Tetrahedron Vol 47, No 30, pp 5901-5918, 1991
Printed in Great Britain

0040-4020/91 $3 00+ 00

INTRAMOLECULAR S_H2' MACROCYCLISATIONS

Jack E. Baldwin, Robert M. Adlington, Mark B. Mitchell and Jeremy Robertson.

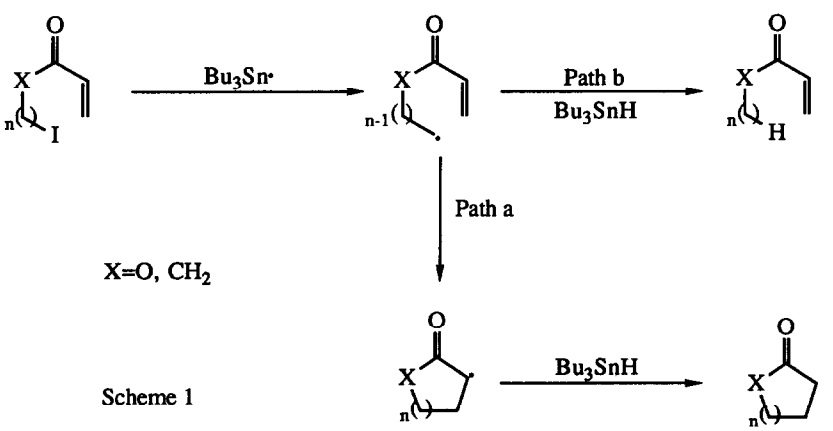
The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QY

(*Received in UK* 25 *April* 1991)

Key Words Radical, selenide, allyltin, macrocyclic lactone, fragmentation

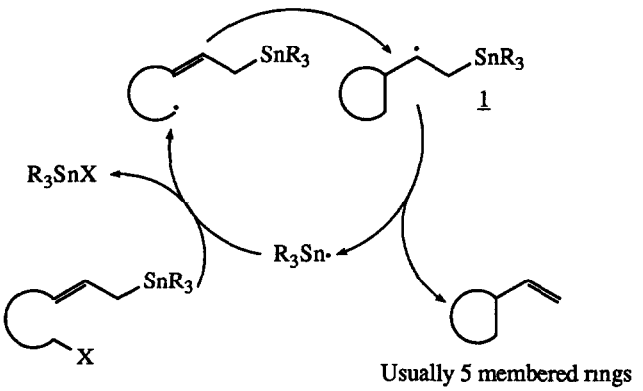
Abstract: *The synthesis of 10-15 membered α-methylene macrocyclic lactones from the functionalised allylstannanes (7e)-(7j) is described Attempts to synthesise analogous 6-9 membered lactones proved unsuccessful, resulting instead in the production of dilactones and AIBN derived adducts*

The application of free radical chain processes to construct macrocyclic rings was first shown to be synthetically viable by Porter, who identified the structural criteria for successful alkyl radical macrocyclisation reactions[1]. Briefly, he demonstrated that radical ring closure should be feasible if it occurs onto sterically unhindered, electronically activated double bonds, leading to ring sizes greater than ten Thus 11-20 membered rings were isolated (15-76% yield) by means of the illustrated macrocyclisation, followed by subsequent reduction (Scheme 1, path a) However, in all cases some direct reduction before cyclisation occurred (Scheme 1, path b) Attempts to circumvent this by either the *in situ* generation of tri-*n*-butyltin hydride from tri-*n*-butyltin chloride and sodium cyanoborohydride or by the slow addition of tri-*n*-butyltin hydride into the reaction vessel did lead to a decrease in the yield of reduced product, but this was generally at the expense of the yield of cyclic product[1] More recently, the direct reduction (path b) has been essentially eliminated by the use of tristrimethylsilylsilane in place of tri-*n*-butyltin hydride[2]



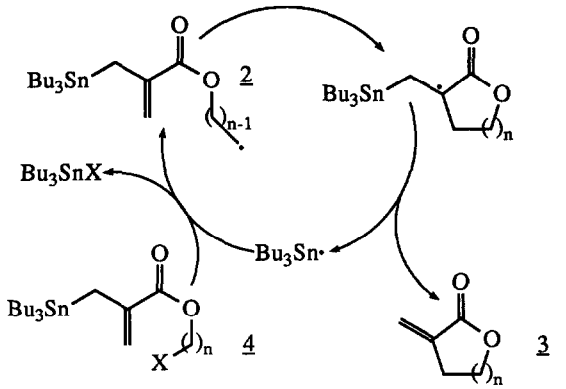
Scheme 1

Keck[3] and Danishefsky[4] have utilised allylic stannanes to synthesise five membered rings, the chain carrying $R_3Sn\cdot$ being generated *in situ* by the rapid fragmentation of the tin-carbon bond in radical (1) (Scheme 2)



Scheme 2

Based upon these observations we proposed that the (ω-alkyl radical) 2-(tri-*n*-butylstannylmethyl)propenoate ester (2) should undergo an intramolecular S_H2' reaction to yield the α-methylene macrocyclic lactones (3) (Scheme 3) As such a chain process would only require catalytic Bu_3SnH/AIBN for initiation, competing reduction of the radical (2) should be essentially eliminated (Scheme 3)

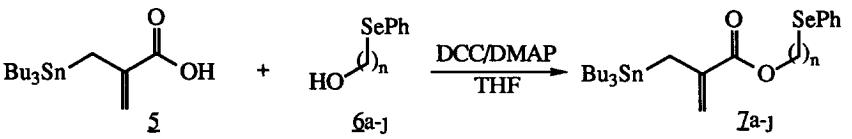


Scheme 3

The criterion for macrocyclisation is satisfied by the substrate (4) since the β-carbon is sterically unhindered while the ester functionality provides electronic activation, and in addition the tri-*n*-butylstannyl group has itself been shown to effect activation of an allyltin double bond relative to an unsubstitued alkene[5a] Another attractive feature was the degeneracy of a potentially undesirable side reaction of allyl stannanes, namely the *in situ* reaction of substrate (4) with trialkylstannyl radicals[5b]

The radical precursors (7a)-(7j) were conveniently prepared by a DCC/DMAP mediated coupling between the stannyl-acid (5) and the ω-phenylselenoalkanols (6a)-(6j), following a modified literature procedure[6] (Scheme

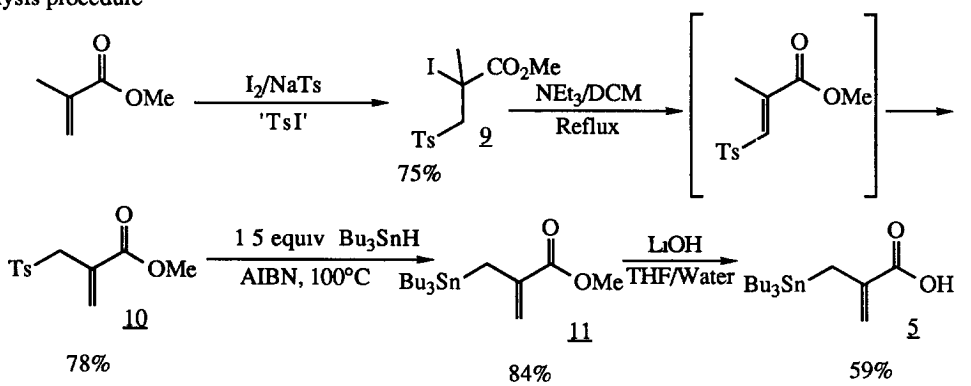
4) The use of selenides as the radical precursor was deemed preferable to either iodides or bromides since the downstream byproduct, trialkylstannyl phenyl selenide, is easier to purify away from desired macrocyclic lactone on silica gel chromatography



n=2	6, 7a	n=8	6, 7g
n=3	6, 7b	n=9	6, 7h
n=4	6, 7c	n=10	6, 7i
n=5	6, 7d	n=11	6, 7j
n=6	6, 7e		
n=7	6, 7f		

Scheme 4

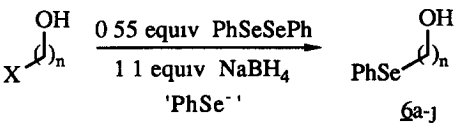
Synthesis of the stannyl-acid (5) was achieved in 4 steps from methyl methacrylate (Scheme 5) The allylic sulphone (10) was prepared by iodosulphonation[7], followed by base catalysed dehydroiodination/isomerisation[8] Conversion to the stannyl-ester (11) was effected by homolytic displacement of the *p*-tolyl sulphonyl group[9] and the acid (5) subsequently obtained by a lithium hydroxide mediated ester hydrolysis procedure[10]



Ts=toluene-*p*-sulphonyl

Scheme 5

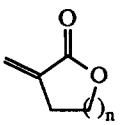
The ω-phenylselenoalkanols (6a)-(6j) were readily obtained from the corresponding ω-haloalkanols[11] by nucleophilic displacement with the phenylselenide anion, produced *in situ* by the reductive cleavage of diphenyl diselenide with sodium borohydride[12] (Scheme 6)



Scheme 6

Cyclisation to the 10-15 membered α-methylene lactones (8e)-(8j) occurred cleanly in moderate to high yield when the substrates (7e)-(7j) were subjected to high dilution (5mM) free radical conditions [cat azobisisobutyronitrile (AIBN), cat Bu_3SnH, benzene, reflux, 48h] Product isolation was effected by removal of the solvent *in vacuo* followed by standard flash chromatography on silica gel (Table 1) Direct reduction of the radical centre was not observed

Table 1

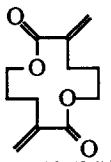
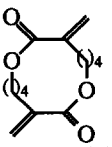
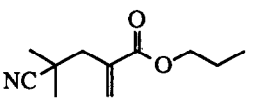
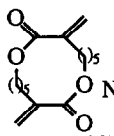
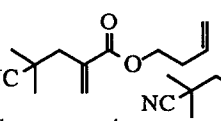
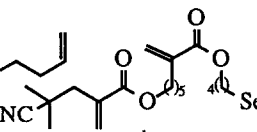
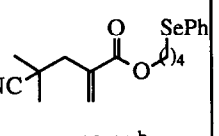
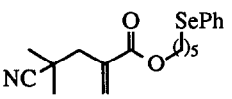


n=2 8a n=8 8g
n=3 8b n=9 8h
n=4 8c n=10 8i
n=5 8d n=11 8j
n=6 8e
n=7 8f

Substrate	Product	Ring size	% Yield
7e	8e	10	54
7f	8f	11	46
7g	8g	12	61
7h	8h	13	50
7i	8i	14	80
7j	8j	15	72

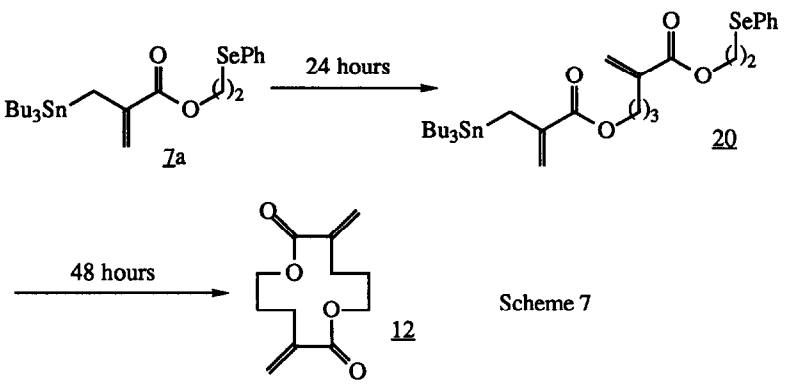
Attempts to synthesise analogous 6-9 membered lactones were unsuccessful, substrates (7a)-(7c) affording the dilactones (12)-(14) in low yield and in addition a variety of minor AIBN derived adducts, while the only isolable product from (7d) was the AIBN adduct (19) (Table 2)

