PART I

Molecular Design for a Novel Organotin Hydride

1.4 Experimental Details

This section provides all the details including experimental procedures, compound characterization and spectral data. Tools used for characterization of compounds have also received brief mentions.

Non-aqueous reactions were performed in oven (150 °C) or flame-dried glass wares, under an atmosphere of dry argon or nitrogen at ambient temperature, unless otherwise stated.

Proton nuclear magnetic resonance \((^1\text{H nmr})\) spectra were recorded on Varian Unity 500 (500 MHz), Varian XL 300 (300 MHz), Varian Gemini 200 (200 MHz), Bruker AC 400 (400 MHz), Bruker AC 300 (300 MHz) or Bruker AC 250 (250 MHz) spectrometers in chloroform-\(d_1\) with residual non-deuterated solvent as internal standard.

Carbon nuclear magnetic resonance \((^{13}\text{C nmr})\) spectra were recorded on Varian Unity 500 (125 MHz), Varian Gemini 200 (50 MHz), Bruker AC 300 (75 MHz) or Bruker AC 250 (62.5 MHz) spectrometers in chloroform-\(d_1\) with deuterated solvent as internal standard.

Chemical shifts for \(\delta_H\) and \(\delta_C\) are quoted in units of parts per million downfield from tetramethylsilane. Signal splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), unresolved multiplet (m), narrow (n), broad (br) or complex, if multiple signals overlap. Coupling constants \(J\) are given in units of hertz (Hz). When they
are observed, up to four bond carbon-tin and three bond proton-tin coupling constants are quoted. When assignment of a signal is ambiguous, carbon-tin coupling constants (if observed) are quoted as $J_{\text{CSn}}$. Average values for $^{117}\text{Sn}$ and $^{119}\text{Sn}$ isotopes are quoted unless they are resolvable ($J_{117\text{Sn}} < J_{119\text{Sn}}$), in which case coupling constants to each isotope are quoted.

Infra-red spectra were recorded on Perkin Elmer 1710 FT and ATI Mattson Genesis Series FT-IR spectrophotometers as evaporated films (dichloromethane) on sodium chloride plates unless otherwise stated. All absorptions shown are strong, unless indicated.

Mass spectra were recorded on a Kratos Concept 1S and Fisons VG Trio 2000 mass spectrometers. The modes of ionization were electron impact (EI) or chemical ionization (CI) using ammonia as the reagent gas. For compounds containing tin, characteristic groups of isotope peaks were observed, and only the most abundant isotope is quoted ($^{120}\text{Sn}$).

Optical rotations were determined on an Optical Activity AA100 polarimeter operating at 589 nm using a 0.25 dm cell. $[\alpha]_D$ values are given in $10^{-1}$ deg cm$^2$ g$^{-1}$.

Crystallographic measurements were made on a Rigaku AFC5R X-ray diffractometer with graphite-monochromated Cu $K_\alpha$ radiation and a 12 KW rotating anode generator.

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected.

Flash chromatography refers to the process of Still$^{37}$ and was carried out using Merck silica gel 60H (40-60 μm, 230-300 mesh) or Rhône-Poulenc Sorbsil C60 silica gel
(40-60 μm) as the stationary phase. Thin layer chromatography (tlc) was performed using Machery Nagel Duren DC-Fertigplatten SIL G-25 UV<sub>254</sub> silica gel glass plates. Detection was by ultra-violet absorption and by treatment with 10% ethanolic dodecamolybdophosphoric acid or aqueous potassium permanganate and subsequent heating.

Petrol refers to the fraction of light petroleum ether which distils in the range 40-60 °C and was redistilled prior to use. Ether refers to diethyl ether. Tetrahydrofuran (THF) was dried over sodium wire and distilled under an atmosphere of nitrogen in the presence of benzophenone as an indicator and was collected once a deep blue colour was obtained. Dichloromethane was dried over calcium hydride and distilled under an atmosphere of nitrogen. Di-iso-propylamine and diethylamine were dried over potassium hydroxide and distilled prior to use. Benzene, toluene and ether were dried over sodium wire. Ethanol and methanol were dried by distillation from the corresponding magnesium alkoxide under an atmosphere of nitrogen. Cyclopentadiene (bp 40 °C) was obtained by cracking dicyclopentadiene (bp 170 °C) and was collected and stored at -78 °C prior to use.

n-Butyllithium was procured as a solution in hexane and was titrated against a standard solution of isopropanol in xylene using N,N'-dipyridyl as indicator. Brine refers to saturated aqueous sodium chloride solution and Rochelle’s salt refers to saturated aqueous potassium sodium tartrate solution. Lithium iodide were dried for a minimum of 48 h on a high vacuum line prior to use. (R) and (S)-α-methoxy-α-(trifluoromethyl) phenylacetic acid (Mosher’s acid), used for determination of the enantiomeric purity of alcohols, was of 99% ee. (R)-Pantolactone was of 99% ee.
I.4.1 Procedures and Characterization of Compounds

I.4.1.1 (E)-3-Triphenylstannylprop-2-en-1-ol, I.19 40

AIBN (25 mg) followed by redistilled propargyl alcohol (0.6 cm³, 10.3 mmol) were added to a deoxygenated (30 min with nitrogen) and stirred solution of triphenyltin hydride (4.1 g, 11.68 mmol, 1.1 eq.) in toluene (20 cm³). The mixture was heated at about 110 °C for 25 h. It was then cooled to ambient temperature, solvent removed under vacuum and the products were separated by a column of silica gel using 20% ether in light petroleum as the eluent. 2-Triphenylstannylprop-2-en-1-ol I.24 (Rf 0.31, 20% ether in light petroleum) was eluted first as a white solid (412.6 mg, 1.01 mmol, 9.8%), mp 108 °C. Found (%): C 62.30, H 5.04, Sn 28.84. \( \text{C}_{21}\text{H}_{20}\text{OSn} \) requires C 61.96, H 4.95, Sn 29.16.

IR (\( \nu_{\text{max}} / \text{cm}^{-1} \)) : 699, 730, 930, 997, 1013, 1073, 1263, 1303, 1428, 1480, 2929, 3062, 3368 (broad, OH).

\( ^1\text{H NMR} \) (\( \delta\text{H ppm} \)) : 1.69 (1H, t, \( ^3J\ 5.90, \text{OH} \)), 4.51 (2H, ddd, \( ^3J\ 5.90, ^4J\ 1.79, ^3J_{\text{SnH}} \) 41.14, \( \text{CH}_2 \)), 5.54 (1H, td, \( ^2J\ 1.79, ^4J\ 1.72, ^3J_{119}\text{SnH} \) 77.73, \( ^3J_{117}\text{SnH} \) 40.2, olefinic), 6.16 (1H, dt, \( ^2J\ 1.79, ^4J\ 1.79, ^3J_{119}\text{SnH} \) 166.58, \( ^3J_{117}\text{SnH} \) 40.2, olefinic), 7.35-7.55 (9H, complex m, aromatic, \( m-\) &
\( p\)-protons), 7.55-7.75 (6H, complex m, \( ^3J_{\text{SnH}}\) 49, aromatic \( o\)-protons).

\[^{13}\text{C} \text{NMR} \ (\delta_{\text{C}} \text{ ppm}) : 68.97 \ (1-\text{C}), \ 126.74 \ (3-\text{C}), \ 128.52 \ (\text{meta}), \ 128.95 \ (\text{para}), \ 137.1 \ (\text{ortho}), \ 138.07 \ (\text{ipso}), \ 152.55 \ (2-\text{C}).

\text{Mass} \ (m/z \text{ Cl}) : 331 \ (M^+ -\text{Ph}, 85\%), \ 348 \ (M^+ -\text{Ph} + \text{NH}_3, 100\%), \ 368 \ (\text{Ph}_3\text{Sn} + \text{NH}_3, 28\%).

Compound \ 1.24 \ was \ followed \ by \ the \ title \ compound \ 1.19 \ (R/0.125) \ as \ a \ white \ solid \ (2.44 \ g, \ 5.99 \ mmol, \ 58.2\%) \ mp \ 120 \ ^\circ \text{C}. \ Found \ (%): \ C \ 62.82, \ H \ 4.71, \ Sn \ 29.90. \ C_{21}H_{20}OSn \ requires \ C \ 61.96, \ H \ 4.95, \ Sn \ 29.16.

\text{IR} \ (\nu_{\text{max}} /\text{cm}^{-1}) : 699, \ 730, \ 997, \ 1013, \ 1074, \ 1263, \ 1428, \ 1480, \ 3062, \ 3393 \ (\text{broad, OH}).

\[^1\text{H} \text{NMR} \ (\delta_{\text{H}} \text{ ppm}) : 1.68 \ (1\text{H}, t, ^3J \ 5.91, \ \text{OH}), \ 4.34 \ (2\text{H}, \text{dd}, ^3J \ 5.9, ^3J \ 4.2, ^4J \ 1.4, \ \text{CH}_2). \]

\hspace{1cm} 6.46 \ (1\text{H}, \text{td}, ^3J \ 19.08, ^3J \ 3.99, ^3J_{\text{SnH}} \ 72.6, \ \text{olefinic}, \ \text{2-CH}). \ 6.62 \ (1\text{H}, \text{td}, ^3J \ 19.08, ^4J \ 1.51, ^2J_{\text{SnH}} \ 91.8, \ \text{olefinic}, \ \text{3-CH}), \ 7.35-7.54 \ (9\text{H}, \text{complex m, aromatic, } m- \& p- \text{protons}), \ 7.54-7.76 \ (6\text{H}, \text{complex m, } ^3J_{\text{SnH}} \ 49, \text{aromatic } o\text{-protons}).

\[^{13}\text{C} \text{NMR} \ (\delta_{\text{C}} \text{ ppm}) : 65.82 \ (\text{CH}_2), \ 123.71 \ (\text{olefinic}), \ 128.56 \ (\text{meta}), \ 129.06 \ (\text{para}), \ 137.0 \ (\text{ortho}), \ 137.95 \ (\text{ipso}), \ 150.78 \ (\text{olefinic}).

