayashi, *Chem. Lett.*, 1990, 1019; T. Mukaiyama, I. Shiina and S. Kobayashi, *Chem. Lett.*, 1991, 1901; S. Kobayashi, Y. Fujishita and T. Mukaiyama, *Chem. Lett.*, 1990, 1455; S. Kobayashi, M. Furuya, A. Ohtsubo and T. Mukaiyama, *Tetrahedron: Asymmetry*, 1991, **2**, 635; T. Mukaiyama, S. Kobayashi, H. Uchiro and I. Shiina, *Chem. Lett.*, 1990, 129; T. Mukaiyama, M. Furuya, A. Ohtsubo and S. Kobayashi, *Chem. Lett.*, 1991, 989; S. Kobayashi, H. Uchiro, I. Shiina and T. Mukaiyama, *Tetrahedron*, 1993, **49**, 1761; S. Kobayashi, A. Ohtsubo and T. Mukaiyama, *Chem. Lett.*, 1991, 831; S. Kobayashi and T. Kawasuji, *Synlett*, 1993, 911.
4 R. Krishnamurti and H. G. Kuivila, *J. Org. Chem.*, 1986, **51**, 4947; D. Young, M. Jones and W. Kitching, *Aust. J. Chem.*, 1986, 563.
5 U.-M. Gross, M. Bartels and D. Kaufmann, *J. Organomet. Chem.*, 1988, **344**, 277; J. M. Chong, G. K. MacDonald, S. B. Park and S. H. Wilkinson, *J. Org. Chem.*, 1993, **58**, 1266.
6 D. Nanni and D. Curran, *Tetrahedron: Asymmetry*, 1996, **7**, 2417; M. Blumenstein, K. Schwarzkopf and J. O. Metzger, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 235.
7 H. Schumann and B. C. Wassermann, *J. Organomet. Chem.*, 1989, **365**, C1.
8 H. Schumann, B. C. Wassermann and J. Pickardt, *Organometallics*, 1993, **12**, 3051.
9 H. Schumann, B. C. Wassermann and F. E. Hahn, *Organometallics*, 1992, **11**, 2803.
10 J. C. Podesta, A. B. Chopa, G. E. Radivoy and C. A. Vitale, *J. Organomet. Chem.*, 1995, **494**, 11; C. A. Vitale and J. C. Podesta, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2407.
11 J. Otera, Y. Yoshinaga, T. Yamaji, T. Yoshioka and Y. Kawasaki, *Organometallics*, 1985, **4**, 1213.
12 P. J. Cox, S. M. S. V. Doidge-Harrison, R. A. Howie, I. W. Nowell, O. J. Taylor and J. W. Wardell, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2017; O. J. Taylor and J. L. Wardell, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 267; L. D. Hall, P. R. Steiner and D. C. Miller, *Can. J. Chem.*, 1978, **57**, 38; K. J. Hale, L. Hough and A. C. Richardson, *Carbohydr. Res.*, 1988, **177**, 259.
13 H. C. Brown and K. S. Bhat, *J. Am. Chem. Soc.*, 1986, **108**, 293, 5919; H. C. Brown and P. K. Jadhav, *J. Org. Chem.*, 1984, **49**, 4089; H. C. Brown and N. N. Joshi, *J. Org. Chem.*, 1988, **53**, 4059.
14 C. R. Johnson and J. F. Kadow, *J. Org. Chem.*, 1987, **52**, 1493.
15 M. Gielen, *Top. Curr. Chem.*, 1982, **104**, 57; G. J. D. Peddle and G. Redl, *J. Chem. Soc., Chem. Commun.*, 1968, 626; M. Gielen, *Top. Stereochem.*, 1980, **12**, 217; M. Gielen and Y. Tondeur, *J. Organomet. Chem.*, 1979, **169**, 265.
16 J. K. Stille and B. L. Groh, *J. Am. Chem. Soc.*, 1987, **109**, 813.
17 J. C. Cochran, L. E. Williams, B. S. Bronk, J. A. Calhoun, J. Fassberg and K. G. Clark, *Organometallics*, 1989, **8**, 804.
18 K. Nozaki, K. Oshima and K. Utimoto, *Tetrahedron*, 1989, **45**, 923.
19 H. X. Zhang, F. Guibe and G. Balavoine, *J. Org. Chem.*, 1990, **55**, 1857; Y. Ichinose, H. Oda, K. Oshima and K. Utimoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3468; H. Miyake and K. Yamamura, *Chem. Lett.*, 1989, 981; J. C. Cochran, B. S. Bronk, K. M. Terrence and H. K. Phillips, *Tetrahedron Lett.*, 1990, **31**, 6621.
20 E. Piers, J. M. Chong and H. E. Morton, *Tetrahedron*, 1989, **45**, 363; E. Piers, T. Wong and K. A. Ellis, *Can. J. Chem.*, 1992, **70**, 2058.
21 L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd edn., Pergamon, 1969, p. 84.
22 I. Fleming and C. Urch, *Tetrahedron Lett.*, 1983, **24**, 4591; J. F. Kadow and C. R. Johnson, *Tetrahedron Lett.*, 1984, **25**, 5255; J. W. Herndon and J. J. Harp, *J. Organomet. Chem.*, 1990, **393**, C1; G. E. Keck and S. D. Tonnies, *Tetrahedron Lett.*, 1993, **34**, 4607.
23 Y. Yamamoto and A. Yanagi, *Chem. Pharm. Bull.*, 1982, **30**, 1731.
24 H. G. Kuivila, *Synthesis*, 1970, 499.
25 W. P. Neumann and J. Pedain, *Tetrahedron Lett.*, 1964, 2461.

26 M. Ochiai, S. Iwaki, T. Ukita, Y. Mitsuura, M. Shiro and Y. Nagao, *J. Am. Chem. Soc.*, 1988, **110**, 4606.
27 F. B. Gonzales and P. A. Bartlett, *Org. Synth.*, 1990, **Coll. Vol. VII**, 164.
28 K. Miura, Y. Ichinose, K. Nozaki, F. Fugami, K. Oshima and K. Utimoto, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 143.
29 E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1975, **44**, 2554.
30 R. Beddoes, R. M. Pratt and E. J. Thomas, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 717.

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