Table 2

Entry	Substrate	Products (% Yield)
1	7a	 12 (34)[a]
2	7b	 13 (25)[b]  15 (5)[b] + unidentified minor adducts
3	7c	 14 (30)[b]  16 (5)[b]  17 (5)[b]  18 (5)[b]
4	7d	 + unidentified minor adducts 19 (21)[a]

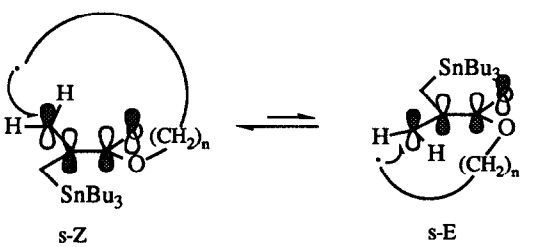
Footnotes a Isolated yield, b Yield estimated from ^1H NMR spectrum after chromatography

In the case of substrate (7a), the dimer species (20) was isolated 24 hours after initiation of the radical reaction On re-exposure to free radical conditions (20) was smoothly converted to the dilactone (12) In a separate experiment the dilactone (12) was obtained directly, 48 hours after initiation of the chain process The dimer species was observed by t l c 24 hours after starting the reaction, but was completely consumed after 2 days (Scheme 7)



Scheme 7

The failure to effect these ring closures can be accounted for in terms of both the traditional problem of slow rate of cyclisation to the 7-9 membered lactones due to considerble Pitzer and transannular strain in the cyclised product, coupled to the requirement that substrates (7a)-(7d) must adopt the unfavourable s-E conformation to accommodate the required radical transition state geometry Only for the longer alkyl chains, presumably n>5, can the desired disposition of reactive centres be adopted while the preferred s-Z conformation[13] is maintained (Figure 1) Consequently intermolecular processes compete effectively for the 6-9 ring closures, even under the high dilution conditions employed, to afford the observed dilactones and AIBN adducts



s-Z s-E

Possible for n>5

Figure 1

Similar initiator derived adducts have been observed during a radical ring expansion study[14], while O-Yang *et al* has reported the formation of mono, di, and trilactone derived species in varying yields when a range of 5 and 6-endo-trig atom transfer radical cyclisations were attempted[15] In contrast to our findings, Boger *et al* failed to effect a 10-endo-trig ring closure, only a dilactone derived species was isolated in low yield[16]

In summary we have synthesised 10 membered or larger α-methylene lactones under free radical conditions, generating the chain carrying tri-*n*-butyl stannyl radical by means of an intramolecular S_H2' fragmentation reaction Smaller ring lactones cannot be made in this fashion due to the effective competition from intermolecular processes over the cyclisation reaction

EXPERIMENTAL SECTION

Infrared (IR) spectra were recorded on a Perkin-Elmer 681 spectrometer with only selected absorbtions being recorded Absorbtion maxima were recorded in cm^{-1} Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini-200 spectrometer Spectra were taken using $CDCl_3$ as solvent with chemical shifts quoted in parts per million (δ p p m) using the residual solvent peak as an internal reference Coupling constants (*J*) are quoted to the nearest 0 5Hz ^{13}C spectra were recorded on a Varian Gemini-200 spectrometer, using DEPT editing when indicated Mass spectra were recorded on a V G Micromass ZAB 1F (IBEI/EI/DCI), a V G 20-250 (DCI/CI) or a V G TRIO 1 (GCMS) spectrometer, with only major isotope peaks for stannanes and selenides being assigned Bulb to bulb distillation refers to distillation at reduced pressure using a horizontal Kugelrohr apparatus, the temperature quoted being that of the heating bath Melting points were obtained using a Buchi 510 capillary melting point apparatus and are uncorrected Microanalyses were performed in the Dyson Perrins Laboratory

Flash chromatography was accomplished on silica gel using Sorbsil™ C60 Preparative plate chromatography (PLC) was carried out on glass plates (20cm x 20cm) coated with silica gel (Blend 41) and with a Kieselgel band Thin layer chromatography was performed on aluminium sheets pre-coated with Merck silica gel 60 F_{254}, plates being visualised by either the quenching of u v fluorescence (λ_{max}=254nm) or by staining with potassium permanganate solution or 10%w/v ammonium molybdate in 2M sulphuric acid, followed by heat

All solvents were distilled before use, tetrahydrofuran (THF) was obtained dry and oxygen free by distillation from sodium/benzophenone ketyl 'Petrol' refers to the fraction of light petroleum ether boiling between 40-60°C Solvents were evaporated at 30°C or below on a Buchi R110 Rotavapor Tri-*n*-butyltin hydride was standardised by comparison of the ^1H NMR integration of the tin hydride resonance and the *n*-butyl resonances All other reagents were used as obtained from commercial sources

Methyl 2-iodo-2-methyl-3-(toluene-p-sulphonyl)propanoate. (9) A solution of methyl methacrylate (25 1ml, 23 5g, 0 24mol), sodium toluene-*p*-sulphinate hydrate (100g, 0 51mol), and iodine (68g, 0 27mol) in methanol (500ml) was stirred at room temperature for 2 5 hours using a mechanical stirrer The solvent was removed *in vacuo* from the resulting viscous brown solution and the residue dissolved in dichloromethane (1000ml) The resulting solution was washed with water (500ml), saturated aqueous sodium bicarbonate (250ml), aqueous sodium thiosulphate (0 5 M, 500ml), dried ($MgSO_4$), and the solvent removed *in vacuo* to yield *methyl 2-iodo-2-methyl-3-(toluene-p-sulphonyl)propanoate* (9) (67 24g, 75%) as a yellow solid, m p 127-133°C (as needles from dichloromethane/petrol) (lit [17] 129-131°C, from dichloromethane/hexane), δ_H (200MHz) 2 44 and 2 46 (2 x 3H, 2 x s, $C\underline{H}_3$ and $ArC\underline{H}_3$), 3 81 (3H, s, $OC\underline{H}_3$), 3 92 (1H, A part of AB, *J* 14Hz, $SC\underline{H}$), 4 48 (1H, B part of AB, *J* 14Hz, $SC\underline{H}$), 7 37 (2H, d, *J* 8Hz, aromatics), and 7 77 (2H, d, *J* 8Hz, aromatics)

Methyl 2-((toluene-p-sulphonyl)methyl)propenoate. (10) To a solution of the iodo-sulphone (9) (67 2g, 0 18mol) in dichloromethane (600ml) was added triethylamine (61.7g, 85ml, 0.61mol) and the solution heated at reflux for 8 hours After cooling, the solution was washed with dilute aqueous hydrochloric acid (450ml), saturated aqueous sodium bicarbonate (230ml), and aqueous sodium thiosulphate (0 5 M; 230ml) The combined aqueous washings were back extracted with dichloromethane (200ml), washed with saturated brine (150ml), and the combined organic phases dried ($MgSO_4$) to yield a viscous red oil after removal of the solvent *in vacuo* Flash chromatography (SiO_2, 2:1 petrol/ether→1 1petrol/ether→2·1 ether/petrol as eluant) afforded *methyl 2-((toluene-p-sulphonyl)methyl)propenoate* (10) (35g, 78%) as a buff coloured solid; m p 39-43°C (lit [18] 41°C from dichloromethane/hexane), ν_{max} ($CHCl_3$) 3030(s, C-H), 2960(m, C-H), 1725(vs, C=O), 1635(m, C=C), 1600(s), 1440(s), 1320(vs), 1148(vs), and 814(s); δ_H (200MHz) 2 45 (3H, s, $ArCH_3$), 3 60 (3H, s, OCH_3), 4 14 (2H, s, allylic H), 5 89 (1H, s, olefinic H), 6.50 (1H, s, olefinic H), 7 33 (2H, d, *J* 8Hz, aromatics), and 7 73 (2H, d, *J* 8Hz, aromatics), *m/z* [CI(NH_3)] 274 (9%), 273 (20), 272 (MNH_4^+, 100), 255 (MH^+, 42), 190 (8), and 108 (10)

Methyl 2-(tri-n-butylstannylmethyl)propenoate. (11) To a degassed solution of methyl 2-((toluene-*p*-sulphonyl)methyl)propenoate (10) (10 0g, 39mmol) in toluene (100ml) was added tri-*n*-butyltin hydride (20 7g, 19 1ml, 1 5 equiv) *via* syringe and AIBN (646mg, 0 1 equiv) The mixture was heated at reflux under an argon atmosphere for 1 hour, followed by removal of the solvent *in vacuo* to yield a viscous yellow oil Flash chromatography (SiO_2, 5% ether/petrol as eluant) afforded *methyl 2-(tri-n-butylstannylmethyl)propenoate* (11) as a colourless oil (12 97g, 84%) (Found C, 52 46, H, 9 06 $C_{17}H_{34}O_2Sn$ requires C, 52 47, H, 8 81%), ν_{max} (thin film) 2950(m, C-H), 2850(w, C-H), 1733(vs, C=O), 1630(m, C=C), 1435(s), 1335(s), 1310(s), 1198(s), and 1170(s), δ_H (200MHz) 0 70-1 02 (15H, m, $Sn((CH_2)_2CH_2CH_3)_3$), 1 18-1 60 (12H, m, $Sn(CH_2CH_2Et)_3$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 58Hz), 3 75 (3H, s, CO_2CH_3), 5 30 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17 5Hz), and 5 83 (1H, d, *J* 1 0Hz olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17 0Hz), δ_C (50 4MHz, DEPT) 168 5 (C=O), 141 2 ($C=CH_2$), 118 8 ($C=CH_2$), 51 7 (OCH_3), 13 5 ($CH_3(CH_2)_3Sn$), 28 6, 27 7,14 8, and 9 5 ($CH_3(CH_2)_3Sn$, and allylic C), *m/z* [EI] 337 (17%), 335 (22), 334 (16), 333 (M^+-*n*-Bu, ^{120}Sn, 100), 332 (34), 331 (74), 330 (25), 329 (41), 219 (15), 179 (27), and 177 (26)

2-(Tri-n-butylstannylmethyl)propenoic acid. (5) To a solution of lithium hydroxide monohydrate (1 1g, 2 equiv) in an 8 1 THF/water mixture (30ml) was added methyl 2-(tri-*n*-butylstannylmethyl)propenoate (11) (5 00g, 13mmol) and the solution heated at reflux with efficient stirring for 36 hours After cooling, the solution was diluted with saturated aqueous ammonium chloride (80ml) and dilute hydrochloric acid was added dropwise until a pH of 6-7 was attained The resulting mixture was extracted with ether (3 x 150ml), dried ($MgSO_4$), and the solvent removed *in vacuo* to yield a yellow oil Flash chromatography (SiO_2, 2% ether/petrol → neat ether as eluant) afforded *2-(tri-n-butylstannylmethyl)propenoic acid* (5) (2 85g, 59%) as a colourless oil ν_{max} (thin film) 3500-2760(br, vs, OH), 2620(s, C-H), 2510(m, C-H), 1690(vs, C=O), 1608(vs, C=C), 1460(vs), 1095(s), 1070(s), 958(s), and 915(vs), δ_H (200MHz) 0 70-1 03 (15H, m, $Sn((CH_2)_2CH_2CH_3)_3$), 1 18-1 60 (12H, m, $Sn(CH_2CH_2Et)_3$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 57 5Hz), 5 42 (1H, s, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 19Hz), and 5 96 (1H, s, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 16 5Hz), δ_C (50 4MHz, DEPT) 174 1 (C=O), 140 9 ($C=CH_2$), 120 8 ($C=CH_2$), 13 4 ($(CH_3(CH_2)_3)_3Sn$), 28 8, 27 2, 14 4,

and 9 5 ($(CH_3(C\underline{H}_2)_3)_3Sn$, and allylic C), *m/z* [CI(NH_3)] 319 (M^+-*n*-Bu, ^{120}Sn, 14%), 317 (10), 312 (19), 310 (16), 309 (15), 308 (100), 307 (49), 306 (79), 305 (38), 304 (47), 293 (15), 291 (40), 290 (16), 289 (29), 287 (16), and 138 (15).