\text{Mass} \ (m/z \text{ Cl}) : 331 \ (M^+ -\text{Ph}, 70\%), \ 348 \ (M^+ -\text{Ph} + \text{NH}_3, 100\%), \ 368 \ (\text{Ph}_3\text{Sn} + \text{NH}_3, 92\%).

\( (\text{Z})\)\-3-Tritylstannylprop-2-en-1-\text{ol} \ 1.23 \ had \ been \ isolated \ when \ the \ reaction \ was 
carried out in dry benzene. Following the same procedure as above, and using 2.28 g
(40.67 mmol) of redistilled propargyl alcohol, 14.46 g (41.19 mmol, 1.01 eq.) of triphenyltin hydride, 25 mg AIBN and 80 cm$^3$ dry benzene, refluxing for 24 h. gradient elution with 10 to 50% ether in light petroleum, (Z)-3-triphenylstannylprop-2-en-1-ol 1.23 (Rf 0.46, 30% ether in light petroleum) was obtained as a white crystalline solid (2.44 g, 6.0 mmol, 14.8%) mp 89 °C. Found (%): C 61.91, H 4.99, Sn 28.84. C$_2$H$_5$OOSn requires C 61.96, H 4.95, Sn 29.16.

IR ($\nu_{max}$/cm$^{-1}$) : 699, 728, 997, 1023, 1073, 1164, 1302, 1427, 1479, 1600, 2986, 3061, 3405 (broad, OH).

$^1$H NMR (δ$_H$ ppm) : 1.41 (1H, t, $^3J_{SnH}$ 5.63, OH), 4.32 (2H, m, CH$_2$), 6.41 (1H, td, $^3J_{SnH}$ 12.78).

$^4$J 1.92, $^2J_{SnH}$ 88.03, olefinic, 3-CH), 7.01 (1H, td, $^3J_{SnH}$ 12.78, $^3J$ 3.85.

$^3J_{SnH}$ 173.18, olefinic, 2-CH), 7.25-7.52 (9H, complex m. aromatic, m- & p- protons), 7.52-7.8 (6H, complex m, $^3J_{SnH}$ 49. aromatic o-protons).

$^{13}$C NMR (δ$_C$ ppm) : 64.24 (CH$_2$), 124.69 (olefinic), 128.38 (meta), 128.6 (para), 136.7 (ortho), 140.79 (ipsos), 148.01 (olefinic).

Mass (m/z CI) : 331 (M$^+$-Ph, 100%).

Compound 1.23 was followed by a mixture of 1.23 and 2-triphenylstannylpropenol 1.24 (Rf 0.38, 2.7 g, 6.64 mmol, 16.3%). Finally (E)-isomer 1.19 (Rf 0.19) was obtained (9.01 g, 22.14 mmol, 54.4%).
I.4.I.2 (E)-3-Triphenylstannylnaldehyde 1.20

\[
\begin{array}{c}
\text{Ph}_3\text{Sn}^+ \quad \text{CHO} \\
1.20
\end{array}
\]

\(\text{MnO}_2\) (24.11 g, 277 mmol, 10 eq, reactivated for 24 h at 115 °C to 130 °C and cooled to ambient temperature in a desiccator) was added to a solution of (E)-alcohol 1.19 (11.29 g, 27.73 mmol) in dichloromethane (100 cm³), and the reaction mixture was stirred at ambient temperature for 24 h under argon. More than 50% reaction was complete within 10 min but subsequently the reaction was slowed down and very trace amount of aldehyde could be seen on tlc after 24 h. The reaction mixture was filtered through celite and the product was purified by column over silica using 20% ether in light petroleum as eluent (Rf 0.55). The title compound 1.20 was obtained as a white solid. mp 102 °C (9.95 g, 24.56 mmol, 88.6%). Found (%): C 62.62, H 4.44, Sn 29.51. \(\text{C}_{21}\text{H}_{18}\text{O}\text{Sn}\) requires C 62.27, H 4.95, Sn 29.30.

\(\text{IR (}\nu_{\text{max}}/\text{cm}^{-1})\) : 699, 730, 997, 1074, 1189, 1429, 1480, 1687(C=O), 3017, 3064

\(\text{H NMR (}\delta_\text{H ppm})\) : 6.85 (1H, dd, \(^3J\text{19.09, }^3J\text{7.42, }^3J_\text{SnH} \text{61.12, olefinic}), 7.4-7.55 \text{ (9H. complex m, aromatic } m- \& p-\text{protons), } 7.55-7.76 \text{ (6H, complex m. } ^3J_\text{SnH} \text{51, aromatic } o-\text{protons), } 8.01 \text{ (1H, d, } ^2J_\text{SnH} \text{19.09, } ^2J_\text{SnH} \text{67.84, olefinic), } 9.62 \text{ (1H, d, } ^3J\text{7.41).}

\(\text{C NMR (}\delta_\text{C ppm})\) : 128.90 (meta), 129.61 (para), 136.12 (ipso), 136.91 (ortho), 149.45 (olefinic), 156.81 (olefinic), 193.19 (aldehydic).

\(\text{Mass (}\text{m/z Cl})\) : 329 (M\(^+\)-Ph, 60%), 346 (M\(^+\)-Ph + NH\(_3\), 100%), 424 (M\(^+\)+NH\(_3\) + H, 10%).
I.4.1.3 (E)-3-Triphenylstannylpropenoic acid I.21

\[
\text{Ph}_3\text{Sn} \overset{\text{CO}_2\text{H}}{\longrightarrow}
\]

A solution of NaClO$_2$ 80% (19.0 g, 168 mmol, 15 eq.) and dihydrogen phosphate dihydrate (13.1 g, 84 mmol, 7.5 eq.) in water (80 cm$^3$) was added dropwise to a solution of aldehyde I.20 (4.54 g, 11.20 mmol) in a mixture of tert-butanol (180 cm$^3$) and 2-methyl-2-butene (90 cm$^3$) over a period of 50 min at ambient temperature. After addition was complete the reaction mixture was stirred for one hour at r.t., diluted with ether (100 cm$^3 \times 2$), and the combined extract was washed with water (100 cm$^3$) followed by brine (100 cm$^3$), dried over magnesium sulphate and filtered through celite.

**Purification:** The solvent was completely removed under vacuum, the residue was redissolved in diethyl ether (50 cm$^3$), and the solution was diluted with light petroleum (50 cm$^3$). When the solution was reduced in volume to about 20 cm$^3$ at r.t., the acid was precipitated as a white solid. After removing the liquor with a pipette, the solid mass was washed with light petroleum (20 cm$^3 \times 2$). After vacuum drying, 4.16 g (9.88 mmol, 88.2%) of the acid I.21 was obtained as a white solid, mp 138 °C. Found (%): C 59.90, H 4.40, Sn 28.07. C$_{21}$H$_{18}$O$_2$Sn requires C 59.90, H 4.31, Sn 28.19.

**IR** ($v_{\text{max}}$/cm$^{-1}$): 697, 728, 997, 1075, 1253, 1290, 1412, 1428, 1480, 1591, 1688 (C=O), 3015, 3064.

**$^1$H NMR** ($\delta_H$ ppm): 6.56 (1H, d, $^3J$ 19.09, $^2J_{\text{SnH}}$ 66.12, olefinic, 3-CH), 7.3-7.5 (9H, complex m, aromatic, m- & p- protons), 7.5-7.74 (6H, complex m, $^3J_{\text{SnH}}$ 50, aromatic o-protons), 8.14 (1H, d, $^3J$ 19.23, $^2J_{\text{SnH}}$ 73.06, olefinic, 2-CH).


\[ ^{13}C \text{NMR} (\delta_{C \text{ ppm}}) : 128.86 \text{ (meta)}, 129.53 \text{ (para)}, 136.42 \text{ (ipso)}, 136.99 \text{ (ortho)}, 138.59 \text{ (olefinic), 150.94 \ (olefinic), 169.61 \ (carbonyl).} \]

\[ \text{Mass (m/}z \text{ Cl) : 326 (40\%), 345 (M}^+\text{-Ph, 35\%), 368 (Ph}_3\text{Sn+ NH}_3, 100\%).} \]

I.4.1.4 Methyl (E)-3-triphenylstannyl propenoate I.3

\[
\begin{array}{c}
\text{Ph}_3\text{Sn} \quad \text{CO}_2\text{Me} \\
\text{I.3} \\
\text{Ph}_3\text{Sn} \quad \text{O} \\
\text{TMS} \\
\text{I.25}
\end{array}
\]

Trimethylsilyldiazomethane (Aldrich, 2.0 M in hexane, 0.4 cm\(^3\), 0.8 mmol, 1.86 eq.) was added to a solution of acid I.21 (181.5 mg, 0.431 mmol) in anhydrous methanol (3.5 cm\(^3\)) and benzene (7 cm\(^3\)) at 0 °C. Evolution of gas was observed instantaneously, and tlc after 2 min showed that reaction was complete. After 5 min reaction was quenched by adding diethyl ether (10 cm\(^3\)), solvent was removed under reduced pressure, and the residue, after column over silica gel using 5% ether in light petroleum as eluent, yielded 170.9 mg (0.393 mmol, 91%) of the title compound I.3 as a white solid, mp 61 °C.

\[ \text{IR (}v_{\text{max}} /\text{cm}^{-1} : 699, 730, 998, 1023, 1075, 1158, 1217, 1261, 1315, 1429, 1480, 1586, 1723 (C=O), 2950, 3015, 3062.} \]

\[ ^1\text{H NMR (}\delta_{H \text{ ppm}} : 3.82 \ (3H, s, OCH}_3, 6.55 \ (1H, d, ^3J 19.23, ^2J_{\text{SnH}} 67, \text{olefinic, 3-CH),} \]

\[ 7.4-7.5 \ (9H, \text{complex m, aromatic, } m- \text{ & } p- \text{protons), 7.5-7.8} \ (6H, \text{complex m, } ^3J_{\text{SnH}} 49, \text{aromatic } o\text{-protons), 8.02 \ (1H, d, } ^3J 19.23, ^3J_{\text{SnH}} 75, \text{olefinic, 2-CH).} \]
While benzene is used as a co-solvent to help in dissolving the acid, the presence of methanol is important for the reaction. If the reaction is carried out without methanol, an almost 1:1 mixture of methyl and trimethylsilylmethyl esters I.25 is obtained. Thus, trimethylsilyldiazomethane (Aldrich, 2.0 M in hexane, 0.6 cm³, 1.2 mmol, 1.71 eq.) was added to a stirred solution of acid I.21 (295.1 mg, 0.701 mmol) in benzene (5 cm³) at 0 °C, quenched with diethyl ether (5 cm³) after 15 min, and purification as above yielded 135.4 mg (0.267 mmol, 38%) of trimethylsilylmethyl 3-triphenylstannylpropenoate I.25 (Rf 0.58, 10% ether in light petroleum) as a colourless liquid.

