Preparation and palladium-catalysed cross-coupling reactions of 3- and 4-tributylstannylfuran-2(5*H*)-ones

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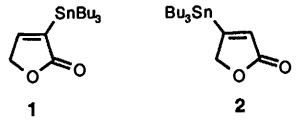
Stannylfuranones 1 and 2 were prepared by ipso radical desulfurative stannylation of phenylsulfanylfuranones 3 and 16. Compounds 1 and 2 underwent Stille coupling reactions with aryl iodides to give 3- and 4-arylfuran-2(5*H*)-ones.

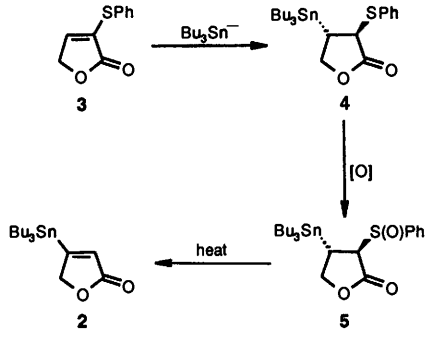
Many natural products contain a furanone ring.[1] Furthermore, the pharmacological activity associated with, in particular, arylfuran-2(5*H*)-ones[2] means that there is a wealth of bioactive *non*-natural products bearing this heterocycle at their heart. There is, however, a corresponding paucity of methods which allow for the *direct* introduction of the furanone moiety to a suitably functionalized precursor, with most synthetic processes allowing the construction of furanones *via* multi-step reaction sequences.[3] We surmised that 3- and 4-tributylstannylfuran-2(5*H*)-ones **1** and **2** would act as precisely such precursors for



1 **2**

direct attachment of furanones to aryl halides: we report here in full[4] the details of our investigations into the synthesis and reactions of these versatile synthetic equivalents.

Our initial proposal to allow preparation of these previously unreported compounds was merely an extension of standard methods for the preparation of 3- and 4-substituted furan-2(5*H*)-ones (Scheme 1). Thus, we thought, conjugate addition of

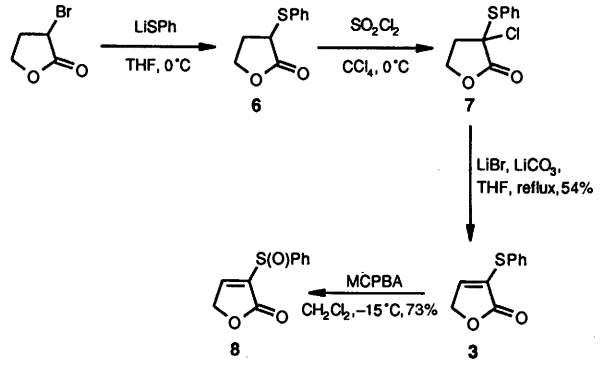


3 **4** **2** **5**

Scheme 1

tributylstannyl anion to 3-phenylsulfanylfuran-2(5*H*)-one **3**[5] should lead to 2-phenylsulfanyl-3-tributylstannyl-γ-butyrolactone **4**, presumably as a mixture of diastereoisomers, although we assumed that the thermodynamically more stable *trans*-diastereoisomer would dominate. A subsequent oxidation reaction would give the corresponding sulfoxide **5** and thermally-induced *syn* elimination would lead to the desired 4-tributylstannylfuran-2(5*H*)-one. We mollified our worries that the relatively oxidatively-labile C–Sn bond[6] would be fragile during the sulfoxide-forming step by realizing that the same stannylsulfoxide **5** would also be available *via* conjugate addition of the same anion to 3-phenylsulfinylfuran-2(5*H*)-one. Once more, thermolysis of **5** would deliver **2**. The *trans* substituted butyrolactone produced from the Michael-addition step would undergo *syn* facile elimination, while any *cis*-compound would be unreactive with respect to elimination. We anticipated that the *cis*-isomer would be readily isomerized to the *trans* in any case.