General Procedure for the preparation of ω-*phenylselenoalkanols*. (6a)-(6j) Sodium borohydride (1 1equiv.) was added in portions to a stirred solution of diphenyl diselenide (0.55 equiv.) in ethanol (≈8ml/mmol of diphenyl diselenide) at 0°C To the resulting colourless solution was added a solution of the appropriate ω-haloalkanol dissolved in the minimum quantity of ethanol The mixture was stirred overnight at either room temperature (in the case of ω-bromoalkanols) or at 50°C (in the case of ω-chloroalkanols) under an argon atmosphere. The solution was diluted with an equal volume of distilled water, extracted thoroughly with ether and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue subjected to flash chromatography (SiO_2, 2 1 petrol/ether as eluant) to yield spectroscopically pure ω-*phenylselenoalkanols* (6a)-(6j)

2-*Phenylselenoethanol* (6a). The standard procedure with diphenyl diselenide (2 06g, 6 6mmol) and 2-bromoethanol (1 50g, 12mmol) afforded the product as a pale yellow oil (1 39g, 58%). ν_{max} (thin film) 3650-3100(br, vs, OH), 3060(s, Ar-H), 2925(vs, C-H), 2870(s, C-H), 1578(vs), 1478(vs), 734(vs), and 688(vs), δ_H (200MHz) 2 10 (1H, t, *J* 6 0Hz, O<u>H</u>), 3 10 (2H, t, *J* 6 5Hz, C<u>H</u>$_2$SePh), 3.78 (2H, ca. quar , *J* 6 5Hz, $CH_2C\underline{H}_2OH$), 7 21-7 39 (3H, m, aromatics), and 7 49-7 61 (2H, m, aromatics), δ_H (200MHz) (+1 drop D_2O) 3 10 (2H, t, *J* 6 5Hz, C<u>H</u>$_2$SePh), 3 78 (2H, t, *J* 6 5Hz, $CH_2C\underline{H}_2OH$), 7.21-7.39 (3H, m, aromatics), and 7 48-7 61 (2H, m, aromatics), *m/z* [CI(NH_3)] 220 (MNH_4^+, ^{80}Se, 15%), 202 (43), 200 (22), 187 (19), 185 (100), 183 (49), 182 (16), 181 (21), 91 (15), and 78 (30)

3-*Phenylselenopropanol* (6b). The standard procedure with diphenyl diselenide (1 85g, 5 9mmol) and 3-bromopropanol (1 50g, 10 8mmol) afforded the product as a pale yellow oil (1.79g, 77%) ν_{max} (thin film) 3640-3100(br, vs, OH), 3058(m, Ar-H), 2930(s, C-H), 2870(s, C-H), 1575(s), 1475(vs), 730(vs), and 688(vs), δ_H (200MHz) 1 45 (1H, br s, O<u>H</u>), 1 98 (2H, ca quin, *J* 7 5Hz, $CH_2C\underline{H}_2CH_2$), 3 20 (2H, t, *J* 7 5Hz, C<u>H</u>$_2$SePh), 3 69-3 83 (2H, m, C<u>H</u>$_2$OH), 7 19-7 35 (3H, m, aromatics), and 7 45-7.59 (2H, m, aromatics), *m/z* [CI(NH_3)] 234 (MNH_4^+, ^{80}Se, 54%), 232 (29), 219 (18), 218 (21), 217 (MH^+, ^{80}Se, 100), 216 (80), 215 (57), 214 (56), 213 (35), 212 (16), 199 (25), 157 (18), 94 (26), 78 (48), and 56 (17)

4-*Phenylselenobutanol* (6c). The standard procedure with diphenyl diselenide (1 73g, 5 5mmol) and 4-chlorobutanol (1 00g, 9 2mmol) afforded the product as a pale orange oil (1 63g, 77%) ν_{max} (thin film) 3640-3100(br, vs, OH), 3078(m, Ar-H), 2938(s, C-H), 2870(s, C-H), 1581(m), 1480(s), 1440(s), 737(s), and 691(s), δ_H (200MHz) 1 30 (1H, br s, O<u>H</u>), 1 61-1 91 (4H, m, $PhSeCH_2(C\underline{H}_2)_2CH_2OH$), 2.96 (2H, t, *J* 7 0Hz, C<u>H</u>$_2$SePh), 3 68 (2H, t, *J* 6 5Hz, C<u>H</u>$_2$OH), 7 18-7 34 (3H, m, aromatics), and 7 42-7.58 (2H, m, aromatics), *m/z* [CI(NH_3)] 248 (MNH_4^+, ^{80}Se, 18%), 231 (MH^+, ^{80}Se, 15), 215 (17), 213 (100), 211 (49), 210 (18), 209 (21), 94 (21), 78 (23), 72 (38), 71 (18), and 70 (29)

5-*Phenylselenopentanol* (6d). The standard procedure with diphenyl diselenide (2 24g, 7.2mmol) and 5-bromopentanol (2 00g, 12 0mmol) afforded the product as a pale yellow oil (2 24g, 77%) ν_{max} (thin film) 3640-3100(br, m, OH), 3078(w, Ar-H), 2938(s, C-H), 2860(m, C-H), 1580(m), 1480(s), 1440(m), 746(s), and 691(s), δ_H (200MHz) 1 30 (1H, br s, O<u>H</u>), 1 40-1 86 (6H, m, $PhSeCH_2(C\underline{H}_2)_3CH_2OH$), 2 94 (2H, t, *J* 7 5Hz, C<u>H</u>$_2$SePh), 3 65 (2H, t, *J* 6 0Hz, C<u>H</u>$_2$OH), 7 18-7 36 (3H, m, aromatics), and 7 41-7 57 (2H, m, aromatics), *m/z* [CI(NH_3)] 264 (17%), 262 (MNH_4^+, ^{80}Se, 100), 260 (48), 258 (21), 245 (MH^+, ^{80}Se, 63), 244 (48), 243 (49), 242 (32), 241 (29), 227 (43), 225 (20), 78 (35), and 58 (17)

6-*Phenylselenohexanol* (6e). The standard procedure with diphenyl diselenide (1.37g, 4.4mmol) and 6-chlorohexanol (1.00g, 7.3mmol) afforded the product as a pale orange oil (1.85g, 98%). $\nu_{max.}$ ($CHCl_3$) 3628(s, OH), 3600-3180(br, s, OH), 3078(m, Ar-H), 3018(vs, C-H), 2938(vs, C-H), 2860(vs, C-H), 1581(vs), 1480(vs), 1440(vs), 1023(vs), and 691(vs), δ_H (200MHz) 1.17-1.82 (8H, m, $PhSeCH_2(C\underline{H}_2)_4CH_2OH$), 2 93 (2H, t, *J* 8.0Hz, $C\underline{H}_2SePh$), 3 64 (2H, t, *J* 6 5Hz, $C\underline{H}_2OH$), 7 18-7.34 (3H, m, aromatics), and 7 42-7.56 (2H, m, aromatics); *m/z* [CI(NH_3)] 278 (19%), 276 (MNH_4^+, ^{80}Se, 100), 274 (53), 272 (24), 271 (23), 259 (MH^+, ^{80}Se, 37), 258 (37), 256 (26), 255 (28), 253 (15), 241 (45), and 239 (24)

7-*Phenylselenoheptanol* (6f). The standard procedure with diphenyl diselenide (1.92g, 6 2mmol) and 7-bromoheptanol (2.00g, 10 3mmol) afforded the product as a pale orange oil which solidified on standing (2 46g, 88%) m p. 33-34°C; ν_{max} ($CHCl_3$) 3620(s, OH), 3600-3100(br, s, OH), 3078(m, Ar-H), 3010(vs, C-H), 2930(vs, C-H), 2860(vs, C-H), 1579(s), 1479(s), 1244(m), 1073(s), and 691(vs); δ_H (200MHz) 1 23-1 82 (10H, m, $PhSeCH_2(C\underline{H}_2)_5CH_2OH$), 2 04 (1H, br s, O$\underline{H}$), 2 92 (2H, t, *J* 7 0Hz, $C\underline{H}_2SePh$), 3.61 (2H, t, *J* 6 5Hz, $C\underline{H}_2OH$), 7 21-7 35 (3H, m, aromatics), and 7 43-7 57 (2H, m, aromatics), *m/z* [CI(NH_3)] 290 (MNH_4^+, ^{80}Se, 69), 288 (39), 286 (17), 273 (MH^+, ^{80}Se, 41), 272 (36), 271 (29), 270 (24), 269 (19), 255 (22), 114 (36), 112 (27), 94 (40), 78 (100), and 58 (18)

8-*Phenylselenooctanol* (6g). The standard procedure with diphenyl diselenide (0 33g, 1 1mmol) and 8-bromooctanol (0 40g, 1 9mmol) afforded the product as a colourless solid (0 52g, 96%). m p. 35-38C, ν_{max} ($CHCl_3$) 3628(m, OH), 3560-3300(br, w, OH), 3060(w, Ar-H), 3015(s, C-H), 2935(vs, C-H), 2860(s, C-H), 1581(m), 1480(s), 1440(s), 1025(s), and 690(s), δ_H(200MHz) 1 32 (8H, br s, $PhSe(CH_2)_2$-$(C\underline{H}_2)_4(CH_2)_2OH$), 1 49-1 80 (4H, m, $PhSeCH_2C\underline{H}_2(CH_2)_4C\underline{H}_2CH_2OH$, 2 92 (2H, t, *J* 7 5Hz, $C\underline{H}_2SePh$), 3 65 (2H, t, *J* 6 5Hz, $C\underline{H}_2OH$), 7 21-7 35 (3H, m, aromatics), and 7 43-7 56 (2H, m, aromatics), *m/z* [CI(NH_3)] 304 (MNH_4^+, ^{80}Se, 22%), 287 (MH^+, ^{80}Se, 22), 285 (20), 172 (16), 146 (21), 129 (19), 128 (18), 127 (30), 126 (17), 125 (17), 124 (16), 112 (24), 109 (18), 95 (17), 94 (80), 93 (37), 81 (20), 80 (20), 79 (15), 78 (100), 77 (24), 71 (28), 70 (18), 69 (19), 58 (31), 56 (29), 55 (18), and 54 (26)