**IR (ν max /cm⁻¹):** 699, 729, 858, 998, 1076, 1152, 1203, 1250, 1318, 1429, 1481, 1720.5 (C=O), 2906, 2956, 3017, 3065.

**¹H NMR (δ_H ppm):** 0.0 (9H, s, Me₃Si), 3.78 (2H, s, CH₂), 6.41 (1H, d, ³J 19.2, ²J_{SnH} 66.9, olefinic, 3-CH), 7.2-7.36 (9H, complex m, aromatic, m- & p-protons), 7.36-7.6 (6H, complex m, ³J_{SnH} 49, aromatic o-protons), 7.82 (1H, d, ³J 19.2, ³J_{SnH} 76.2, olefinic, 2-CH).

**¹³C NMR (δ_C ppm):** -3.03 (Me₃Si), 58.04 (CH₂), 128.74 (meta), 129.37 (para), 136.72 (ipso), 136.96 (ortho), 139.25 (olefinic), 146.3 (olefinic), 165.53 (carbonyl).
Further elution gave the methyl ester I.3 (Rf 0.41) as a white solid (137.4 mg, 0.316 mmol, 45%). It should be noted that large excess of trimethylsilyldiazomethane and longer reaction time have a detrimental effect over the desired product. Thus, when Trimethylsilyldiazomethane (Aldrich, 2.0 M in hexane, 1.5 cm³, 3.0 mmol, 5.9 eq.) was added to a solution of acid I.21 (215.1 mg, 0.511 mmol) in anhydrous methanol (3 cm³) and benzene (1 cm³) at 0 °C, reaction mixture stirred for 2 h at 0 °C and 2 h at ambient temperature, 170 mg (0.462 mmol, 90%) of triphenyltin hydroxide was obtained after purification by column using methanol as the eluent.

I.4.1.4.1 Methyl (E)-3-triphenylstannylpropenoate I.3 by conjugate addition of triphenyltin hydride to methyl propiolate

AIBN (24 mg) followed by triphenyltin hydride (21.27 g, 60.59 mmol, 1.2 eq.) in benzene (60 cm³) were added to a deoxygenated (15 min with nitrogen) solution of methyl propiolate (4.5 cm³, 50.58 mmol) in benzene (140 cm³). The reaction mixture was refluxed for 24 h. After cooling to ambient temperature solvent was removed under reduced pressure and the products were purified and separated in five batches by column using 5% ether in light petroleum as eluent. Methyl (Z)-3-triphenylstannylpropenoate
I.11 (R_f 0.35, 5% ether in light petroleum) was eluted first followed by methyl 2-triphenylstannylpropenoate I.12 (R_f 0.24) and methyl (E)-3-triphenylstannylpropenoate I.3 (R_f 0.18). Fractions containing I.11 mixed with I.12 and I.12 mixed with I.3 were collected from different batches and separated again by column. In total 11.28 g (25.93 mmol, 51.3%) of I.11 was obtained as a white crystalline solid, mp 59 °C.

IR (ν_max /cm⁻¹) : 699, 728, 823, 997, 1074, 1221, 1341, 1429, 1480, 1710 (C=O), 2951, 3014, 3063.

¹H NMR (δ_H ppm) : 3.68 (3H, s, OCH₃), 7.09 (1H, d, ³ J 12.23, ² J_SnH 144, olefinic, 3-CH), 7.3-7.7 (9H, complex m, aromatic, m- & p- protons), 7.52 (1H, d, ³ J 12.23, olefinic, 2-CH), 7.7-7.8 (6H, complex m, ³ J_SnH 50, aromatic o-protons).

¹³C NMR (δ_C ppm) : 51.92 (OMe), 128.29 (meta), 128.64 (para), 136.88 (ortho), 137.38 (ipso), 139.88 (olefinic), 152.11 (olefinic), 167.79 (carbonyl).

Mass (m/z CI) : 359 (M⁺-Ph, 100%).

Yield of I.12, a white crystalline solid, mp 80 °C, was 212.8 mg (0.489 mmol, 0.97%).

Found (%): C 60.28, H 4.62, Sn 27.64. C₂₂H₂₆O₂Sn requires C 60.73, H 4.63, Sn 27.28.

IR (ν_max /cm⁻¹) : 699, 730, 978, 1074, 1114, 1278, 1428, 1480, 1692 (C=O), 2952, 3012, 3061.

¹H NMR (δ_H ppm) : 3.82 (3H, s, OCH₃), 6.27 (1H, d, ² J 2.06, ³ J_SnH 68.67, olefinic), 7.29 (1H, d, ² J 2.06, ³ J_SnH 138, olefinic), 7.4-7.6 (9H, complex m, aromatic, m- & p- protons), 7.6-7.8 (6H, complex m, ³ J_SnH 51, aromatic o-protons).
\( ^{13}C \) NMR (\( \delta_{C} \) ppm) : 51.1 (OMe), 128.62 (meta), 129.18 (para), 137.11 (ortho), 137.50 (ipso), 143.45 (olefinic), 169.69 (carbonyl).

**Mass** (\( m/z \) Cl) : 376 (\( M^{+} \)-Ph + NH\(_3\), 100%), 454 (\( M^{+} \) + NH\(_3\) + H, 12%); (EI) 359 (\( M^{+} \)-Ph, 100%).

Total yield of I.3 was 6.29 g (14.46 mmol, 28.59%).

I.4.1.5 (R)-4,4-Dimethyl-2-oxotetrahydrofuran-3-yl (E)-3-triphenylstannylpropenoate I.27

DMAP (13 mg, 0.1 mmol, 0.21 eq.) followed by DCC (207 mg, 1.00 mmol, 2 eq.) dissolved in dichloromethane (1 cm\(^3\)) were added to a stirred solution of acid I.21 (209.3 mg, 0.497 mmol) and (R)-pantolactone (88 mg, 0.676 mmol, 1.36 eq.) in dichloromethane (2 cm\(^3\)) at ambient temperature. Precipitate could be observed within a few seconds. After stirring at ambient temperature for one hour, the reaction mixture was diluted with diethyl ether (5 cm\(^3\)), filtered through glass wool and the precipitate was washed with diethyl ether repeatedly. Solvent was removed from the combined filtrate, and purification of the residue over silica by gradient elution using 20 to 40% ether in light petroleum yielded 225 mg (0.422 mmol, 85%) of the *title compound* I.27 as a white
solid, mp 129-130 °C, [α]_D^{21} +4.07°. Found (%): C 60.92, H 5.12, Sn 22.06. C_{27}H_{26}O_{4}Sn requires C 60.82, H 4.92, Sn 22.26.

**IR (v_{max}/cm^{-1}):** 699, 730, 997, 1013, 1077, 1148, 1200, 1249, 1301, 1370, 1429, 1481, 1731 (C=O), 1799 (C=O), 2932, 2968, 3016, 3065.

**^{1}H NMR (δ_{H} ppm):** 1.18 (3H, s, Me), 1.28 (3H, s, Me), 4.08 (1H, d, 2J 9.06, CHH), 4.12 (1H, d, 2J 9.06, CHH), 5.49 (1H, s, OCH), 6.63 (1H, d, 3J 19.23, 2J_{SnH} 64.5, olefinic, 3-CH), 7.35-7.54 (9H, complex m, aromatic, m- & p- protons), 7.54-7.75 (6H, complex m, 3J_{SnH} 50, aromatic o-protons), 8.17 (1H, d, 2J 2.06, 3J_{SnH} 138, olefinic, 2-CH).

**^{13}C NMR (δ_{C} ppm):** 19.93 (Me), 23.03 (Me), 40.36 (4'-C), 75.33 (3'-C), 76.21 (5'-C), 128.88 (meta), 129.54 (para), 136.33 (ipso), 136.99 (ortho), 137.25 (olefinic 3-C), 150.79 (olefinic 2-C), 163.12 (carbonyl 1-C), 172.33 (carbonyl 2'-C).

**Mass (m/z Cl):** 457 (M^{+}-Ph, 30%), 552 (M^{+} + NH_{3} + H, 65%); (EI) 457 (M^{+}-Ph, 45%).

Concentration is an important factor in this reaction. When the concentration of the acid was increased from 0.09 M to 0.166 M in a reaction of identical scale, the yield of (R)-pantolactonyl ester 10 was increased from 73% to 85%.
1.4.1.6 (E)-N-Benzyl-3-triphenylstannyIpropenamide 1.28

Benzylamine (125 µL, 1.144 mmol, 2 eq.) followed by DCC (242 mg, 1.173 mmol, 2 eq.) in dichloromethane (1 cm³) was added to a stirred solution of acid 1.21 (241.3 mg, 0.573 mmol) and DMAP (15 mg, 0.123 mmol, 0.21 eq.) in dichloromethane (1 cm³) at ambient temperature. The reaction mixture was stirred at ambient temperature for 22 h before being diluted with ether (5 cm³), filtered through glass-wool, and the precipitate was washed repeatedly with ether. Solvent was removed from the combined filtrate, and the residue, after column over silica using 20% ether in light petroleum as eluent, yielded N-[(Z)-3-triphenylstannylpropenoyl]-N,N'-dicyclohexylurea 1.30 (R, 0.62, 30% ether in light petroleum) as a white solid (17.1 mg, 0.027 mmol, 4.8%), mp 126-127 °C.