We commenced our programme of synthesis with the preparation of 3-phenylsulfanylfuran-2(5*H*)-one **3** using a modification of the method of Uda and co-workers (Scheme 2).[5] Thus, nucleophilic attack by lithium thiophenolate upon 2-



6 **7** **8** **3**

Scheme 2

bromo-γ-butyrolactone gave 2-phenylsulfanyl-γ-butyrolactone **6** in excellent yield. Reaction of **6** with sulfuryl chloride gave 2-chloro-2-phenylthio-γ-butyrolactone **7**[7] in 88% yield, and this compound underwent conjugative elimination of HCl upon reaction with a mixture of lithium bromide and lithium carbonate to give **3** in 54% overall yield from commercially available and inexpensive 2-bromobutyrolactone. We then turned our attention to oxidation of this sulfide, which was, we found, optimal using *m*-chloroperbenzoic acid (MCPBA); upon reaction of **3** with MCPBA we obtained sulfinylfuranone **8** in 73% yield. Use of other oxidants (such as sodium periodate or OXONE®) proved a less efficient entry to **8**. The newly formed S-centred asymmetric centre of the sulfinylfuranone exerted an influence upon the relatively distant C-5 protons of the molecule, as shown by the compound's ^{1}H NMR spectrum, which exhibited a broad AB-type resonance indicating a diastereotopicity of these hydrogen atoms. With the required furanones in hand, we then began our studies of their reactions with various metal tributylstannylates; this reaction was, and is (to the best of our knowledge) unreported by other workers, although there are several reports of Michael addition of both carbon and sulfur-centred nucleophiles to these furanones.[8,9,10]

Our numerous attempts at conjugate addition reactions of a

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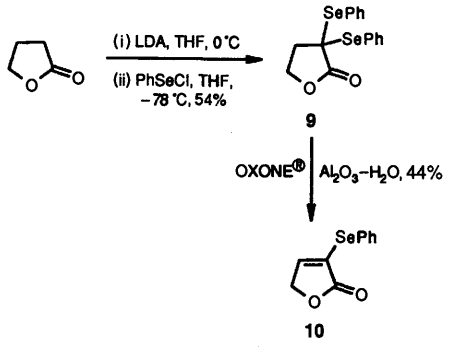
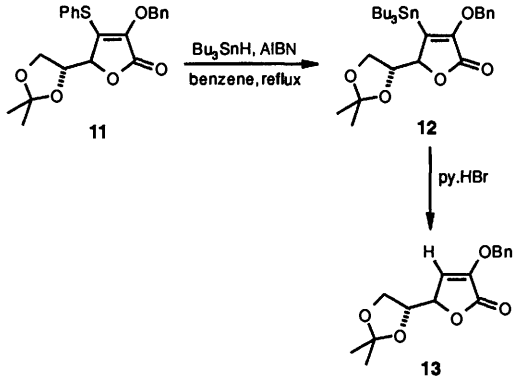
variety of tributylstannyl anion equivalents with 3-phenylsulfanylfuranone met with limited success: reaction with tributylstannyllithium in THF prepared according to the method of Still[11] gave 2-phenylsulfanyl-3-tributylstannyl-γ-butyrolactone **4** as a diastereoisomeric mixture (the ratio in which was unity) in 19% yield. An improvement was observed when bis(tributylstannyl) copper lithium[12] was utilized as stannyl source, with **4** being obtained in 44% yield after chromatography, again as a 1:1 mixture of diastereoisomers. Resolving to tackle the question of these rather poor yields at a later stage, we examined the oxidation and subsequent thermolytic elimination reaction of **4**. Exposure of the diastereoisomeric mixture (~1:1, *cis*:*trans*) to one equivalent of MCPBA at −20 °C gave, after removal of solvent *in vacuo*, a solid residue which was dissolved in benzene and the resulting solution was heated at reflux for 18 h. From the crude reaction mixture, after flash column chromatography, we obtained the desired 4-tributylstannylfuran-2(5*H*)-one **2** in 23% yield from stannyl sulfide **4**. The yield of **2** could be increased slightly (to 27%, in fact) when OXONE® and 'wet' alumina[13] were employed as oxidant. Several other oxidation processes were examined but none of these alternatives led to an improvement in yield, and the presence of furan-2(5*H*)-one in both crude and purified product mixtures suggested that the conditions being employed were causing elimination of the sulfur and stannyl functionality, with the C–Sn bond being sufficiently nucleophilic to displace a phenylsulfanyl leaving group.[14] Disappointingly, attempted Michael additions of stannylates to sulfinylfuranone **8** yielded no trace of stannyl sulfoxide **5**, presumably due to the increased nucleofugacity of phenylsulfinite relative to phenylthiolate: in other words, the eliminative decomposition reaction which, we believed, led to production of significant amounts of furan-2(5*H*)-one from the reaction of stannylate with **3** was even faster in stannyl sulfinylfuranone **5**. In an attempt to improve the yield of stannylfuranone **2** obtained from thermolysis of **5**, we looked, briefly, into the viability of utilizing a phenylselanyl group in place of the phenylsulfanyl group of **3**, because of the well-documented ease of thermolytic elimination of phenylseleninic acid relative to phenylsulfinic acid. Thus, 3-phenylselanylfuran-2(5*H*)-one **10** was prepared according to the sequence of reactions outlined diagrammatically in Scheme 3. Firstly, γ-