9-*Phenylselenononanol* (6h). The standard procedure with diphenyl diselenide (1 10g, 3 5mmol) and 9-bromononanol (2 00g, 9 0mmol) afforded the product as a colourless solid (1.89g, 70%) m p 46-47°C, ν_{max} ($CHCl_3$) 3628(m, OH), 3560-3460(br, w, OH), 3018(s, C-H), 2934(vs, C-H), 2860(vs, C-H), 1580(m), 1480(s), 1440(s), 1024(s), and 691(s), δ_H (200MHz) 1 31 (10H, br s, $PhSe(CH_2)_2(C\underline{H}_2)_5(CH_2)_2OH$), 1 50-1 80 (4H, m, $PhSeCH_2C\underline{H}_2(CH_2)_5C\underline{H}_2CH_2OH$), 2 93 (2H, t, *J* 7 5Hz, $C\underline{H}_2SePh$), 3 65 (2H, t, *J* 7 0Hz, $C\underline{H}_2OH$), 7 20-7 35 (3H, m, aromatics), and 7 43-7 57 (2H, m, aromatics), *m/z* [CI(NH_3)] 318 (MNH_4^+, ^{80}Se, 44%), 316 (19), 301 (MH, ^{80}Se, 21%), 300 (17), 283 (64), 282 (21), 281 (31), 94 (24), 93 (21), 78 (100), and 58 (18)

10-*Phenylselenodecanol* (6i). The standard procedure with diphenyl diselenide (0 29g, 9 3mmol) and 10-bromodecanol (0 40g, 1 8mmol) afforded the product as a colourless solid (0 48g, 90%). m p 52-53°C, ν_{max} ($CHCl_3$) 3628(m, OH), 3078(w, Ar-H), 3015(m, C-H), 2938(vs, C-H), 2860(s, C-H), 1582(m), 1480(s), 1440(m), 1025(m), and 691(m), δ_H (200MHz) 1 29 (12H, br s, $PhSe(CH_2)_2(C\underline{H}_2)_6(CH_2)_2OH$), 1 50-1 78 (4H, m, $PhSeCH_2C\underline{H}_2(CH_2)_6C\underline{H}_2CH_2OH$), 2 93 (2H, t, *J* 7 5Hz, $C\underline{H}_2SePh$), 3 65 (2H, quar , *J* 6 0Hz, $C\underline{H}_2OH$), 7 21-7 35 (3H, m, aromatics), and 7 43-7 57 (2H, m, aromatics), *m/z* [IBEI] 314 (M^+, ^{80}Se, 65%), 312 (33), 160 (17), 158 (100), 157 (37), 156 (55), 155 (29), 154 (23), 97 (19), 91 (18), 83 (34), 78 (25), 69 (57), 55 (73), and 43 (23)

11-*Phenylselenoundecanol* (6j). The standard procedure with diphenyl diselenide (1 16g, 3 7mmol) and 11-bromoundecanol (1.70g, 6 8mmol) afforded the product as a pale yellow solid (2.20g, 98%) m p 54-55°C; ν_{max} ($CHCl_3$) 3628(m, OH), 3580-3100(br, w, OH), 3078(w, Ar-H), 3010(s, C-H), 2934(vs, C-H), 2860(vs, C-H), 1582(m), 1480(s), 1440(s), 1024(s), and 691(s), δ_H (200MHz) 1.28 (14H, br s, $PhSe(CH_2)_2(\underline{CH_2})_7(CH_2)_2OH$), 1 50-1.81 (4H, m, $PhSeCH_2\underline{CH_2}(CH_2)_7\underline{CH_2}CH_2OH$), 2.92 (2H, t, *J* 7 5Hz, $\underline{CH_2}SePh$), 3 66 (2H, t, *J* 6.5Hz, $\underline{CH_2}OH$), 7 20-7.32 (3H, m, aromatics), and 7.45-7.58 (2H, m, aromatics), *m/z* [DCI(NH_3)] 348 (20%), 347 (20), 346 (MNH_4^+, ^{80}Se, 96), 344 (54), 343 (26), 342 (22), 330 (29), 329 (MH^+, ^{80}Se, 74), 328 (100), 327 (43), 326 (63), 325 (34), 324 (21), 311 (30), and 272 (27).

General Procedure for the preparation of ω-*phenylselenoalkyl* 2-(*tri*-n-*butylstannylmethyl)propenoate* esters. (7a)-(7j) To a mixture of the desired ω-phenylselenoalkanol (6a)-(6j) (1 1 equiv), 2-(tri-*n*-butylstannylmethyl)propenoic acid (5) (1 equiv.), and DMAP (0.1 equiv) stirring in dry THF (≈3ml per mmol of stannyl-acid) under an argon atmosphere was added a solution of DCC (1 1 equiv) in dry THF (≈2ml per mmol of stannyl-acid) dropwise, *via* syringe After stirring overnight at room temperature the resulting white precipitate of dicyclohexylurea was filtered off, thoroughly washed with ether and the collected filtrate washed with saturated aqueous sodium bicarbonate and saturated aqueous brine The solvent was subsequently removed *in vacuo* to yield an oil which was purified by flash chromatography (SiO_2, 1% ether/petrol as eluant) to afford spectroscopically pure esters (7a)-(7j)

2-*Phenylselenoethyl* 2-(*tri*-n-*butylstannylmethyl)propenoate* (7a). The standard procedure afforded the product as a pale yellow oil (0 66g, 72%) from 2-phenylselenoethanol (6a) (0 35g, 1 73mmol) and the stannyl-acid (5) (0 60g, 1 60mmol) (Found C, 51 75, H, 7 38 $C_{24}H_{40}O_2SeSn$ requires C, 51 64, H, 7 22%), ν_{max} (thin film) 3060(w, Ar-H), 2955(vs, C-H), 2920(vs, C-H), 2870(s, C-H), 2850(s, C-H), 1714(vs, C=O), 1613(m, C=C), 1162(vs), 1090(s), and 689(s), δ_H (200MHz) 0 68-1 08 (15H, m, $Sn((CH_2)_2\underline{CH_2}CH_3)_3$), 1 16-1 68 (12H, m, $Sn(\underline{CH_2}\underline{CH_2}Et)_3$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 59 5Hz), 3 13 (2H, t, *J* 7 0Hz, $\underline{CH_2}SePh$), 4 35 (2H, t, *J* 7.0Hz, $CO_2\underline{CH_2}$), 5 30 (1H, s, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 18 0Hz), 5 81 (1H, s, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 16 5Hz), 7 20-7 36 (3H, m, aromatics), and 7 48-7 62 (2H, m, aromatics), δ_C (50 4MHz, DEPT) 167 7 ($\underline{C}$=O), 141 1 ($\underline{C}$=CH_2), 133 0 (aromatic), 129 3 (aromatic), 127 4 (aromatic), 119 1 (C=$\underline{C}H_2$), 63 9 (O$\underline{C}H_2$), 25 2 ($\underline{C}H_2SePh$), 28 9, 27 2, 14 7, 9 5 ($Sn((\underline{C}H_2)_3CH_3)_3$ and allylic C), and 13 5 ($Sn((CH_2)_3\underline{C}H_3)_3$), *m/z* [DCI($NH_3$)] 507 (15%), 505 (30), 504 (MH^+-*n*-Bu, ^{80}Se, ^{120}Sn, 30), 503 (87), 502 (43), 501 (100), 500 (52), 499 (78), 498 (26), 497 (33), 475 (23), 473 (24), 471 (19), 403 (35), 401 (27), 399 (16), 308 (41), 307 (15), 306 (33), 305 (19), 185 (71), 184 (35), and 113 (22)

3-*Phenylselenopropyl* 2-(*tri*-n-*butylstannylmethyl)propenoate* (7b). The standard procedure afforded the product as a pale yellow oil (0 52g, 55%) from 3-phenylselenopropanol (6b) (0 38g, 1 73mmol) and the stannyl-acid (5) (0 60g, 1 60mmol) (Found C, 52 69, H, 7 69 $C_{25}H_{42}O_2SeSn$ requires C, 52 47, H, 7 40%), ν_{max} (thin film) 3062(w, Ar-H), 2950(s, C-H), 2920(s, C-H), 2865(m, C-H), 2850(m, C-H), 1715(s, C=O), 1615(m, C=C), 1170(s), 1092(m) ,735(m), and 690(m), δ_H (200MHz) 0 70-1 05 (15H, m, $Sn((CH_2)_2\underline{CH_2}CH_3)_3$), 1 20-1 68 (12H, m, $Sn(\underline{CH_2}\underline{CH_2}Et)_3$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 59 0Hz), 2 00-2 12 (2H, m, $CO_2CH_2\underline{CH_2}CH_2SePh$), 2 98 (2H, t, *J* 7 0Hz, $\underline{CH_2}SePh$), 4 23 (2H, t, *J* 6 5Hz, $CO_2\underline{CH_2}$), 5 32 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 19 0Hz), 5 81 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer

satellites ^4J Sn 16.5Hz), 7.21-7.35 (3H, m, aromatics), and 7.47-7 58 (2H, m, aromatics); δ_C (50 4MHz, DEPT) 167 9 (C=O), 141 3 (C=CH_2), 132 9 (aromatic), 129.9 ($CSeCH_2$), 129 2 (aromatic), 127 1 (aromatic), 118 7 (C=CH_2), 63.9 (OCH_2), 29.1, 23.8 (CH_2CH_2SePh), 28 9, 27 2, 14.7, 9 5 ($Sn((CH_2)_3CH_3)_3$ and allylic C), and 13 5 ($Sn((CH_2)_3CH_3)_3$), *m/z* [DCI(NH_3)] 519 (35%), 518 (MH^+-*n*-Bu, ^{80}Se, ^{120}Sn, 27), 517 (91), 516 (43), 515 (100), 514 (53), 512 (27), 511 (34), 199 (93), 197 (47), 196 (18), and 195 (20).