IR (νmax /cm⁻¹): 699, 728, 803, 1074, 1231, 1291, 1349, 1385, 1428, 1451, 1480, 1526, 1638 (C=O), 1680 (C=O), 2855, 2932, 3063, 3309 (N-H).

¹H NMR (δH ppm): 1.0-1.9 (20H, complex m, cyclohexyl methylene), 3.6 (1H, unresolved m, cyclohexyl methine), 3.95 (1H, unresolved m, cyclohexyl methine), 6.5 (1H, s, NH), 7.21 (1H, d, 3J 11.5. JSnH
63, olefinic), 7.22-7.3 (9H, complex m, aromatic, m- & p-protons), 7.38 (1H, d, 3J 11.5, olefinic), 7.5-7.7 (6H, complex m.
3J_{SNH} 49, aromatic o-protons).

13C NMR (δC ppm) : (24.36, 25.20, 25.38, 26.04, 30.82, 32.44 cyclohexyl methylene carbons), (49.71, 56.08 cyclohexyl methine carbons). (127.73, 128.08, 128.36, 136.79, 137.02, 137.27 aromatic and olefinic carbons), (141.25, 153.24 carbonyl carbons).

Mass (m/z Cl) : 426 (65%), 504 (10%), 551 (M+Ph, 23%), 629 (M+ + H, 5%).

Compound I.30 was followed by N-[((E)-3-triphenylstannypropenoyl]-N,N'-
dicyclohexylurea I.29 (Rf 0.28) as a feathery light white solid (76.5 mg, 0.122 mmol.
21.3%), mp 166-167 °C.

IR (νmax /cm⁻¹) : 699, 728, 986, 1076, 1229, 1292, 1348, 1362, 1429, 1451,1526. 1640
(C=O), 1704 (C=O), 2855, 2932, 3064, 3298 (N-H).

1H NMR (δH ppm) : 0.8-1.9 (20H, complex m, cyclohexyl methylenes). 3.49 (1H.
unresolved m, cyclohexyl methine), 3.92 (1H, unresolved m.
cyclohexyl methine), 6.7 (1H, d, 3J 18.54, 2J_{SNH} 67.2. olefinic. 3-
CH), 6.95 (1H, s broad, NH), 7.2-7.4 (9H, complex m. aromatic.
m- & p- protons), 7.4-7.6 (6H, complex m, 3J_{SNH} 49, aromatic o-
protons). 7.83 (1H, d, 3J 18.54, 3J_{SNH} 79, olefinic, 2-CH).

13C NMR (δC ppm) : (24.6, 25.17, 25.34, 26.17, 30.78, 32.49 cyclohexyl methylene carbons), (49.7, 56.51 cyclohexyl methine carbons). 128.73
(aromatic m-carbons), 129.36 (aromatic p-carbons). 136.69
(aromatic ipso), 136.93 (aromatic o-carbon), 140.64 (olefinic, 3-C), 144.69 (olefinic, 2-C), 153.65 (carbonyl), 165.61 (carbonyl).

**Mass (m/z Cl)**: 426 (35%), 504 (35%), 551 (M⁺-Ph, 52%), 629 (M⁺ + H, 10%).

Finally, 182.3 mg (0.357 mmol, 62%) of the *title compound* **I.28** was recovered as a white solid, mp 148 °C. Found (%): C 65.77, H 4.92, N 2.75, Sn 22.66. C₂₈H₂₅NOSn requires C 65.92, H 4.94, N 2.75, Sn 23.26.

**IR (νmax /cm⁻¹)**: 698, 728, 996, 1023, 1075, 1250, 1333, 1428, 1453, 1480, 1548, 1642 (C=O), 2850, 2919, 3063, 3275 (N-H).

**¹H NMR (δH ppm)**: 4.43 (2H, d, 3J 5.63, CH₂), 5.78 (1H, unresolved & broad, NH), 6.33 (1H, d, 3J 18.82, 2JₙₜₙH 69, olefinic, 3-CH), 7.1-7.36 (14H, complex m, benzylic Ph and m- & p- protons), 7.36-7.6 (6H, complex m, 3JₙₜₙH 50, o-protons), 7.73 (1H, d, 3J 18.82, 3JₙₜₙH 77.25, olefinic, 2-CH).

**¹³C NMR (δC ppm)**: 43.8 (CH₂), (127.58, 127.97 benzylic Ph), 128.69 (*meta*), 129.32 (*para*), 136.84 (*ipso*), 137.96 (*ortho*), 141.58 (olefinic), 141.69 (olefinic), 163.98 (carbonyl).

**Mass (m/z Cl)**: 434 (M⁺-Ph, 35%), 512 (M⁺ + H, 42%); (EI) 434 (M⁺-Ph, 25%).
Diethylamine (51 μL, 0.494 mmol, 2 eq.) followed by DCC (102 mg, 0.494 mmol, 2 eq.) in dichloromethane (0.5 cm³) was added to a stirred solution of acid 1.21 (104 mg, 0.247 mmol) and DMAP (6 mg, 0.049 mmol, 0.2 eq.) in dichloromethane (1 cm³) at ambient temperature. The reaction mixture was then refluxed for 26 h at 35-40 °C, quenched with ether (2 cm³), filtered through glass-wool, and the precipitate was washed repeatedly with ether. Solvent was removed from the combined filtrate under reduced pressure, and the products were separated by column over silica using 20% ether in light petroleum as eluent. *N-[(Z)-3-triphenylstannylpropenoyl]-N,N'-dicyclohexylurea* 1.30 (Rf 0.62, 30% ether in light petroleum) was recovered first (82.1 mg, 0.132 mmol, 53%) followed by the compound 1.29 (Rf 0.28, 42.2 mg, 0.067 mmol, 27%). The title compound 1.32 (Rf 0.14) was finally recovered as a pasty mass (21.1 mg, 0.044 mmol, 18%).

**IR** (vmax /cm⁻¹): 697, 728, 994, 1073, 1131, 1260, 1426, 1479, 1577, 1630, 2849, 2925, 2972, 3063, 3322.

**¹H NMR** (δH ppm): 1.14 (3H, t, 3J 7.14, CH₃), 1.19 (3H, t, 3J 7.14, CH₃), 3.35 (2H, q, 3J 7.14, CH₂), 3.48 (2H, q, 3J 7.14, CH₂), 6.89 (1H, d, 3J 18.67, Si-Sn, olefinic, 3-CH), 7.3-7.5 (9H, complex m, aromatic m- & p-.
protons), 7.5-7.7 (6H, complex m, $^3J_{SNH}$ 49, aromatic o-protons).

7.88 (1H, d, $^3J$ 18.67, $^3J_{SNH}$ 85.8, olefinic, 2-CH).

$^{13}$C NMR ($\delta$ ppm): 13.03 (Me), 14.74 (Me), 41.00 (CH$_2$), 42.15 (CH$_2$), 128.6 (meta).

129.2 (para), 136.93 (ortho), 137.23 (ipso), 139.38 (olefinic),

141.85 (olefinic), 164.51 (carbonyl).

Mass ($m/z$ Cl): 400 (M$^+$-Ph, 40%), 478 (M$^+$+ H, 25%); (EI) 400 (M$^+$-Ph, 45%).

Attempted reaction with pyrrolidine was not successful. The acid preferentially coupled with dicyclohexylurea to form compounds I.30 and I.29. Thus, to a stirred solution of acid I.21 (140.8 mg, 0.334 mmol) and DMAP (4 mg, 0.033 mmol, 0.1 eq.) in dichloromethane (0.5 cm$^3$), pyrrolidine (36 μL, 0.435 mmol, 1.3 eq.) followed by DCC (138 mg, 0.668 mmol, 2 eq.) in dichloromethane (0.5 cm$^3$) were added, and the reaction mixture was stirred at ambient temperature for 26 h. After removal of the precipitate, and separation and purification of the products as above, 13.5 mg of a mixture consisting of compound I.30 and another compound (not identified) was recovered first followed by the compound I.29 (41 mg, 0.065 mmol, 19.6%).
Part 1.4

I.4.1.8  *(1RS,2RS,3SR,4SR)-Methyl 3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate 1.34*.

![Methyl 3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate 1.34](image)

Freshly prepared cyclopentadiene (20 cm³, 281 mmol, 20 eqvt) was added to a deoxygenated (15 min with nitrogen) solution of ester 1.3 (6.07 g, 13.95 mmol) in benzene (100 cm³), and the reaction mixture was refluxed for 24 h. After cooling to ambient temperature, the solvent was removed under reduced pressure, and the product was purified by column over silica using 10% ether in light petroleum as the eluent. The *title compound 1.34* along with a minor isomer (88:12) was obtained as a white solid (6.66 g, 13.29 mmol, 95%), mp 100°C.

**IR** (*ν*<sub>max</sub>/cm<sup>-1</sup>): 699, 728, 1021, 1074, 1197, 1255, 1332, 1428, 1480, 1731 (C=O), 2987, 3063.

**IR** *NMR* (δ<sub>H</sub> ppm): 1.33 (1H, d, *J* 8.52, 7-CHH), 1.39 (1H, d, *J* 8.52, 7-CHH), 1.95 (1H, dd, *J* 5.02, *J* 2.4, *J*<sub>SnH</sub> 37.84, 3-CH), 3.21 (1H, s broad, *J*<sub>SnH</sub> 23.55, 4-CH), 3.3-3.4 (overlapping signals of 1-CH & 2-CH), 3.66 (3H, s, OCH₃), 5.93 (1H, dd, *J* 5.55, *J* 2.4, olefinic, 6-CH), 6.36 (1H, dd, *J* 3.03, olefinic, 5-CH), 7.33-7.52 (9H, complex m, aromatic, m- & p-protons), 7.52-7.6 (6H, complex m, *J*<sub>SnH</sub> 42, aromatic, o-protons).

**13C NMR** (δ<sub>C</sub> ppm): 27.31 (CH, C-3), 46.0 (CH), 46.69 (CH), 47.07 (CH), 49.30 (CH₂, 7-C), 51.49 (OMe), 128.53 (*meta*), 128.92 (*para*), 130.40
(olefinic), 137.24 (ortho), 138.29 (ipso), 138.88 (olefinic), 174.97 (carbonyl).