Scheme 3

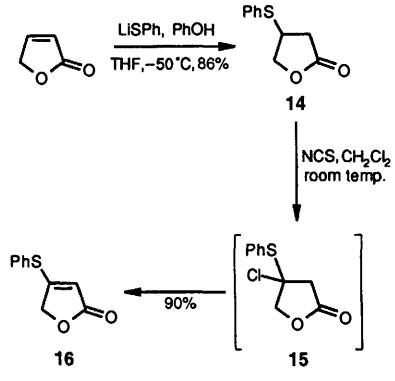
butyrolactone was doubly selanylated by sequential deprotonation and reaction with excess phenylselanyl chloride from −78 °C to ambient temperature. The product of this reaction was 2,2-bis(phenylselanyl)-γ-butyrolactone **9**, which was isolated in moderate yield (54%) after flash chromatography. Single elimination of phenylseleninic acid occurred smoothly when **9** was oxidized at room temperature using the OXONE®–alumina conditions earlier referred to. Thus was obtained, in 44% yield (55% based on unreacted starting material isolated during flash chromatography), 3-(phenylselanyl)furan-2(5*H*)-one **10**. Sadly, **10** was as bad a precursor to stannylbutyrolactones as was sulfinylfuranone **8**, with only unidentifiable products arising from its reaction with a variety of tributylstannylates.[15] Thus the notion of preparing stannylfuranones **1** and **2** *via* sequential addition–elimination reactions was abandoned.

Casting our eyes over the literature, we found that the preparation of a highly substituted 4-tributylstannylfuranone **12** has been reported by White and co-workers[16] to involve a desulfurative stannylation reaction, first reported a year earlier by Miyasaka *et al.*[17] Thus, when the White group attempted to reductively desulfurize phenylsulfanylfuranone **11**, they found that they unexpectedly obtained **12** in good yield. Compound **12** was protiodestannylated to give their desired product, furanone **13**, in a separate reaction with acid (Scheme 4). These



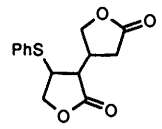
Scheme 4

authors did not examine the generality of the desulfurative stannylation reaction. Miyasaka and co-workers had previously found that phenylsulfanyluracil derivatives could also be ipso-stannylated upon reaction with tributylstannane in the presence of AIBN; apart from commenting upon the unusual nature of this transformation, the latter authors also failed to examine the range of this reaction. We therefore chose to turn the focus of our synthetic efforts towards radical stannylation of 4-phenylsulfanylfuran-2(5*H*)-one **16**, since this reaction involved a structurally similar substrate to that examined in White's report. As a starting point then, we had need of 4-phenylsulfanylfuran-2(5*H*)-one; this material was synthesized in two steps from furan-2(5*H*)-one (Scheme 5). Addition of a 1:1



Scheme 5

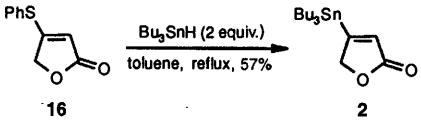
mixture of furan-2(5*H*)-one and phenol to a solution of lithium thiophenoxide in THF at −50 °C gave, after work-up and flash chromatography, 3-phenylsulfanyl-γ-butyrolactone **14** in 86% yield.[7] Phenol is present to protonate the enolate resulting from conjugate addition of thiophenoxide, thereby preventing this enolate from reacting in a Michael fashion with starting material to give bislactone **17**, which byproduct is produced in significant amounts when phenol is not present in the reaction mixture. *S*-Chlorination of **14** using *N*-chlorosuccinimide, followed by rearrangement gave 3-chloro-3-phenylsulfanyl-γ-butyrolactone **15** as an intermediate which could not be isolated because, under the reaction conditions, elimination of HCl



17

occurred to give 4-phenylsulfanylfuran-2(5*H*)-one **16** directly in 90% yield.[18]

With an efficient route to our substrate for the Miyasaka reaction in hand, we proceeded to the stannylation reaction. We were pleased to observe that the desulfurative stannylation reaction of **16** in the presence of two equivalents of tributyltin hydride and a sub-stoichiometric amount of AIBN in refluxing toluene gave 4-tributylstannylfuran-2(5*H*)-one **2**, isolated in 57% yield after flash chromatography (Scheme 6). The infrared