4-Phenylselenobutyl 2-(tri-n-butylstannylmethyl)propenoate **(7c).** The standard procedure afforded the product as a colourless oil (0.38g, 59%) from 4-phenylselenobutanol (6c) (0 27g, 1 17mmol) and the stannyl-acid (5) (0.40g, 1 06mmol). ν_{max} (thin film) 3078(w, Ar-H), 2958(vs, C-H), 2928(vs, C-H), 2878(s, C-H), 2858(s, C-H), 1714(vs, C=O), 1615(m, C=C), 1170(vs), 1093(s), 737(s), and 690(s); δ_H (200MHz) 0 70-1 07 (15H, m, $Sn((CH_2)_2CH_2CH_3)_3$), 1 17-1 68 (12H, m, $Sn(CH_2CH_2Et)_3$), 1 72-1 88 (4H, m, $OCH_2(CH_2)_2CH_2SePh$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 58 0Hz), 2 94 (2H, t, *J* 7.0Hz, CH_2SePh), 4 13 (2H, t, *J* 6 0Hz, CO_2CH_2), 5 29 (1H, d, *J* 1 5Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 19 5Hz), 5 78 (1H, d, *J* 1.5Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17 0Hz), 7 20-7 33 (3H, m, aromatics), and 7 44-7 56 (2H, m, aromatics), δ_C (50 4MHz, DEPT) 168 0 (C=O), 141 4 (C=CH_2), 132 8 (aromatic), 129 2 (aromatic), 127 0 (aromatic), 118 6 (C=CH_2), 64 0 (OCH_2), 28 6, 26 5 (CH_2), 28 9, 27 2, 14 7, 9 5 ($Sn((CH_2)_3CH_3)_3$ and allylic C), and 13 5 ($Sn((CH_2)_3CH_3)_3$), *m/z* [IBEI] 533 (35%), 532 (33), 531 (M^+-*n*-Bu, 92), 530 (50), 529 (100), 528 (51), 527 (72), 526 (30), 319 (60), 317 (36), 315 (31), 277 (23), 273 (20), 235 (37), 233 (31), 179 (62), 177 (64), 69 (40), and 55 (48)

5-Phenylselenopentyl 2-(tri-n-butylstannylmethyl)propenoate **(7d).** The standard procedure afforded the product as a colourless oil (0 26g, 41%) from 5-phenylselenopentanol (6d) (0 28g,1 20 mmol) and the stannyl-acid (5) (0 40g, 1 06mmol) ν_{max} (thin film) 3078(w, Ar-H), 2958(vs, C-H), 2930(vs, C-H), 2875(s, C-H), 2858(s, C-H), 1713(vs, C=O), 1613(s, C=C), 1172(vs),1094(s), 736(s), and 690(s), δ_H (200MHz) 0 70-1 04 (15H, m, $Sn((CH_2)_2CH_2CH_3)_3$), 1 18-1 81 (28H, m, $Sn(CH_2CH_2Et)_3$ and $CO_2CH_2(CH_2)_3CH_2$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 59 0Hz), 2 93 (2H, t, *J* 7 5Hz, CH_2SePh), 4 12 (2H, t, *J* 6 5Hz, CO_2CH_2), 5 30 (1H, d, *J* 1 5Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 18 5Hz), 5 81 (1H, d, *J* 1 5Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17 0Hz), 7 21-7 37 (3H, m, aromatics), and 7 45-7 57 (2H, m, aromatics), δ_C (50 4MHz) 168 0 (C=O), 141 4 (C=CH_2), 132 7 (aromatic), 130 5 ($CSeCH_2$), 129 1 (aromatic), 126 8 (aromatic), 118 6 (C=CH_2), 64 5 (OCH_2), 29 6, 28 0, 27 5, 26 1 (CH_2), 28 9, 27 2, 14 7, 9 5 ($Sn((CH_2)_3CH_3)_3$ and allylic C), and 13 5 ($Sn((CH_2)_3CH_3)_3$), *m/z* [IBEI] 545 (M^+-*n*-Bu, ^{80}Se, ^{120}Sn, 9%), 543 (11), 541 (8), 235 (18), 229 (28), 228 (18), 227 (100), 225 (65), 224 (24), 223 (29), 179 (26), 177 (23), 175 (18), and 69 (18)

6-Phenylselenohexyl 2-(tri-n-butylstannylmethyl)propenoate **(7e).** The standard procedure afforded the product as a colourless oil (0 41g, 61%) from 6-phenylselenohexanol (6e) (0 30g, 1 16mmol) and the stannyl-acid (5) (0 40g, 1 06mmol) (Found C, 54 46, H, 8 04 $C_{28}H_{48}O_2SeSn$ requires C, 54 74, H, 7 88%), ν_{max} (thin film) 3078(w, Ar-H), 2960(vs, C-H), 2930(vs, C-H), 2859(s, C-H), 1714(vs, C=O), 1617(m, C=C), 1582(w), 1172(vs), 736(m), and 691(m), δ_H (200MHz) 0 70-1 06 (15H, m, $Sn((CH_2)_2CH_2CH_3)_3$), 1 19-1 81 (20H, m, $Sn(CH_2CH_2Et)_3$ and $CO_2CH_2(CH_2)_4CH_2$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 53 0Hz), 2 93 (2H, t, *J* 7 0Hz, CH_2SePh), 4 12 (2H, t, *J* 6 0Hz, CO_2CH_2), 5 30 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn

17 0Hz), 5 81 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17 0Hz), 7 20-7 32 (3H, m, aromatics), and 7 45-7.55 (2H, m, aromatics), δ_C (50 4MHz) 168.1 (C=O), 141 5 (C=CH_2), 132 6 (aromatic), 130.6 (C$SeCH_2$), 129.1 (aromatic), 126 8 (aromatic), 118 5 (C=CH_2), 64 6 (OCH_2), 29 9, 28 4, 27 7, 27.6, 25.4 (CH_2), 28 9, 27 2, 14 7, 9.5 (Sn((CH_2)$_3CH_3$)$_3$ and allylic C), and 13.5 (Sn((CH_2)$_3CH_3$)$_3$), *m/z* [IBEI] 559 (M^+-*n*-Bu, ^{80}Se, ^{120}Sn, 19%), 557 (19), 555 (15), 319 (19), 317 (16), 243 (18), 241 (100), 239 (56), 237 (23), 235 (27), 233 (21), 179 (47), 177 (44), 175 (26), and 55 (42)

***7-Phenylselenoheptyl* 2-*(tri*-n-*butylstannylmethyl)propenoate* (7f).** The standard procedure afforded the product as a colourless oil (0 48g, 72%) from 7-phenylselenoheptanol (6f) (0 32g, 1 2mmol) and the stannyl-acid (5) (0.40g, 1.06mmol) ν_{max} (thin film) 3078(w, Ar-H), 2958(s, C-H), 2930(vs, C-H), 2858(s, C-H), 1713(s, C=O), 1613(m, C=C), 1172(s), 738(m), and 691(m), δ_H (200MHz) 0 70-1 04 (15H, m, Sn((CH_2)$_2$CH_2CH_3)$_3$), 1 18-1 81 (22H, m, Sn(CH_2CH_2Et)$_3$ and CO_2CH_2(CH_2)$_5$$CH_2$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 58 5Hz), 2 94 (2H, t, *J* 7 5Hz, CH_2SePh), 4 12 (2H, t, *J* 6 5Hz, CO_2CH_2), 5 30 (1H, d, *J* 1 5Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 18 5Hz), 5 81 (1H, d, *J* 1 5Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17 0Hz), 7 22-7 34 (3H, m, aromatics), and 7 46-7 57 (2H, m, aromatics), δ_C (50 4MHz) 168 1 (C=O), 141 5 (C=CH_2), 132 5 (aromatic), 130 7 (C$SeCH_2$), 129 1 (aromatic), 126 7 (aromatic), 118 5 (C=CH_2), 64 7 (OCH_2), 29 9, 29 5, 28 6, 28 5, 26 8, 25 7 (CH_2), 28 8, 27 2, 14.7, 9 5 (Sn((CH_2)$_3CH_3$)$_3$ and allylic C), and 13 5 (Sn((CH_2)$_3$CH_3)$_3$), *m/z* [IBEI] 575 (28%), 574 (25), 573 (M^+-*n*-Bu, ^{80}Se, ^{120}Sn, 84), 572 (43), 571 (100), 570 (59), 569 (67), 567 (21), 391 (23), 389 (34), 388 (33), 319 (78), 317 (39), 315 (27), 277 (25), 275 (40), 273 (22), 255 (71), 253 (32), 235 (45), 233 (29), 205 (22), 179 (73), 177 (53), and 175 (32)

***8-Phenylselenooctyl* 2-*(tri*-n-*butylstannylmethyl)propenoate* (7g).** The standard procedure afforded the product as a colourless oil (0 47g, 67%) from 8-phenylselenooctanol (6g) (0.33g, 1 15mmol) and the stannyl-acid (5) (0 40g, 1 06mmol) ν_{max} (thin film) 2960(m, C-H), 2930(s, C-H), 2860(m, C-H), 1715(m, C=O), 1618(w, C=C), 1465(w), 1175(m), 1093(w), and 738(w), δ_H (200MHz) 0 70-1 06 (15H, m, Sn((CH_2)$_2$CH_2CH_3)$_3$), 1 18-1 79 (24H, m, Sn(CH_2CH_2Et)$_3$ and CO_2CH_2(CH_2)$_6$$CH_2$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 58.0Hz), 2 91 (2H, t, *J* 7 0Hz, CH_2SePh), 4.12 (2H, t, *J* 6 0Hz, CO_2CH_2), 5 29 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 18 0Hz), 5 82 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17 0Hz), 7 18-7 32 (3H, m, aromatics), and 7 42-7 54 (2H, m, aromatics), δ_C (50 4MHz, DEPT) 168 1 (C=O), 141 5 (C=CH_2), 132 5 (aromatic), 130 8 (C$SeCH_2$), 129 1 (aromatic), 126 7 (aromatic), 118 5 (C=CH_2), 64 7 (OCH_2), 30 0, 29 6, 29 0, 28 5, 28 0, 27 7, 25 8 (CH_2), 28 9, 27 2, 14 7, 9 5 (Sn((CH_2)$_3CH_3$)$_3$ and allylic C), and 13 5 (Sn((CH_2)$_3$CH_3)$_3$), *m/z* [IBEI] 587 (M^+-57, ^{80}Se, ^{120} Sn, 18%), 585 (20), 583 (15), 513 (20), 511 (68), 510 (37), 509 (100), 508 (42), 507 (61), 505 (25), 319 (43), 317 (35), 315 (20), 235 (32), 233 (22), 179 (40), 177 (37), and 175 (29)

***9-Phenylselenononyl* 2-*(tri*-n-*butylstannylmethyl)propenoate* (7h).** The standard procedure afforded the product as a colourless oil (0 36g, 50%) from 9-phenylselenonanol (6h) (0 35g, 1 17mmol) and the stannyl-acid (5) (0 40g, 1 06mmol) (Found C, 56 35, H, 8 65 $C_{31}H_{54}O_2SeSn$ requires C, 56 59, H, 8 29%), ν_{max} (thin film) 3078(w, Ar-H), 2960(s, C-H), 2930(s, C-H), 2860(m, C-H), 1714(m, C=O), 1617(w, C=C), 1175(m), 1092(w), and 738(w), δ_H (200MHz) 0 70-1 04 (15H, m, Sn((CH_2)$_2$CH_2CH_3)$_3$), 1.18-1 80 (26H, m, Sn(CH_2CH_2Et)$_3$ and CO_2CH_2(CH_2)$_7$$CH_2$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer

satellites ^2J SnCH 58.0Hz), 2.91 (2H, t, J 7.5Hz, CH_2SePh), 4 12 (2H, t, J 7.5Hz, CO_2CH_2), 5.29 (1H, d, J 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17.5Hz), 5.81 (1H, d, J 1.0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 18.5Hz), 7.18-7.32 (3H, m, aromatics), and 7.42-7 53 (2H, m, aromatics), δ_C (50 4MHz) 168.1 (C=O), 141.5 ($C=CH_2$), 132.5 (aromatic), 129.1 (aromatic), 126 7 (aromatic), 118 5 ($C=CH_2$), 64.8 (OCH_2), 30 0, 29.6, 29.2, 29 0, 28.5, 27.7, 25.8 (CH_2), 28.9, 27.2, 14 7, 9 5 ($Sn((CH_2)_3CH_3)_3$ and allylic C), and 13 5 ($Sn((CH_2)_3CH_3)_3$), *m/z* [IBEI] 603 (34%), 602 (32), 601 (M^+, ^{80}Se, ^{120}Sn, 98), 600 (53), 599 (100), 598 (54), 597 (71), 596 (28), 595 (32), 391 (24), 389 (27), 387 (22), 322 (67), 319 (59), 317 (42), 315 (25), 292 (22), 277 (23), 275 (23), 273 (19), 235 (41), 233 (32), 179 (61), 177 (61), 175 (43), 91 (38), 86 (99), 85 (67), 84 (38), 83 (43), 69 (35), 57 (27), 55 (52), 51 (39), and 49 (51)