**Mass (m/z Cl)**: 351 (Ph₃Sn, 5%), 368 (Ph₃Sn+NH₃, 10%), 425 (M⁺-Ph, 35%), 442 (M⁺-Ph+NH₃, 100%); (EI) 351 (Ph₃Sn, 100%), 425 (M⁺-Ph, 20%), 502 (M⁺, 2%).

I.4.1.9 (1RS,2SR,3SR,4SR)-Methyl 2-benzyl-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate I.36.²

\[ \text{SnPh}_3 \]
\[ \text{CO}_2\text{Me} \]
\[ \text{Ph} \]

[I.36]

\( n \)-Butyl lithium (1.34 mol dm\(^{-3}\) in hexane, 5.9 cm\(^3\), 7.906 mmol, 1.3 eqvt) was added slowly to a stirred solution of diethylamine (1.0 cm\(^3\), 9.67 mmol, 1.6 eqvt) in tetrahydrofuran (40 cm\(^3\)) at 0 °C. The solution was stirred for 15 min, and then cooled to -78 °C before the addition of ester I.34 (3.03 g, 6.046 mmol) in tetrahydrofuran (20 cm\(^3\)). The mixture was stirred at -78 °C for 1 h and then benzylbromide (1.4 cm\(^3\), 11.8 mmol, 1.95 eqvt) was added drop wise. After stirring for a further 1.5 h, the reaction mixture was warmed up to ambient temperature over 1 hour. Solvent was removed under reduced pressure, the residue diluted with ethyl acetate (100 cm\(^3\)), organic phase washed with water (50 cm\(^3\)) and brine (50 cm\(^3\)), and was dried over magnesium sulphate. After column over silica using light petroleum and 10% ether in light petroleum as eluents, 2.64 g (4.46 mmol, 74%) of the *title compound* I.36 was obtained as a white solid, mp
131 °C. Found(%): C 68.94, H 5.51, Sn 19.95. C_{34}H_{32}O_2Sn requires C 69.06, H 5.45, Sn 20.07.

**IR (v_{max} /cm^{-1})**: 699, 728, 1073, 1181, 1231, 1247, 1331, 1428, 1480, 1708 (C=O), 2950, 3061.

**\(^1\)H NMR (δ_H ppm)**: 1.28 (1H, d, J 8.92, 7-CH/H), 1.41 (1H, d, J 8.92, 7-CH/H), 1.74 (1H, d, J 2.47, J_{SnH} 49.31, 3-CH), 2.68 (1H, d, J 13.32, PhCH/H), 3.14 (1H, d, J 13.32, PhCH/H), 3.22 (1H, s broad, J_{SnH} 27.74, 4-CH), 3.31 (1H, s broad, 1-CH), 3.55 (3H, s, OMe), 6.30 (1H, dd, J 5.1, 3 J 3.02, olefinic, 6-CH), 6.54 (1H, dd, J 5.1, 3 J 3.02, olefinic, 5-CH), 7.0-7.2 (5H, complex m, benzylic Ph), 7.2-7.4 (9H, complex m, aromatic, m- & p-protons), 7.4-7.65 (6H, complex m, J_{SnH} 46.28, aromatic, o-protons).

**\(^{13}\)C NMR (δ_C ppm)**: 37.04 (CH), 45.34 (CH_2), 46.60 (CH), 48.00 (CH_2), 51.43 (CH), 52.30 (OMe), 59.8 (2-C) 126.56, 127.83, 128.22, 128.99, 132.25, 137.35 (ortho in Ph_3Sn), 137.85 quarternary carbon), 140.79, 142.14 (quarternary carbon), 179.88 (C=O).

**Mass (m/z Cl)**: 449 (10%), 368 (Ph_3Sn+NH_3, 10%), 515 (M^+-Ph, 100%); (EI) 449 (50%), 351 (Ph_3Sn, 100%), 592 (M^+, 8%), 515 (M^+-Ph, 30%).
1.4.1.10 \((1\text{RS},2\text{RS},3\text{RS},4\text{SR})\)-3-Benzyl-3-hydroxymethyl-2-
tri phenylstannyl bicyclo[2.2.1]hept-5-ene I.41.

Diisobutylaluminium hydride (1.0 M in dichloromethane, 35 cm\(^3\), 35 mmol, 4.0
eqv) was added to a stirred solution of ester I.36 (5.11 g, 8.64 mmol) in dichloromethane
(100 cm\(^3\)) at ambient temperature. After stirring for 2.5 h at ambient temperature the
reaction mixture was cooled to 0°C and quenched with methanol (20 cm\(^3\)). It was then
warmed up to ambient temperature, saturated Rochelle’s salt solution (75 cm\(^3\)) added and
stirred for about 3 h until the gelatinous precipitate was completely dissociated. Organic
phase was separated and the aqueous phase was extracted with dichloromethane (50 cm\(^3\)
x 3). The combined organic phase was dried over magnesium sulphate. solvent
evaporated under reduced pressure, and the product was purified by column over silica
using 10% ether in light petroleum as the eluent. The \textit{title compound} I.41 (4.19 g, 7.44
mmol, 86%) was obtained as a white solid, mp 126 °C. Found(%): C 70.49, H 5.56, Sn
20.37. \(\text{C}_{33}\text{H}_{32}\text{O}_{3}\text{Sn}\) requires C 70.36, H 5.73, Sn 21.07.

\textbf{IR} (\(\nu_{\text{max}}\) / cm\(^{-1}\)) : 700, 728, 908, 996, 1023, 1073, 1257, 1327, 1427, 1453, 1480, 1494.
2882, 2964, 3061, 3561 (m, sh, OH).

\textbf{\(^1\text{H NMR}\) (\(\delta_{\text{H}}\) ppm) :} 1.24 (1H, dd, \(^3J\ 4.94, \(^3J\ 4.94, \(^3J\ 2.61, \text{OH}), 1.31 (2H, \text{ broad & unresolved, overlapping of 2-H & 7-CH(H), 1.58 (1H, d, }^2J\ 9.06, 7-
\text{CH(H)}, 2.43 (1H, s broad, 4-CH), 2.48 (1H, d, }^2J\ 13.32, \text{ PhCH/H).}\

\[\text{SnPh}_3\]
\[\text{OH}\]

\[\text{Ph}\]
2.74 (1H, d, $^2J$ 13.32, PhCH), 3.07 (1H, s broad, $^3J_{SnH}$ 27.6, 1-CH), 3.21 (1H, dd, $^2J$ 10.03, $^3J$ 4.94, CHHOH), 3.37 (1H, dd, $^2J$ 10.03, $^3J$ 2.61, CHHOH), 6.24 (1H, dd, $^3J$ 5.49, $^3J$ 2.88, olefinic, 5-CH), 6.31 (1H, dd, $^3J$ 5.49, $^3J$ 2.88, olefinic, 6-CH), 7.0-7.34 (14H, complex m, benzylic Ph and m- & p- protons in Ph$_3$Sn), 7.34-7.6 (6H, complex m, $^3J_{SnH}$ 43.88, o-protons in Ph$_3$Sn).

$^{13}$C NMR ($\delta$ ppm) : 35.80 (CH), 42.72 (CH$_2$), 46.64 (CH), 47.50 (CH$_2$), 48.35 (CH), 51.41 (quaternary C-3), 66.96 (CH$_2$), 126.07, 128.25 (m-carbons in Ph$_3$Sn), 128.31, 129.87, 133.41 (olefinic), 137.10 (ortho), 138.76 (olefinic), 139.32, 141.77.

Mass (m/z CI) : 368 (Ph$_3$Sn+NH$_3$, 5%), 487 (M$^+$-Ph 100%).

I.4.1.11 (1RS,2SR,3SR,4SR)-2-Benzyl-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde I.42.

Dimethylsulfoxide (2.5 cm$^3$, 35.2 mmol, 4.4 eqvt) was added to a stirred solution of oxalyl chloride (1.5 cm$^3$, 17.2 mmol, 2.14 eqvt) in dichloromethane (80 cm$^3$) at -78 °C. After 5 min, alcohol I.41 (4.52 g, 8.02 mmol) in dichloromethane (50 cm$^3$) was added, and the reaction mixture was stirred for 15 min before adding trimethylamine (10.1 cm$^3$,
72.46 mmol, 9.0 eqvt). After 5 min the reaction mixture was stirred at 0 °C for 30 min and for one hour at ambient temperature. Quenched with water (100 cm³), organic phase separated, washed with water (50 cm³ x 4) and dried over magnesium sulphate. Product was purified by recrystallization. Solvent was completely removed and the solid was redissolved in ether (250 cm³), diluted with light petroleum (50 cm³) and the volume was reduced to about 50 cm³ under reduced pressure. It was refrigerated, the liquor removed by pipette and the white crystalline solid was washed repeatedly with light petroleum. After vacuum drying yield was 4.17 g (7.43 mmol, 92.6%), mp 140°C. Found(%): C 70.37, H 5.31, Sn 20.68. C₃₃H₃₀OSn requires C 70.62, H 5.39, Sn 21.15.

**IR** (νmax /cm⁻¹) : 699, 728, 907, 1072, 1328, 1427, 1454, 1480, 1711.5 (C=O), 2961.3061.

**¹H NMR** (δH ppm) : 1.02 (1H, d, ²J 9.07, 7-CHH), 1.26 (1H, d, ²J 9.07, 7-CHH), 1.45 (1H, d, ⁴J 2.75, ²JSnH 45, 3-CH), 2.63 (1H, d, ²J 13.87, PhCHH). 3.09 (1H, s broad, 1-CH), 3.20 (1H, d, ²J 13.87, PhCHH), 3.21 (1H, s broad, 4-CH), 6.29 (1H, dd, ³J 5.5, ³J 3.02, olefinic, 6-CH). 6.60 (1H, dd, ³J 5.5, ³J 3.02, olefinic, 5-CH), 6.9-7.2 (5H, complex m, benzylic Ph), 7.2-7.4 (9H, complex m, aromatic, m- & p-protons in Ph₃Sn), 7.4-7.6 (6H, complex m, ³JSnH 44, α-protons in Ph₃Sn), 9.74 (1H, s, CHO).