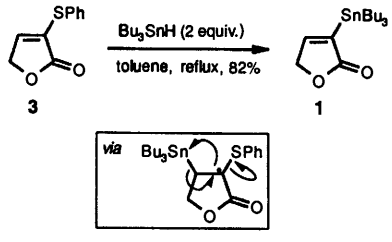


16 2

Scheme 6

spectrum of **2** showed an interesting split C=O stretching band. This fine structure is very characteristic of furan-2(5*H*)-ones bearing a hydrogen in the 3-position and has been explained by invoking a Fermi resonance between the carbonyl absorption $\nu_{(C=O)}$ and the overtone bending frequency $2\gamma_{(CH)}$.[19] Stannylfuranone **2** is, therefore, readily accessible on a multigram scale in three steps from commercially available 2-bromo-γ-butyrolactone.

With 4-tributylstannylfuran-2(5*H*)-one now available, attention was turned to the synthesis of the 3-stannylated compound. A reaction analogous to that used above was attempted between tributyltinhydride and 3-phenylsulfanylfuran-2(5*H*)-one in the presence of AIBN (Scheme 7). In this case benzene



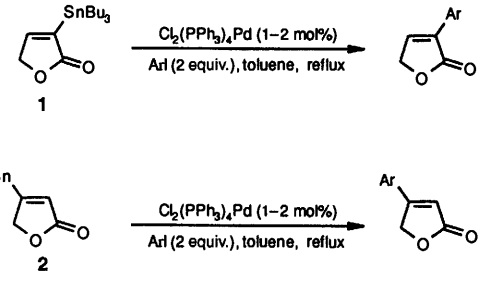
3 1

Scheme 7

was used as solvent, since we had concerns over the stability of stannane **1** and wished, therefore, to lower the temperature reached at reflux. We were gratified to observe smooth formation of the prized 3-tributylstannylfuran-2(5*H*)-one **1**, which was isolated in 82% yield after flash chromatography, and also interested to witness that not only was **1** obtained in higher yield than **2**, but that this more efficient reaction had also occurred more rapidly and at a lower temperature. Furthermore, when we turned our attention to the mechanism of this process, we found that it is not possible to invoke an addition–elimination explanation to rationalize formation of **1**. It may be that a stannyl shift is involved in formation of **1** and that the higher yield obtained is merely a reflection of the diminished capability for Michael addition that **1** exhibits. The mechanism underlying this reaction is at present under scrutiny in our laboratory.

With both stannanes now readily available on multigram scale, some of their uses as synthetic equivalents for incorporation of a furan-2(5*H*)-one structural unit were investigated.

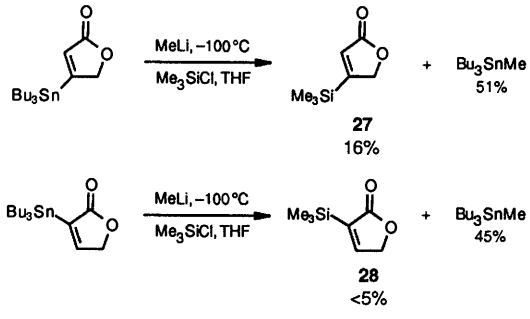
Initial attempts at palladium-catalysed cross-coupling reactions (Stille reactions[22]) of both 3- and 4-stannylfuranones with iodobenzene using DMF as solvent and bis(acetonitrile)dichloropalladium(II) (1–2 mol%) as catalyst were unsuccessful. Since the reaction mixture became black, depositing palladium metal, but starting materials still survived, we presumed that the catalyst (known to be highly active) was simply being consumed without inducing reaction. Use of the less active tetrakis(triphenylphosphine)palladium(0) catalyst and toluene as solvent gave, after prolonged reflux, trace amounts of 3- and 4-phenylfuran-2(5*H*)-ones **18** and **19**. After much study, it transpired that the optimal conditions for the cross-coupling reaction employed 5 mol% of dichlorobis(triphenylphosphine)palladium(II) (a catalyst possessing relatively intermediate activity) in a refluxing toluene solution containg stannane and two equivalents of aryl iodide (Scheme 8).



Scheme 8

This proved to be a general method for preparation of both 3- and 4-arylfuran-2(5*H*)-ones; the products prepared by this reaction are recorded in Table 1.