10-*Phenylselenodecyl* 2-(*tri*-n-*butylstannylmethyl)propenoate (7i). The standard procedure afforded the product as a colourless oil (0.32g, 44%) from 10-phenylselenodecanol (6i) (0.37g, 1 18mmol) and the stannyl-acid (5) (0 40g, 1 06mmol) (Found· C, 57 25, H, 8 72 $C_{32}H_{56}O_2SeSn$ requires C, 57 33, H, 8 42%), ν_{max} (thin film) 2930(s, C-H), 2860(m, C-H), 1712(m, C=O), 1615(w, C=C), 1175(m), 738(w) and 690(w), δ_H (200MHz) 0 70-1 06 (15H, m, $Sn((CH_2)_2CH_2CH_3)_3$), 1 20-1 80 (28H, m, $Sn(CH_2CH_2Et)_3$ and $CO_2CH_2(CH_2)_8CH_2$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 58 0Hz), 2 94 (2H, t, J 7 0Hz, CH_2SePh), 4 12 (2H, t, J 7 0Hz, CO_2CH_2), 5 30 (1H, d, J 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 19 0Hz), 5 82 (1H, d, J 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 18 0Hz), 7 21-7 33 (3H, m, aromatics), and 7 43-7 54 (2H, m, aromatics), δ_C (50 4MHz, DEPT) 168 1 (C=O), 141 5 ($C=CH_2$), 132 5 (aromatic), 129 1 (aromatic), 126 7 (aromatic), 118 5 ($C=CH_2$), 64 8 (OCH_2), 30 0, 29 7, 29 3, 29 1, 28 5, 25 8 (CH_2), 28 9, 27 2, 14 7, 9 5 ($Sn((CH_2)_3CH_3)_3$ and allylic C), and 13 5 ($Sn((CH_2)_3CH_3)_3$), *m/z* [IBEI] 617 (50%), 616 (49), 615 (M^+-*n*-Bu, ^{80}Se, ^{120}Sn, 100), 614 (67), 613 (98), 612 (64), 611 (80), 610 (42), 609 (47), 319 (56), 317 (44), 315 (32), 291 (30), 235 (41), 233 (36), 231 (23), 205 (24), 179 (50), 177 (48), 175 (33), 69 (24), and 55 (26)

11-*Phenylselenoundecyl* 2-(*tri*-n-*butylstannylmethyl)propenoate (7j). The standard procedure afforded the product as a colourless oil (0 42g, 56%) from 11-phenylselenoundecanol (6j) (0 38g, 1 16mmol) and the stannyl-acid (5) (0 40g, 1 06mmol) (Found C, 57 67, H, 8 79 $C_{33}H_{58}O_2SeSn$ requires C, 57 91, H, 8 54%), ν_{max} (thin film) 3060(w, Ar-H), 2920(vs, C-H), 2850(vs, C-H), 1710(vs, C=O), 1610(s, C=C), 1460(s), 1170(vs), 1090(s), 730(s), and 688(s), δ_H (200MHz) 0 70-1 03 (15H, m, $Sn((CH_2)_2CH_2CH_3)_3$), 1.18-1 79 (30H, m, $Sn(CH_2CH_2Et)_3$ and $CO_2CH_2(CH_2)_9CH_2$), 1 98 (2H, s, allylic H, this resonance shows tin isotopomer satellites ^2J SnCH 58 5Hz), 2 94 (2H, t, J 7 5Hz, CH_2SePh), 4 12 (2H, t, J 7 0Hz, CO_2CH_2), 5 29 (1H, d, J 1 5Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 18 0Hz), 5 81 (1H, d, J 1 5Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17 5Hz), 7 21-7 35 (3H, m, aromatics), and 7 46-7 56 (2H, m, aromatics), δ_C (50 4MHz) 168 1 (C=O), 141 5 ($C=CH_2$), 132.5 (aromatic), 130 9 ($CSeCH_2$), 129 0 (aromatic), 126 5 (aromatic), 118 5 ($C=CH_2$), 64 7 (OCH_2), 29 8, 29 5, 29 0, 28 5, 28 3, 27 5, 25 3 (CH_2), 28 9, 27 1, 14 5, 9 5 ($Sn((CH_2)_3CH_3)_3$ and allylic C), and 13 5 ($Sn((CH_2)_3CH_3)_3$), *m/z* [DCI(NH_3)] 686 (MH^+, ^{80}Se, ^{120}Sn, 22%), 685 (23), 684 (16), 631 (27), 630 (19), 629 (MH^+-*n*-Bu, ^{80}Se, ^{120}Sn, 54), 628 (29), 627 (52), 626 (30), 625 (35), 624 (15), 623 (17), 312 (20), 310 (16), 309 (16), 308 (100), 307 (38), 306 (70), 305 (32), and 304 (48)

General Procedure for the preparation of 2-*methylene alkanolides*. (8e)-(8j) To a degassed solution of the desired ω-phenylselenoalkyl 2-(tri-*n*-butylstannylmethyl)propenoate ester (7e)-(7j) in

benzene (5mM solution) was added tri-*n*-butyltin hydride (≈0.1 equiv) *via* syringe and AIBN (0.05-0.1 equiv.) The mixture was heated at reflux under an argon atmosphere for 48 hours, recharging the system with a catalytic quantity of AIBN after approximately every 12 hours The solvent was subsequently removed *in vacuo*, and the residue purified as detailed below

2-*Methylene nonan*-9-*olide* (8e). The standard procedure was followed using 6-phenylselenohexyl 2-(tri-*n*-butylstannylmethyl)propenoate (7e) (320mg, 0.5mmol) and tri-*n*-butyltin hydride (8µl, 0 03mmol) The residue was purified by flash chromatography (SiO_2, 1% ether/petrol as eluant) followed by PLC (SiO_2; neat petrol as eluant) to yield spectroscopically pure 2-*methylene nonan*-9-*olide* (8e) (47mg, 54%) as a colourless oil ν_{max} (thin film) 2956(s, C-H), 2938(s, C-H), 2876(m, C-H), 1721 (vs, C=O), 1633(m, C=C), 1294(s), 1188(vs), 1150(s), and 830(C=C, m); δ_H (200MHz) 1.10-1 84 (10H, m, $OCH_2(CH_2)_5$), 2.48 (2H, t, *J* 6 0Hz, $C{=}CCH_2$), 4 35 (2H, ca.t, *J* 5.0Hz, OCH_2), 5 48 (1H, d, *J* 1.5Hz, olefinic H), and 6 15 (1H, d, *J* 1 5Hz, olefinic H), δ_C (50 4MHz) 168 4 (C=O), 142.7 ($C{=}CH_2$), 125 9 ($C{=}CH_2$), 66 4 (OCH_2), 29 2, 28 5, 26 2, 24 8, 24 2, and 22 6 (-CH_2-), *m/z* [CI(NH_3)] 186 (MNH_4^+, 86%), 169 (MH^+, 100), and 123 (19)

2-*Methylene decan*-10-*olide* (8f). The standard procedure was followed using 7-phenylselenoheptyl 2-(tri-*n*-butylstannylmethyl)propenoate (7f) (375mg, 0.6mmol) and tri-*n*-butyltin hydride (10µl, 0 04mmol) The residue was purified by flash chromatography (SiO_2, 1% ether/petrol as eluant) followed by bulb to bulb distillation (b p ≈135°C/0 05mmHg) to yield spectroscopically pure 2-*methylene decan*-10-*olide* (8f) (50mg, 46%) as a colourless oil ν_{max} (thin film) 2958(s, C-H), 2938(s, C-H), 2860(m, C-H), 1725 (s, C=O), 1633(m, C=C), 1465(m), 1292(s), 1210(m), 1175(s), and 820(C=C, m), δ_H (200MHz) 1 20-1.78 (12H, m, $OCH_2(CH_2)_6$), 2 38 (2H, t, *J* 6 5Hz, $C{=}CCH_2$), 4.18 (2H, ca t, *J* 5 0Hz, OCH_2), 5.47 (1H, d, *J* 2 0Hz, olefinic H), and 6 20 (1H, d, *J* 2.0Hz, olefinic H), δ_C (50 4MHz) 168 1 (C=O), 142 4 ($C{=}CH_2$), 126.1 ($C{=}CH_2$), 65 6 (OCH_2), 28 4, 28 1, 26 1, 24 9, 24 6, 23 9, and 21.6 (-CH_2-), *m/z* [CI(NH_3)] 200 (MNH_4^+, 100%), 183 (MH^+, 57), and 137 (17)

2-*Methylene undecan*-11-*olide* (8g). The standard procedure was followed using 8-phenylselenooctyl 2-(tri-*n*-butylstannylmethyl)propenoate (7g) (330mg, 0 5mmol) and tri-*n*-butyltin hydride (10µl, 0 04mmol) The residue was purified by flash chromatography (SiO_2, 2% ether/petrol as eluant) to yield analytically pure 2-*methylene undecan*-11-*olide* (8g) (60mg, 61%) as a colourless oil (Found. C, 73 66, H, 10 67 $C_{12}H_{20}O_2$ requires C, 73 43, H, 10 27%), ν_{max} (thin film) 2938(vs, C-H), 2865(s, C-H), 1725 (vs, C=O), 1638(w, C=C), 1468(s), 1296(s), 1173(vs), 941(m), and 815(C=C, m), δ_H (200MHz) 1 25-1 49 (10H, br s, $C{=}C(CH_2)_2(CH_2)_5$), 1 49-1 66 (2H, m, $C{=}CCH_2CH_2$), 1 67-1 80 (2H, m, OCH_2CH_2), 2 36 (2H, t, *J* 7 0Hz, $C{=}CCH_2$), 4 24 (2H, ca t, *J* 5 0Hz, OCH_2), 5 45 (1H, d, *J* 1 0Hz, olefinic H), and 6 07 (1H, d, *J* 1 0Hz, olefinic H), δ_C (50 4MHz, DEPT) 168 3 (C=O), 142 5 ($C{=}CH_2$), 125 0 ($C{=}CH_2$), 65 0 (OCH_2), 30 9, 26 1, 25 5, 25 4, 25 2, 23 6, and 23 3 (-CH_2-), *m/z* [CI(NH_3)] 214 (MNH_4^+, 81%), 197 (MH^+, 100), and 151 (17), 95 (20), 81 (18), and 58 (22)

2-*Methylene dodecan*-12-*olide* (8h). The standard procedure was followed using 9-phenylselenononyl 2-(tri-*n*-butylstannylmethyl)propenoate (7h) (283mg, 0 43mmol) and tri-*n*-butyltin hydride (8µl, 0 03mmol) The residue was purified by flash chromatography (SiO_2, 1% ether/petrol as eluant) followed by bulb to bulb distillation (b p ≈135°C/0 05mmHg) to yield analytically pure 2-*methylene dodecan*-12-*olide* (8h) (44mg, 50%) as a colourless oil (Found C, 74 52, H, 10 91 $C_{13}H_{22}O_2$ requires C, 74 24, H, 10 54%), ν_{max} (thin film) 2938(s, C-H), 2868(m, C-H), 1723 (vs, C=O), 1635(w, C=C), 1465(m),1301(m), 1175(s),

and 818(C=C, w); δ_H (200MHz) 1 20-1 59 (14H, br s, C=CCH$_2$(CH$_2$)$_7$), 1.60-1.78 (2H, m, OCH$_2$CH$_2$), 2.32 (2H, t, *J* 8 0Hz, C=CCH$_2$), 4.20 (2H, ca.t, *J* 5.0Hz, OCH$_2$), 5.48 (1H, d, *J* 1.5Hz, olefinic H), and 6.14 (1H, d, *J* 1 5Hz, olefinic H); δ_C (50.4MHz, DEPT) 168 2 (C=O), 141.9 (C=CH$_2$), 125.7 (C=CH$_2$), 65.4 (OCH$_2$), 31 8, 27 4, 26 6, 26.5, 25 1, 24 8, 24 6, and 24 2 (-CH$_2$-); *m/z* [CI(NH$_3$)] 228 (MNH$_4^+$, 47%), 212 (11) and 211 (MH$^+$, 100).