**¹³C NMR** (δC ppm) : 30.95 (CH), 42.93 (CH₂), 46.44 (CH₂), 46.79 (CH), 48.69 (CH). 63.70 (quaternary C-2), 126.70, 127.92 (meta), 127.98, 128.5. 129.07, 130.9 (olefinic), 136.68, 137.19 (ortho), 141.52 (olefinic). 141.82, 205.93 (C=O).
Mass (m/z Cl): 368 (Ph₃Sn+NH₃, 48%), 419 (77%), 485 (M⁺-Ph, 100%).

I.4.1.12 (1RS,2RS,3RS,4SR)-3-Benzyl-2-chlorodiphenylstannylibicyclo[2.2.1]hept-5-ene-3-carbaldehyde oxime I.45.

\[
\text{I.45}
\]

Sodium acetate (24.7 mg, 0.301 mmol, 2.3 eqvt) and hydroxylamine hydrochloride (18.2 mg, 0.262 mmol, 2 eqvt), were added everyday to a solution of aldehyde I.42 (73.4 mg, 0.131 mmol) in anhydrous methanol (1.5 cm³) and benzene (2 cm³), and the reaction mixture was stirred for 13 days at ambient temperature. All together 211.2 mg (2.57 mmol, 19.65 eqvt) of sodium acetate and 166.9 mg (2.40 mmol, 18.33 eqvt) of hydroxylamine hydrochloride were added. The reaction was monitored by tlc, and it was observed that an intermediate was formed before it was converted to stable product. Formation of both the intermediate and the product were slow. After 13 days neither aldehyde (Rf 0.49, 10% ether in light petroleum) nor the intermediate (Rf 0.29) could be observed. Solvent was removed under reduced pressure, the residue dissolved in water, extracted with dichloromethane, and the extract was dried over magnesium sulphate. The product (Rf 0.11) was purified by a short column of silica eluted with 20% ether in light petroleum. The title compound I.45 (43.9 mg, 0.082 mmol, 62.6%) was obtained as a solid, mp 106°C.
IR (ν\text{max} / \text{cm}^{-1}) : 699, 732, 756, 906, 959, 1072, 1268, 1429, 1454, 1481, 2918, 2963, 3053, 3254, 3431, 3610.

\(^1\text{H}\) NMR (δ\text{H} ppm): 1.47 (1H, d, 2\text{J} 9.2, 7-CHH), 1.52 (1H, d, 2\text{J} 9.2, 7-CHH), 1.66 (1H, d, 4\text{J} 2.47, 2\text{J_{Sat}} 61, 2-CH), 2.69 (1H, d, 2\text{J} 13.46, \text{PhCHH}), 2.97 (1H, s, 4-CH), 3.04 (1H, d, 2\text{J} 13.46, \text{PhCHH}), 3.52 (1H, s, 3\text{J_{SnH}} 34.88), 6.31 (1H, dd, 3\text{J} 5.49, 3\text{J} 3.02, \text{olefinic}, 5-CH), 6.57 (1H, dd, 3\text{J} 5.49, 3\text{J} 3.02, \text{olefinic}, 6-CH), 6.93 (1H, s, NOH), 7.0-7.5 (13H, complex m, aromatic), 7.6-7.85 (2H, complex m, aromatic, two of the four \text{o}-protons in \text{ClPh}_2\text{Sn}), 7.92 (1H, s, \text{CH= N}).

\(^{13}\text{C} \) NMR (δ\text{C} ppm): 39.68 (CH), 45.25 (CH\text{2}), 45.7(CH), 47.24 (CH\text{2}), 51.32 (CH), 54.62 (quaternary 3-C), (126.98, 128.59, 128.79, 128.83, 128.97, 129.26, 129.77, 131.50, 135.53, 135.53, 135.83, 136.65, 140.8, aromatic & olefinic), 162.92 (CH= N).

Mass (m/z Cl): 212 (100%), 458 (M\text{+}-\text{Ph}, 3%), 500 (M\text{+}-^{35}\text{Cl}, 35%), 535 (M\text{+}, 2%). (ES) 500 (M\text{+}-^{35}\text{Cl}, 100%).

During work up some amount of the product \textbf{I.45} got converted to another compound (probably a compound derived from \textbf{I.45} by replacing Cl with OH) which appeared on the base line and could not be recovered in enough quantity for characterization.
I.4.1.13 (1RS,2RS,3RS,4SR)-3-Benzyl-2-triphenylstannylbicyclo[2.2.1]hept-5-ene-3-carbaldehyde O-methyloxime 1.46 and (1RS,2RS,3RS,4SR)-3-Benzyl-2-chlorodiphenylstannylbicyclo[2.2.1]hept-5-ene-3-carbaldehyde O-methyloxime 1.47.

Sodium acetate (23.4 mg, 0.285 mmol, 1.5 eqvt) and methoxyamine hydrochloride (22.1 mg, 0.265 mmol, 1.4 eqvt) were added everyday to a solution of aldehyde 1.42 (107 mg, 0.190 mmol) in anhydrous methanol (2.5 cm³) and benzene (2.5 cm³), and the reaction mixture was stirred for 13 days at ambient temperature. All together 147 mg (1.79 mmol, 9.43 eqvt) of sodium acetate and 138 mg (1.65 mmol, 8.70 eqvt) of methoxyamine hydrochloride were added. The reaction was monitored by tlc, and it was observed that the oxime 1.46 (Rf 0.63, 10%, ether in light petroleum) starts appearing above the aldehyde (Rf 0.49) in the first few days. Before the aldehyde could react completely, the compound 1.47 (Rf 0.18) started to appear below the aldehyde. Formation of both the product were slow. When the aldehyde almost disappeared, solvent was removed under reduced pressure, the residue dissolved in water, extracted with dichloromethane, the extract dried over magnesium sulphate, and the products were separated by column over silica by gradient elution using 10 to 30% ether in light petroleum. The oxime 1.46 (62 mg, 0.105 mmol, 55%) was recovered as a white solid, mp
115 °C. Found (%): C 68.96, H 5.80, N 2.44, Sn 19.70. C₃₄H₃₃NOSn requires C 69.18, H 5.63, N 2.37, Sn 20.11.

**IR** ($\nu_{\text{max}}$ /cm$^{-1}$): 700, 729, 908, 1045, 1072, 1427, 1453, 1480, 1494, 2963, 3061.

**$^1$H NMR** ($\delta_H$ ppm): 1.48-1.55 (2H, overlapping signals of 2-CH & 7-CHH), 1.81 (1H, d, $^2J$ 7.83, 7-CHH), 2.80 (1H, d, $^2J$ 13.32, PhCHH), 2.87 (1H, d, $^2J$ 13.32, PhCHH), 2.93 (1H, s, 4-CH), 3.21 (3H, s, OCH₃), 3.25 (1H, s, 3 $^J_{\text{SnH}}$ 41, 1-CH), 6.31 (1H, dd, $^3J$ 5.36, $^3J$ 2.89, olefinic, 5-CH), 6.45 (1H, dd, $^3J$ 5.36 2.89, olefinic 6-CH), 7.15-7.6 (20H, complex m, aromatic), 7.62 (1H, s, CH=N).

**$^{13}$C NMR** ($\delta_C$ ppm): 36.15 (CH), 46.31 (CH₂), 46.58(CH), 47.45(CH₂), 50.86 (CH), 52.08 (3-C), 60.92 (OMe), [126.59, 128.03, 128.47, 128.56, 130.00, 131.33, 136.80, 137.13, 137.83 (quaternary), 140.11 (quaternary), 142.79, aromatic & olefinic], 158.13 (CH=N).

**Mass** (m/z Cl): 514 (M+·Ph, 100%), no other major fragment; (ES+) 393 (20%), 447 (100%), no other major fragment.

Further elution gave the compound 1.47 (17.6 mg, 0.032 mmol, 17%) also as a white solid. Found (%): C 62.14, H 5.16, N 2.08, Cl 6.58. C₂₈H₂₈NOClSn requires C 61.29, H 5.14, N 2.55, Cl 6.46.

**IR** ($\nu_{\text{max}}$ /cm$^{-1}$): 701, 733, 788, 908, 998, 1038, 1072, 1266, 1326, 1430, 1454, 1481, 1495, 2874, 2968, 3052.

**$^1$H NMR** ($\delta_H$ ppm): 1.52 (1H, dd, $^2J$ 9.2, $^4J$ 2.2, 7-CHH), 1.58 (1H, d, $^2J$ 9.2, 7-CHH), 1.65 (1H, d, $^2J$ 2.48, $^2J_{\text{SnH}}$ 60.42, 2-CH), 2.75 (1H, d, $^2J$ 13.6,
PhCHH), 2.99 (1H, s, 4-CH), 3.00 (1H, d, $^2J$, 13.6, PhCHH), 3.25 (3H, s, OCH$_3$), 3.51 (1H, s, $^3J_{SnH}$ 35.43, 1-CH), 6.32 (1H, dd, $^3J$ 5.5, $^3J$ 3.02, olefinic, 5-CH), 6.56 (1H, dd, $^3J$ 5.5, $^3J$ 3.02, olefinic, 6-CH), 7.1-7.5 (13H, complex m, aromatic), 7.8-7.88 (2H, complex m, two of the four o-protons in ClPh$_2$Sn), 7.93 (1H, s, CH=N).

$^{13}$C NMR ($\delta_C$ ppm) : 39.02 (CH), 45.58 (CH$_2$), 45.84 (CH), 47.41 (CH$_2$), 51.41 (CH), 54.12 (quaternary 3-C), 62.03 (OMe), 127.01, 128.39, 128.57, 128.82, 128.86, 129.26, 130.01, 131.46, 135.55, 136.39, 136.72 (quaternary), 140.42, 140.79 (quaternary), 142.98 (quaternary), 163.01 (CH=N).