Given the well-known ability of alkylstannanes to act as precursors to alkyllithiums *via* transmetallation, we briefly investigated the suitability of stannanes **1** and **2** as such reagents (Scheme 9). Thus, **2** was treated sequentially at very low



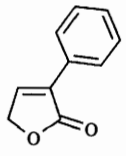
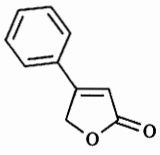
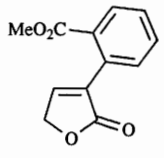
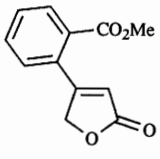
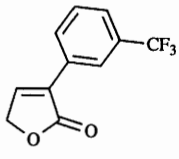
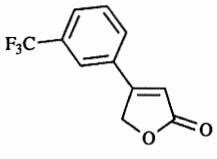
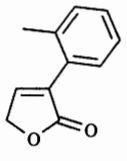
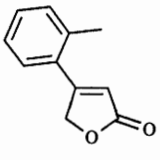
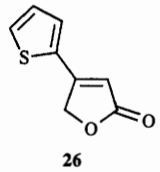
Scheme 9

temperature with methyllithium[23] and trimethylsilyl chloride. The two products of the reaction were 4-trimethylsilylfuran-2(5*H*)-one **27** and methyltributyltin, isolated in yields of 16 and 51%, respectively. This low yield of silane was reproducible, as was the yield of tetraalkyltin, the latter indicating that transmetallation of (at least) slightly more than half of the starting stannane was occurring. Unfortunately, despite exhaustive variation in the reaction conditions, these yields could not be improved upon. In the case of stannane **1**, very small amounts of 3-trimethylsilylfuran-2(5*H*)-one **28**[24] and methyltributyltin were isolated under analogous conditions. Use of other electrophiles (such as methyl iodide, benzyl or allyl bromides) did not give products of alkylation, and no starting materials were returned. Use of Lipshutz's copper-based transmetallation methodology[25] was similarly unsuccessful.

Thus, stannylfuranones do not seem to hold promise as precursors to the corresponding organolithiums.

In conclusion, we have achieved syntheses and cross-coupling reactions with aryl iodides of the previously unknown 3- and 4-tributylstannylfuran-2(5*H*)-ones. Further delineation of other

Table 1 Furanones prepared by palladium-catalysed coupling of stannanes **1** and **2** with aryl iodides

Product	Yield (%)
 **18**	45
 **19**	65
 **20**	65
 **21**	72
 **22**	23
 **23**	61
 **24**	36
 **25**	76
 **26**	58

metal-catalysed reactions of these stannanes is currently underway in our laboratory.

Experimental

General

All organic solvents were distilled prior to use and all reagents were purified by standard procedures.[15] Light petroleum refers to the fraction with the boiling range 40–60 °C. Diethyl ether, THF and DME were distilled from sodium benzophenone ketyl; toluene from sodium; dichloromethane, triethylamine, diisopropylamine and acetonitrile from calcium hydride, and pyridine and diisopropylethylamine from potassium hydroxide.

Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 881 spectrophotometer. Mass spectra were recorded on a VG9090 mass spectrometer or on a Fisons Autospec machine. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-270 spectrometer. Unless otherwise stated, deuteriochloroform was used as solvent and tetramethylsilane (TMS) was used as the internal standard. Chemical shifts (δ) in ^{1}H NMR spectra are expressed in ppm downfield from tetramethylsilane, and in ^{13}C NMR, relative to the internal solvent standard. Coupling constants (J) are quoted in Hz.

Reactions involving chemicals or intermediates sensitive to air and/or moisture were performed under a nitrogen atmosphere in flame- or oven-dried apparatus. Flash column chromatography[16] was performed using Merck kieselgel 60 or Fluka kieselgel 60 silica. Analytical thin layer chromatography (TLC) was performed on precoated Merck kieselgel 60 F_{254} aluminium-backed plates and were visualized under UV conditions at 254 nm, and by staining with an acidic ammonium molybdate spray.

2-Phenylsulfanyl-γ-butyrolactone 6

To a suspension of lithium thiophenolate (28.68 g, 217 mmol) in THF (160 ml) was added α-bromo-γ-butyrolactone (35.85 g, 217 mmol) in THF (80 ml) at 0 °C over 30 min. The reaction mixture was allowed to warm to room temperature and stirred for 48 h. The mixture was partitioned between water (200 ml) and diethyl ether (200 ml), the layers separated and the aqueous phase extracted with diethyl ether (100 ml). The combined organic layers were washed with brine (200 ml), dried ($MgSO_4$) and evaporated to give *lactone* **6** as a clear liquid (40.1 g, 95%); $\delta_H(CDCl_3)$ 7.6–7.25 (5 H, m, Ph), 4.2 (2 H, m, CH_2O), 3.9 (1 H, dd, CHSPh), 2.7 (1 H, m, CH_2CH_2O), 2.3 (1 H, m, CH_2CH_2O); $\delta_C(CDCl_3)$ 175.0, 133.5, 131.6, 129.0, 128.6, 66.5, 44.3, 29.9.