2-Methylene tridecan-13-olide **(8i).** The standard procedure was followed using 10-phenylselenodecyl 2-(tri-*n*-butylstannylmethyl)propenoate (7i) (470mg, 0 70mmol) and tri-*n*-butyltin hydride (10µl, 0 04mmol). The residue was purified by flash chromatography (SiO_2; 1% ether/petrol as eluant) followed by bulb to bulb distillation (b.p. ≈140°C/0.05mmHg) to yield spectroscopically pure *2-methylene tridecan-13-olide* (8i) (125mg, 80%) as a colourless oil. ν_{max} (thin film) 2930(vs, C-H), 2860(s, C-H), 1722(vs, C=O), 1635(w, C=C), 1463(m), 1302(s), 1170(s), and 818 (C=C, w), δ_H (200MHz) 1 20-1.59 (16H, m, C=C(CH$_2$)$_8$), 1 60-1 78 (2H, m, OCH$_2$CH$_2$), 2 33 (2H, t, *J* 7 0Hz, C=CCH$_2$), 4.26 (2H, ca t, *J* 6 0Hz, OCH$_2$), 5 47 (1H, d, *J* 2.0Hz, olefinic H), and 6 09 (1H, d, *J* 2 0Hz, olefinic H), δ_C (50.4MHz) 167.9 (C=O), 141 8 (C=CH$_2$), 125 1 (C=CH$_2$), 63 8 (OCH$_2$), 32 7, 27 4, 26 5, 26.1, 25 8, 25.5, 25 1, 23 9, and 22 8 (-CH$_2$-), *m/z* [CI(NH$_3$)] 242 (MNH$_4^+$, 38%), 226 (12), and 225 (MH$^+$, 100).

2-Methylene tetradecan-14-olide **(8j).** The standard procedure was followed using 11-phenylselenoundecyl 2-(tri-*n*-butylstannylmethyl)propenoate (7j) (420mg, 0 61mmol) and tri-*n*-butyltin hydride (10µl, 0 04mmol) The residue was purified by flash chromatography (SiO_2, 5% ether/petrol as eluant) followed by PLC (SiO_2, neat petrol as eluant) to yield analytically pure *2-methylene-tetradecan-14-olide* (8j) (110mg, 72%) as a colourless oil (Found C, 75 40, H, 11 27 $C_{15}H_{26}O_2$ requires C, 75 58, H, 10 99%); ν_{max} (thin film) 2920(s, C-H), 2855(m, C-H), 1721 (s, C=O), 1630(m, C=C), 1460(m), 1303(m), 1175(s), and 820(w, C=C), δ_H (200MHz) 1 20-1 55 (18H, br s, C=CCH$_2$(CH$_2$)$_9$), 1 62-1 78 (2H, m, OCH$_2$CH$_2$), 2.34 (2H, t, *J* 7 0Hz, C=CCH$_2$), 4 22 (2H, ca t, *J* 5 0Hz, OCH$_2$), 5 48 (1H, d, *J* 1 0Hz, olefinic H), and 6.15 (1H, d, *J* 1 0Hz, olefinic H), δ_C (50 4MHz, DEPT) 168 2 (C=O), 141 5 (C=CH$_2$), 125.5 (C=CH$_2$), 64 5 (OCH$_2$), 32 5, 28 1, 26 3, 26.1, 24 8, and 24 6 (-CH$_2$-), *m/z* [CI(NH$_3$)] 256 (MNH$_4^+$, 44%), 240 (14), 239 (MH$^+$, 100), 109 (15), 95 (24), 81 (25) and 58 (27)

Attempted preparation of 2-Methylene pentan-5-olide **(8a).** The standard procedure was followed using 2-phenylselenoethyl 2-(tri-*n*-butylstannylmethyl)propenoate (7a) (500mg, 0 89mmol) and tri-*n*-butyltin hydride (10µl, 0 04mmol) After 24 hours t l c of the reaction mixture revealed an intensely staining spot at R_f 0 6 (10% ether/petrol) A portion of the mixture was removed and subjected to PLC (10% ether/petrol), whence the spot was identified as the dimer species (20) To a degassed solution of the dimer (20) (40mg, 0 06mmol) in benzene (20ml) was added tri-*n*-butyltin hydride (2µl, 0 008mmol) *via* syringe and AIBN (1mg, 0 1equiv) The mixture was heated at reflux for 3 hours, and the solvent subsequently removed *in vacuo* The residue was subjected to PLC (10% ether/petrol) whence the dilactone *1,7-dioxa-2,8-dioxo-3,9-dimethylene cyclododecane* (12) (5mg) was isolated

In a separate experiment the standard procedure was followed using 2-phenylselenoethyl 2-(tri-*n*-butylstannylmethyl)propenoate (7a) (488mg, 0 87mmol) and tri-*n*-butyltin hydride (10µl, 0 04mmol) The intense spot corresponding to the dimer species (20) was observed after 24h, but had disappeared after a further 24 hours, being replaced by a spot with R_f 0 2 (10% ether/petrol) corresponding to the dilactone (12) The solvent was removed *in vacuo* and the residue subjected to flash chromatography (SiO_2; 10% ether/petrol as eluant) to yield the dilactone *1,7-dioxa-2,8-dioxo-3,9-dimethylene cyclododecane* (12) (33mg, 34%) as a

colourless oil ν_{max} (thin film) 2950(s, C-H), 2925(s, C-H), 2870(m, C-H), 1720(vs, C=O), 1630(s, C=C), 1290(vs), 1200(vs), 1160(vs), 948(s), and 812(m), δ_H (200MHz) 1.81-1 98 (4H, m, 2 x C=CCH$_2$CH$_2$), 2.54 (4H, t, *J* 6 5Hz, 2 x C=CCH$_2$), 4.20 (4H, ca.t , *J* 5 5Hz, 2 x OCH$_2$), 5.51 (2H, d, *J* 1.0Hz, 2 x olefinic H), and 6 08 (2H, d, *J* 1.0Hz, 2 x olefinic H); *m/z* [CI(NH$_3$)] 243 (12%), 242 (MNH_4^+, 100), 225 (MH^+, 11), 132 (11), 130 (39), and 113 (31)

1-*Phenylseleno*-3,9-*dioxa*-4,10-*dioxo*-5,11-*dimethylene*-12-(*tri*- n -*butylstannylmethyl*) *dodecane* (20). ν_{max} (liquid film) 3060(w, Ar-H), 2950(vs, C-H), 2865(s, C-H), 2850(s, C-H), 1716(vs, C=O), 1630(w, C=C), 1611(m, C=C), 1318(s), 1298 (s), 1169(s), 810(m), and 732(s); δ_H (200MHz) 0.70-1 04 (15H, m, Sn((CH$_2$)$_2$CH$_2$CH$_3$)$_3$), 1 16-1.68 (12H, m, Sn((CH$_2$)$_2$Et)$_3$), 1 78-1 95 (2H, m, OCH$_2$CH$_2$CH$_2$C=C), 1 98 (2H, s, Bu$_3$SnCH$_2$, this resonance shows tin isotopomer satellites ^2J SnCH 61Hz), 2 39 (2H, t, *J* 7.5Hz, C=CCH$_2$), 3.14 (2H, t, *J* 7.0Hz, CH$_2$SePh), 4.16 (2H, t, *J* 6 5Hz, OCH$_2$(CH$_2$)$_2$C=C), 4 40 (2H, t, *J* 7 5Hz, OCH$_2$CH$_2$SePh), 5 30 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 18Hz), 5 58 (1H, d, *J* 1 0Hz, olefinic H), 5.83 (1H, d, *J* 1 0Hz, olefinic H, this resonance shows tin isotopomer satellites ^4J Sn 17.5Hz), 6 17 (1H, d, *J* 1 0Hz, olefinic H), 7 22-7 34 (3H, m, aromatics), and 7 51-7 63 (2H, m, aromatics), *m/z* [DCI(NH$_3$)] 615 (M^+-*n*-Bu, ^{80}Se, ^{120}Sn, 33%), 614 (18), 613 (36), 612 (19), 611 (29), 447 (17), 408 (34), 407 (20), 406 (35), 405 (25), 404 (30), 403 (40), 402 (26), 401 (28), 400 (22), 393 (23), 391 (70), 390 (26), 389 (70), 388 (34), 387 (55), 389 (19), 385 (24), 308 (100), 307 (38), 306 (80), 305 (33), 304 (50), and 185 (29)

***Attempted preparation of* 2-*Methylene*-*hexan*-6-*olide* (8b).** The standard procedure was followed using 3-phenylselenopropyl 2-(tri-*n*-butylstannylmethyl)propenoate (7b) (356mg, 0.62mmol) and tri-*n*-butyltin hydride (10µl, 0 04mmol) Examination of the reaction mixture by t l.c after 24 and 48 hours revealed analogous behaviour to that described for the attempted preparation of 2-methylene hexan-6-olide (8a) The solvent was removed *in vacuo* and the residue subjected to flash chromatography (SiO_2; 10% ether/petrol as eluant) to yield a mixture of the dilactone 1,8-*dioxa*-2,9-*dioxo*-3,10-*dimethylene cyclotetradecane* (13) (25%)† and the co-running AIBN adduct (15) (5%)† (combined mass 21mg) as a colourless oil. The flash column was subsequently flushed with ethyl acetate to yield a complex mixture of unidentified AIBN adducts (50mg)