Mass ($m/z$ Cl) : 514 (M$^+$-35Cl, 100%), no other major fragment; (ES$^+$) 513 (M$^+$-35Cl-H, 100%), 514 (M$^+$-35Cl, 98%), no other major fragment; (EI) 309 (60%), 406 (25%), 472 (M$^+$-Ph, 35%).

When more equivalents of methoxyamine hydrochloride and sodium acetate were added to reduce reaction time the compound 1.47 became major as compared to 1.46. Thus addition of 1.236 g (15.07 mmol, 29.84 eqvt) of sodium acetate and 1.107 mg (13.25 mmol, 26.24 eqvt) of methoxyamine hydrochloride to 284 mg (0.505 mmol) of aldehyde L.42 in anhydrous methanol (5 cm$^3$) and benzene (5 cm$^3$) over 9 days, yielded 91.4 mg (0.154 mmol, 31%) of L.46 and 149.9 mg (0.273 mmol, 54%) of L.47. Higher temperature did not help either. Thus, 111.8 mg (0.199 mmol) of aldehyde L.42 was refluxed with 49.9 mg (0.608 mmol, 3.06 eqvt) of sodium acetate and 46.8 mg (0.554 mmol, 2.78 eqvt) of methoxyamine hydrochloride in anhydrous methanol (2 cm$^3$) and benzene (2 cm$^3$) for
45 h to yield 28.2 mg (0.048 mmol, 24%) of oxime I.46. Starting material (12%) was also recovered. It appeared that the compound I.47 was also formed but was converted to another compound (probably a compound derived from I.47 with Cl replaced by OH) which appeared on the base line and could not be recovered in enough quantity for characterization.


Hydrazine hydrate (5 cm³) was added to solution of aldehyde I.42 (323 mg, 0.575 mmol) in anhydrous ethanol (10 cm³) and benzene (6 cm³). The reaction mixture was refluxed for 47 h, solvent removed under reduced pressure, the residue diluted with water, extracted with ether (50 cm³ x 4), the combined extract was washed with brine and dried over magnesium sulphate. Chromatography over silica with 10% ether in light petroleum as eluent yielded 0.230 g (0.398 mmol, 69%) of the hydrazone I.49 as a foaming white solid, mp 60 °C. Found (%): C 68.60, H 6.01, N 4.81, Sn 19.94. C₃₃H₃₄N₂Sn requires C 68.65, H 5.94, N 4.85, Sn 20.56.

IR (νmax/cm⁻¹): 701, 730, 1071, 1264, 1426, 1452, 1479, 1495, 1603, 2870, 2938, 3059.
$^1$H NMR ($\delta_{\text{H}}$ ppm): 1.21 (1H, d, $^2$J 9.75, 7-CH$_2$), 1.48-1.65 (3H, complex m. overlapping signals of one proton from each of 5-CH$_2$, 6-CH$_2$ and 7-CH$_2$), 1.65-1.88 (2H, complex m, overlapping signals of one proton from each of 5-CH$_2$ & 6-CH$_2$), 2.11-2.33 (2H. unresolved m, overlapping signals of 2-CH & 4-CH), 2.63 (1H. s, $^3$J$_{\text{SnH}}$ 39.5, 1-CH), 2.87 (1H, d, $^2$J 13.46, PhCH$\equiv$H), 3.14 (1H. d. $^2$J 13.46, PhCH$\equiv$H), 4.67 (2H, s, NH$_2$), 6.90 (1H, s, CH=N), 7.1-7.4 (14H, complex m, aromatic), 7.4-7.6 (6H, complex m. $^2$J$_{\text{SnH}}$ 43, o-protons in Ph$_3$Sn).

$^{13}$C NMR ($\delta_{\text{C}}$ ppm): 23.71 (CH$_2$), 34.24 (CH$_2$), 37.19 (CH$_2$), 41.31 (CH), 42.08 (CH). 43.18 (CH$_2$), 44.82 (CH), 53.15 (quaternary 3-C), [126.31 127.63, 127.91, 128.35, 129.79, 136.89, 138.41 (quaternary). 144.55 (quaternary), aromatic], 152.61 (CH=N).

Mass (m/z Cl): 501 (M$^+$-Ph, 100%), accurate mass of (M$^+$-Ph) measures 501.1359. C$_{33}$H$_{34}$N$_2$Sn requires 501.1352; (ES+) 501 (M$^+$-Ph, 100%). 527 (72%). 541 (42%), 619 (12%).
1.4.1.15 *(1RS,2RS,3SR,4SR)-3-Triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde I.50.

Freshly prepared cyclopentadiene (4.9 cm³, 69 mmol, 20 eq.) was added to a deoxygenated (1 h with nitrogen) solution of aldehyde I.20 (1.4 g, 3.45 mmol) in benzene (50 cm³), and the reaction mixture was refluxed overnight (22 h), cooled to ambient temperature, solvent removed under reduced pressure, and the product was purified by column over silica using 10% ether in light petroleum as the eluent. The *title compound* I.50 along with a minor isomer (85:15) was obtained as a viscous liquid which crystallized to a white solid on standing, mp 90-92 °C, yield 1.50 g (3.18 mmol, 92%).


**IR** (ν_{max} / cm⁻¹): 699, 728, 997, 1073, 1331, 1428, 1480, 1714 (C=O), 2715, 2809, 2867, 2971, 3062.

**¹H NMR** (δ_H ppm): 1.32 (1H, d, ²J 8.66, 7-CHH), 1.39 (1H, d, ²J 8.51, 7-CHH), 1.97 (1H, dd, ³J 5.22, ⁴J 2.34, ³J_{SnH} 36.4, 3-CH), 3.28 (1H, s broad, 1-CH or 4-CH), 3.30 (1H, complex m, 2-CH), 3.37 (1H, s broad, 1-CH or 4-CH), 5.93 (1H, dd, ³J 5.56, ³J 2.7, olefinic), 6.36 (1H, dd, ³J 5.43, ³J 3.0, olefinic), 7.3-7.5 (9H, complex m, aromatic m- & p-protons), 7.5-7.7 (6H, complex m, ³J_{SnH} 46, aromatic o-protons), 9.84 (1H, d, ³J 2.06, CHO).
$^{13}$C NMR (δC ppm): 24.73, 46.44, 49.2, 55.81, 128.73 (meta), 129.05 (para), 129.51 (olefinic), 137.27 (ortho), 137.97 (ipso), 139.22 (olefinic), 203.86 (C=O).

Mass (m/z Cl): 368 (Ph$_3$Sn + NH$_3$, 12%), 395 (M$^+$ - Ph, 6%), 512 (M$^+$ - Ph + NH$_3$, 100%), 490 (M$^+$ + NH$_3$ + H, 23%); (El) 472 (M$^+$, 32%), 351 (Ph$_3$Sn, 100%).

I.4.1.16 (Dibromomethyl)triphenylstannane I.16.

$n$-Butyl lithium (1.50 M in hexane, 20 cm$^3$, 30 mmol) was added to a stirred solution of diisopropylamine (5 cm$^3$, 35.7 mmol) in THF (35 cm$^3$) and anhydrous diethyl ether (50 cm$^3$) at 0 °C. After stirring for 15 min the solution was cooled to -90 °C (methanol/liquid nitrogen bath) before addition of dibromomethane (3.7 cm$^3$, 52.7 mmol) in THF (15 cm$^3$). The reaction mixture was stirred for 15 min and triphenyltinchloride 95% (9.7 g, 23.9 mmol) in THF (25 cm$^3$) was added. This was allowed to warm up to -60°C and quenched with saturated ammonium chloride solution (10 cm$^3$). After warming upto a ambient temperature solvent was removed under reduced pressure, and the residue diluted with water (200 cm$^3$) and light petroleum (300 cm$^3$) was filtered through celite. Organic phase was separated, and the aqueous phase was extracted with light petroleum (100 cm$^3$ x 2). The combined organic phases (about 500 cm$^3$) were dried over magnesium sulphate and the product was purified by column chromatography using gradient elution.
of 5 to 20% ether in light petroleum. The title compound (dibromomethyl)triphenylstannane I.16 (Rf 0.64, 10% ether in light petroleum) was obtained as a white solid (6.7 g, 12.8 mmol, 53.6%), mp 103°C. Found(%): C 43.38, H 3.05, Br 28.92, Sn 22.66. C_{19}H_{16}Br_{2}Sn requires C 43.65, H 3.08, Br 30.57, Sn 22.7.

IR (\nu_{\text{max}} / \text{cm}^{-1}): 697, 728, 996, 1073, 1426, 1480, 3048, 3063.

\(^1\)H NMR (\delta_{\text{H}} \text{ ppm}): 5.74 (1H, s, methine), 7.4-7.6 (9H, complex m, aromatic, \text{m-} \& \text{p-} protons), 7.6-7.9 (6H, complex m, \text{ J_{SnH} 49}, aromatic, \text{o-}protons).

\(^{13}\)C NMR (\delta_{\text{C}} \text{ ppm}) : 25.52 (methine), 128.83 (meta), 129.88 (para), 136.04 (ipso).

137.18 (ortho).

Mass (m/z Cl): 368 (Ph\text{3Sn+NH}_3, 8%), 462 (M^+ - Ph + NH\text{3}, 35%), 479 (8%), 523 (M^+ + H, 12%), 540 (M^+ + NH\text{2} + H, 15%).

A minor product (Rf 0.47), probably bis(dibromomethyl)diphenylstannane, could be detected on TLC but could not be recovered in enough quantity for characterization.

I.4.1.17 (E)-1-Triphenylstannyldec-1-ene I.17.

![Diagram of (E)-1-Triphenylstannyldec-1-ene](image)

Anhydrous and deoxygenated DMF (0.8 cm\(^3\), 10 mmol) was added to stirred slurry of CrCl\(_2\) (1.33 g, 10 mmol) in dry and deoxygenated THF (16 cm\(^3\)). After stirring for 15 min a solution of \text{n-nonanal} (175 \text{ \mu l}, 1.0 mmol) and dibromomethyl(triphenyl)stannane (1.04 g, 2 mmol) in dry and deoxygenated THF (4
cm<sup>3</sup>) was added dropwise. The flask was covered with aluminium foil to protect from light and Lil (535 mg, 4mmol) in dry and deoxygenated THF (4cm<sup>3</sup>) was added dropwise. The reaction mixture was stirred for 46 h at ambient temperature before it was quenched with water (30 cm<sup>3</sup>), extracted with light petroleum (25 cm<sup>3</sup> x 3) and diethyl ether (25 cm<sup>3</sup> x 3), combined extract washed with water (30 cm<sup>3</sup> x 2) and brine (30 cm<sup>3</sup> x1) and dried over magnesium sulphate. Column chromatography eluting with 1% ether in light petroleum gave 193.3 mg (0.395 mmol, 39.5%) of the title compound 1.17 as an oily liquid. Found (%); C 68.95, H 7.23, Sn 24.49. C<sub>28</sub>H<sub>34</sub>Sn requires C 68.74, H 7.00, Sn 24.26.

**IR** (v<sub>max</sub>/cm<sup>-1</sup>): 656, 699, 727, 997, 1023, 1075, 1189, 1301, 1376, 1428, 1464, 1480, 1598, 2853, 2924, 2955, 3015, 3063.

**<sup>1</sup>H NMR** (δ<sub>H</sub> ppm): 0.97 (3H, t, <sup>3</sup>J 7.0, CH<sub>3</sub>), 1.37 (10H, unresolved s, 5 to 9 methylenes), 1.53 (2H, unresolved m, 4-CH<sub>2</sub>), 2.33 (2H, unresolved m, 3-CH<sub>2</sub>), 6.26 (1H, d, <sup>3</sup>J 18.82, olefinic), 6.35 (1H, d, <sup>3</sup>J 18.82, olefinic), 7.35-7.55 (9H, complex m, aromatic, m- & p-protons), 7.55-7.8 (6H, complex m, <sup>3</sup>J<sub>SnH</sub> 47, aromatic, o-protons).

**<sup>13</sup>C NMR** (δ<sub>C</sub> ppm): 14.11 (CH<sub>3</sub>), 22.67, 28.59, 29.16, 29.27, 29.43, 31.85, 37.81, 122.91 (olefinic), 128.43 (meta), 128.86 (para), 137.02 (ortho), 138.71 (ipso), 153.94 (olefinic).

**Mass** (m/z Cl): 351 (Ph<sub>3</sub>Sn, 15%), 368 (Ph<sub>3</sub>Sn+NH<sub>3</sub>, 100%), 430 (M<sup>-</sup>-Ph+NH<sub>3</sub>, 20%); (ES+) 351 (Ph<sub>3</sub>Sn, 85%), 392 (47%), 450 (100%); (El) 274 (Ph<sub>2</sub>Sn, 42%), 351 (Ph<sub>3</sub>Sn, 55%), 413 (M<sup>-</sup>-Ph, 65%).
Some amount of 1.17 was recovered as a mixture with side products and rejected. The side products detected are Ph$_3$SnCH$_3$ and Ph$_3$SnCH$_2$.

1.4.1.18 Preparation of (-)-dibenzyl D-tartrate 1.18.

Dibenzyl D-(-)-tartrate was prepared according to the literature procedure.\textsuperscript{41} However, as the literature $^1$H nmr spectrum was found quite different, all spectral data are recorded here again.

To a 500 cm$^3$ round-bottomed flask equipped with a Dean-Stark trap, a reflux condenser, a nitrogen bubbler, and a stir bar were added 25 g (0.167 mol) of D-(-)-tartaric acid, 35.2 g (33.7 cm$^3$, 0.326 mol, 1.95 eqvt) of benzyl alcohol, 1.76 g (5 mol\%) of $p$-toluenesulfonic acid, and 110 cm$^3$ of benzene. The solution was refluxed until evolution of water had ceased (24 h) and was then brought to r.t. Isooctane (150 cm$^3$) was added, and the precipitate was filtered off and then redissolved in ethylacetate (300 cm$^3$). After being washed with sodium bicarbonate (75 cm$^3$ x 2) and brine (50 cm$^3$ x 1) the organic solution was dried over magnesium sulfate, filtered, and concentrated. The residue was dissolved in 200 cm$^3$ of toluene, and the product was precipitated out by addition of 200 cm$^3$ of isooctane. After filtration and drying under high vacuum (1 mb, 36 h), 36.41 g
(66%) of the title compound I.18 as a white solid was obtained, mp 49.6 °C. Found (%): C 66.14, H 5.36; C_{18}H_{18}O_{6} requires C 65.45, H 5.49.

**IR (νmax /cm\(^{-1}\))**: 698, 750, 1089, 1218, 1266, 1455, 1744 (C=O), 3483 (medium, broad, OH).

**\(^1\)H NMR (δH ppm)**: 3.36 (1H, d, \(^3\)J 7.55, OH), 4.68 (1H, d, \(^3\)J 7.27, CH), 5.29 [1H, d (AB type), \(^2\)J 12.09, CHH], 5.35 [1H, d (AB type), \(^2\)J 12.08, CHH], 7.41 (5H, s, Ph).

**\(^{13}\)C NMR (δC ppm)**: 68.00 (CH\(_2\)), 72.07 (CH), 128.34 (ortho), 128.62 (meta & para), 134.72 [C-1 in Ph (ipso)], 171.31 (carbonyl).

**Mass (m/z Cl)**: 348 (M\(^+\) + NH\(_3\) + H, 100%), no other major fragment.

### I.4.2 X-Ray crystal structure determinations

#### I.4.2.1 Crystal data for (1RS,2SR,3SR,4SR)-methyl 2-benzyl-3-triphenylstannylbicyclo[2.2.1]hept-5-ene-2-carboxylate I.36.

C\(_{34}\)H\(_{32}\)O\(_2\)Sn, \(M=591.32\), C-centred monoclinic, space group Cc (#9), \(a=9.692(5)\) Å, \(b=67.57(4)\) Å, \(c=9.795(5)\) Å, \(U=5575(5)\) Å\(^2\), \(β=119.63(3)^°\) (by least squares refinement on diffractometer angles of 17 carefully centred reflections in the range 28.84<\(2θ<31.28^°\)), \(Z=8, \ Dc=1.409\ \text{g cm}^{-3}, \ μ=75.14\ \text{cm}^{-1}, \ F(000)=2416.00\), colourless needle, crystal dimensions 0.25x0.10x0.05 mm.\(^{42-46}\)
I.4.2.2 Crystal data for \((\text{cSRS,2SR,3SR,4SR})-2\text{-benzyl-3-triphenylstannylbicyclo}[2.2.1]\text{hept-5-ene-2-carbaldehyde I.42.}\)

\[\text{C}_{33}\text{H}_{30}\text{O}_{11}\text{Sn}, \quad M=561.29, \quad \text{primitive triclinic, space group } P1 \text{ (#2), } \alpha=13.912(7), \]

\[b=16.820(8), \quad c=11.615(6) \text{ Å}, \quad U=2659(2) \text{ Å}^2, \quad \alpha=91.10(4) ^\circ, \quad \beta=90.07(4) ^\circ, \quad \gamma=78.13(4) ^\circ\]

(by least squares refinement using setting angles of 22 carefully centred reflections in the range \(14.53<\theta<20.68^\circ\)), \(Z=4, \quad D_c=1.402 \text{ g cm}^{-3}, \quad \mu=9.85 \text{ cm}^{-1}, \quad F(000)=1144.00\).

colourless block, crystal dimensions 0.20x0.30x0.40 mm.\(^{42-45, 47}\)

I.4.2.3 Crystal data for \((\text{cSRS,2SR,3RS,4SR})-3\text{-benzyl-2-chlorodiphenylstannylbicyclo}[2.2.1]\text{hept-5-ene-carbaldehyde oxime I.45.}\)

\[\text{C}_{31}\text{H}_{36}\text{NOSnCl}, \quad M=608.77, \quad \text{primitive monoclinic, space group } P2_1/n \text{ (#14), } \alpha=11.870(7), \]

\[b=14.311(3), \quad c=17.597(6) \text{ Å}, \quad U=2960(2) \text{ Å}^2, \quad \beta=98.02(4) ^\circ \text{ (by least squares refinement using setting angles of 25 carefully centred reflections in the range } 40.79<\theta<49.42^\circ\text{).} \]

\(Z=4, \quad D_c=1.366 \text{ g cm}^{-3}, \quad \mu=79.07 \text{ cm}^{-1}, \quad F(000)=1248.00\), colourless block, crystal dimensions 0.30x0.20x0.20 mm.\(^{42-45, 48}\)

I.4.2.4 Crystal data for \((\text{cSRS,2SR,3RS,4SR})-3\text{-benzyl-2-chlorodiphenylstannylbicyclo}[2.2.1]\text{hept-5-ene-3-carbaldehyde O-methyloxime I.47.}\)

\[\text{C}_{28}\text{H}_{28}\text{NOSnCl}, \quad M=548.68, \quad \text{primitive monoclinic, space group } P2_1 \text{ (#4), } \alpha=9.128(2), \]

\[b=30.712(6), \quad c=9.907(2) \text{ Å}, \quad U=2529.3(8) \text{ Å}^2, \quad \beta=114.39(1) ^\circ \text{ (by least squares refinement using setting angles of 24 carefully centred reflections in the range } 28.50<\theta<31.32^\circ\text{).} \]

\(Z=4, \quad D_c=1.441 \text{ g cm}^{-3}, \quad \mu=91.62 \text{ cm}^{-1}, \quad F(000)=1112.00\). colourless needle, crystal dimensions 0.25x0.12x0.15 mm.\(^{42-45, 49}\)
References to Parts 1.2 to 1.4


17. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ (e-mail: deposit@ccdc.cam.ac.uk)


46. Data deposited at the Cambridge Crystallographic Data Centre; deposition number CCDC 167852.
47. Data deposited at the Cambridge Crystallographic Data Centre; deposition number CCDC 167853.

48. Data deposited at the Cambridge Crystallographic Data Centre; deposition number CCDC 167855.

49. Data deposited at the Cambridge Crystallographic Data Centre; deposition number CCDC 167854.