1,8-*dioxa*-2,9-*dioxo*-3,10-*dimethylene cyclotetradecane* (13) ν_{max} (thin film, mixture of dilactone and AIBN adduct (15)) 2945(s, C-H), 2870(m, C-H), 2238(w, C≡N), 1715(br, vs, C=O), 1632(s, C=C), 1300(vs), 1265(s), 1195(vs), 1050(s), and 820(s), δ_H (200MHz) 1.59-1 79(8H, m, 2 x C=CCH$_2$(CH$_2$)$_2$), 2.36 (4H, t, *J* 6 5Hz, 2 x C=CCH$_2$), 4 24 (4H, ca t , *J* 5.0Hz, 2 x OCH$_2$), 5 48 (2H, d, *J* 1 0Hz, 2 x olefinic H), and 6 13 (2H, d, *J* 1 0Hz, 2 x olefinic H), δ_C (50 4MHz) 167 5 (C=O), 141 9 (C=CH$_2$), 126 1 (C=CH$_2$), 63 3 (OCH$_2$), 32 8, 28 0, and 25 2 (CH$_2$), *m/z* [CI(NH$_3$), GCMS] 270 (MNH_4^+, 100%), 253 (MH^+, 33), 127 (28) and 109 (17)

4-*oxa*-5-*oxo*-6-*methylene*-8-*cyano*-8-*methyl*-*nonane* (15). ν_{max} (thin film, mixture of dilactone (13) and AIBN adduct) as previously recorded, δ_H (200MHz) 0 98 (3H, t, *J* 7 0Hz, CH$_2$CH$_3$), 1 36 (6H, s, (CH$_3$)$_2$C), 2 03 (2H, ca sex *J* 7 0Hz, OCH$_2$CH$_2$CH$_3$), 2 60 (2H, s, allylic H), 4 14 (2H, t, *J* 7 0Hz, OCH$_2$), 5 88 (1H, s, olefinic H), 6 43 (1H, s, olefinic H), *m/z* [CI(NH$_3$), GCMS] 214 (11%), 213 (MNH_4^+, 100), 196 (MH^+, 8), and 153 (8)

***Attempted preparation of* 2-*Methylene heptan*-7-*olide* (8c).** The standard procedure was followed using 4-phenylselenobutyl 2-(tri-*n*-butylstannylmethyl)propenoate (7c) (300mg, 0 51mmol) and tri-*n*-

† Yield estimated from ^{1}H NMR spectrum

butyltin hydride (10µl, 0.04mmol). Examination of the reaction mixture by t.l c. after 24 and 48 hours revealed analogous behaviour to that previously described for the attempted preparation of 2-methylene hexan-6-olide (8a) The solvent was removed *in vacuo* and the residue subjected to flash chromatography (SiO_2, 10% ether/petrol as eluant) to yield a mixture of the dilactone 1,9-*dioxa*-2,10-*dioxo*-3,11-*dimethylene cyclohexadecane* (14) (30%)† and the co-running AIBN adduct (16) (5%)† (combined mass 27mg) as a colourless oil. The flash column was subsequently flushed with ethyl acetate to yield a mixture of AIBN adducts (108mg), which were subsequently separated by PLC (SiO_2, 20% ether/petrol as eluant) to afford the two products (17) (5%)† and (18) (5%)

1,9-*dioxa*-2,10-*dioxo*-3,11-*dimethylene cyclohexadecane* (14). ν_{max} (thin film; mixture of dilactone and AIBN adduct (16)) 2938 (m, C-H), 2865 (w, C-H), 2240(w, C≡N), 1721 (s, C=O), 1631 (w, C=C), 1183 (s) and 818 (w), δ_H (200MHz) 1 23-1.85 (12H, m, 2 x C=CCH$_2$(C$\underline{H}_2$)$_3$), 2.39 (4H, t, *J* 6.5Hz, 2 x C=CC$\underline{H}_2$), 4.18 (4H, ca t , *J* 5 0Hz, 2 x OC$\underline{H}_2$), 5 49 (2H, d, *J* 1 0Hz, 2 x olefinic H), and 6 11 (2H, d, *J* 1 0Hz, 2 x olefinic H), *m/z* [CI(NH$_3$), GCMS] 299 (18%), 298 (MNH$_4^+$, 100), 281 (MH$^+$, 28), and 95 (13)

5-*oxa*-6-*oxo*-7-*methylene*-9-*cyano*-9-*methyl decene* (16). ν_{max} (thin film, mixture of dilactone (14) and AIBN adduct) as previously recorded, δ_H (200MHz) 1 35 (6H, s, (C$\underline{H}_3$)$_2$C), 2 46 (2H, ca quar , *J* 6 5Hz, CH$_2$=CHC$\underline{H}_2$), 2 61 (2H, s, allylic H), 4 24 (2H, t, *J* 6 5Hz, CO$_2$C$\underline{H}_2$), 5.05-5 21 (2H, m, C$\underline{H}_2$=CH), 5 70-5 86 (1H, m, CH$_2$=C$\underline{H}$), 5 88 (1H, s, olefinic H), 6 46 (1H, s, olefinic H); *m/z* [CI(NH$_3$), GCMS] 226 (13%), 225 (MNH$_4^+$, 100), 208 (MH$^+$, 16), and 54 (13)

1-*Phenylseleno*- 5,13 -*dioxa*-6,14-*dioxo*-7,15-*dimethylene*-17-*cyano*-17-*methyl octadecane* (17). ν_{max} (thin film) 2932(m, C-H), 2858(m, C-H), 2238(w, C≡N), 1718(s, C=0), 1632(m, C=C), 1180(m), 783(m), and 691(m), δ_H (200MHz) 1 20-1 88 (10H, m, PhSeCH$_2$(C$\underline{H}_2$)$_2$ and CO$_2$CH$_2$(CH$_2$)$_3$CH$_2$C=C), 1 36 (6H, s, (C$\underline{H}_3$)$_2$C), 2 31 (2H, t, *J* 7 5Hz, CH$_2$C$\underline{H}_2$C=C), 2 60 (2H, s, (CH$_3$)$_2$(CN)CC$\underline{H}_2$), 2 97 (2H, t , *J* 6 0Hz, C$\underline{H}_2$SePh), 4 18 (4H, t, *J* 6 0Hz, 2 x CO$_2$C$\underline{H}_2$), 5.53 (1H, d, *J* 1 0Hz, olefinic H), 5 88 (1H, d, *J* 1 0Hz, olefinic H), 6 12 (1H, d, *J* 1 0Hz, olefinic H), 6 43 (1H, d, *J* 1 0Hz, olefinic H), 7.21-7 33 (3H, m, aromatics), and 7 46-7 56 (2H, m, aromatics)

1-*Phenylseleno*-5-*oxa*-6-*oxo*-7-*methylene*-9-*cyano*-9-*methyl decane* (18). ν_{max} (thin film) 2938(m, C-H), 2238(w, C≡N), 1716(s, C=O), 1630(m, C=C), 1181(m), 783(m), and 691(m), δ_H (200MHz) 1 35 (6H, s, (C$\underline{H}_3$)$_2$C), 1 82 (4H, m, OCH$_2$(C$\underline{H}_2$)$_2$), 2 59 (2H, s, allylic H), 2 95 (2H, t, *J* 6 5Hz, C$\underline{H}_2$SePh), 4 19 (2H, t, *J* 6 5Hz, CO$_2$C$\underline{H}_2$), 5 77 (1H, d, *J* 1 0Hz, olefinic H), 6 49 (1H, d, *J* 1 0Hz, olefinic H), 7 22-7 32 (3H, m, aromatics), and 7 47-7 56 (2H, m, aromatics)

***Attempted preparation of* 2-*Methylene*-*octan*-8-*olide* (8d).** The standard procedure was followed using 5-phenylselenopentyl 2-(tri-*n*-butylstannylmethyl)propenoate (7d) (236mg, 0 39mmol) and tri-*n*-butyltin hydride (6µl, 0 02mmol) After 48 hours there was no evidence of the formation of the dilactone by t l c , although the starting material had been consumed The tributyltin phenylselenide was removed by flash chromatography (SiO_2, 1% ether/petrol as eluant) and the polar residue flushed off the column with ethyl acetate (85mg) This was subjected to PLC, whence the adduct (19) was isolated (30mg, 21%). The remainder of the residue consisted of unidentified AIBN adducts

1-*Phenylseleno*-6-*oxa*-7-*oxo*-8-*methylene*-10-*cyano*-10-*methyl undecane* (19) δ_H (200MHz) 1 38 (6H, s, (C$\underline{H}_3$)$_2$C), 1 40-1 86 (6H, m, OCH$_2$(C$\underline{H}_2$)$_3$), 2 60 (2H, s, allylic H), 2 93 (2H, t, *J* 7 5Hz, C$\underline{H}_2$SePh), 4 18 (2H, t, *J* 7 0Hz, CO$_2$C$\underline{H}_2$), 5 87 (1H, olefinic H), 6 42 (1H, s, olefinic H), 7 22-7 31 (3H, m, aromatics), and 7 47-7 55 (2H, m, aromatics)

REFERENCES AND NOTES

1 Porter, N A , Chang, V H T *J Am Chem Soc* , 1987, 109, 4976 Porter, N A , Chang, V H T , Magnin, D R ; Wright, B T *J Am Chem Soc* , 1988, 110, 3554

2 See for example. Hitchcock, S A , Pattenden, G *Tetrahedron Lett* , 1990, 31, 3641 Cox, N J , Mills, S D , Pattenden, G *Tetrahedron Lett* , 1989, 30, 621

3 Keck, G E , Enholm, E J *Tetrahedron Lett* , 1985, 26, 3311

4 Danishefsky, S.J , Panek, J S *J Am Chem Soc* , 1987, 109, 917

5 a) Curran, D P., van Elburg, P A , Giese, B , Gilges, S *Tetrahedron Lett* , 1990, 31, 2861
b) Baldwin, J E , Adlington, R M , Birch, D J , Crawford, J A , Sweeney, J B *J Chem Soc , Chem Commun* , 1986, 1339.

6 Ziegler, F E , Berger, G D *Synth Comm* , 1979, 9, 539

7 da Silva Corrêa, C M M , Waters, W A *J Chem Soc (C)*, 1968, 1874

8 Harvey, I W , Phillips, E D , Whitham, G H *J Chem Soc , Chem Commun* , 1990, 481

9 Ueno, Y , Ohta, M , Okawara, M *J Organomet Chem* , 1980, 197, C1

10 Patel, D V ; VanMiddlesworth, F , Donaubauer, J , Gannett, P , Sih, C J *J Am Chem Soc* , 1986, 108, 4603

11 Either purchased commercially or prepared from the corresponding diols by the method of Kang, S , Kim, W , Moon, B *Synthesis*, 1985, 1161

12 Sharpless, K B , Young, M W , Lauer, R F *Tetrahedron Lett* , 1973, 1979 Grieco, P A , Miyashita, M *Tetrahedron Lett* , 1974, 1869 Scarborough Jr , R M , Smith III, A B *Tetrahedron Lett* , 1977, 4361 Sharpless, K B , Lauer, R F *J Am Chem Soc* , 1973, 95, 2697

13 Oki, M , Nakanishi, H *Bull Chem Soc Japan*, 1970, 43, 2558

14 Baldwin, J.E , Adlington, R M , Robertson, J *Tetrahedron*, in press 1991

15 Barth, F , O-Yang, C *Tetrahedron Lett* , 1990, 31, 1121

16 Boger, D L , Mathvink, R J *J Am Chem Soc* , 1990, 112, 4008

17 Nájera, C , Baldó, B , Yus, M *J Chem Soc , Perkin Trans I*, 1988, 1029

18 Nájera, C , Mancheño, B , Yus, M *Tetrahedron Lett* , 1989, 30, 3837