2-Chloro-2-phenylsulfanyl-γ-butyrolactone 7

To a solution of α-phenylsulfanyl-γ-butyrolactone (24.0 g, 124 mmol) in CCl_4 (140 ml) at 0 °C under nitrogen was added sulfuryl chloride (20.0 g, 148 mmol) in CCl_4 (60 ml) dropwise over 1 h. The yellow solution was stirred for a further 2 h at 0 °C. The reaction mixture was then *very cautiously* poured into saturated aqueous $NaHCO_3$ (200 ml), the layers separated and the aqueous phase extracted with CH_2Cl_2 (2 × 100 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (200 ml), water (200 ml) and brine (200 ml), dried ($MgSO_4$) and evaporated to give *lactone* **7** as a yellow gum which crystallized on cooling (24.9 g, 88%); $\delta_H(CDCl_3)$ 7.7–7.35 (5 H, m, Ph), 4.35 (2 H, m, CH_2O), 2.75 (2 H, m, CH_2CH_2O); $\delta_C(CDCl_3)$ 169.6, 136.4, 130.6, 129.1, 127.8, 71.9, 65.3, 39.9.

3-Phenylsulfanylfuran-2(5*H*)-one 3[5]

A solution of 2-chloro-2-phenylsulfanyl-γ-butyrolactone (9.0 g, 39.4 mmol) in THF (40 ml) was added to a mixture of lithium bromide (11.6 g, 140 mmol) and lithium carbonate (8.86 g, 135 mmol) in THF (40 ml) and the mixture heated at reflux for 30 min, by which time it was orange–brown in

colour. The inorganic salts were filtered through Celite and the filtrate evaporated to a brown oil. The residue was taken up in CH_2Cl_2 (50 ml), and washed with dilute aqueous $NaHCO_3$ (50 ml) and brine (50 ml), dried ($MgSO_4$) and evaporated to give a red oil (7.51 g, 99%) which crystallized on cooling. Recrystallization from ethanol gave pure *furanone* **3** as slightly orange crystals (4.93 g, 65%); $\delta_H(CDCl_3)$ 7.6–7.35 (5 H, m, Ph), 6.63 (1 H, t, *J* 2.01, vinylic), 4.78 (2 H, d, *J* 2.01, CH_2O); $\delta_C(CDCl_3)$ 170.4, 140.7, 133.8, 132.3, 129.7, 129.5, 129.3, 71.3.

2-Phenylsulfanyl-3-tributylstannyl-γ-butyrolactone 4

To a solution of diisopropylamine (0.40 ml, 2.86 mmol) in THF (6 ml) at 0 °C under nitrogen was added BuLi (2.43 M; 1.18 ml, 2.86 mmol). After stirring for 5 min, tributyltin hydride (0.77 ml, 2.86 mmol) was added at 0 °C and the yellow solution stirred for 15 min. After cooling to −78 °C, copper(I) iodide (270 mg, 1.43 mmol) was added and the mixture warmed to −20 °C for 10 min before recooling to −78 °C. At this temperature a solution of 3-phenylsulfanylfuran-2(5*H*)-one (250 mg, 1.30 mmol) in THF (4 ml) was added and the mixture stirred for 45 min, by which time TLC indicated consumption of sulfide. Water (10 ml) was added and the mixture warmed to room temperature and partitioned between diethyl ether (20 ml) and water (20 ml). The layers were separated and the aqueous phase extracted with diethyl ether (20 ml). The combined organic phases were washed with brine (20 ml), dried ($MgSO_4$) and evaporated. Column chromatography using diethyl ether–light petroleum (1:3) as eluent afforded *lactone* **4** as a mixture of isomers (*cis*:*trans* ~1:1) (272 mg, 44%); 1st isomer: $\delta_H(CDCl_3)$ 7.6–7.25 (5 H, m, Ph), 4.62–4.45 (2 H, m, C*H*$_2$O), 3.85 (1 H, d, *J* 7.5, PhSC*H*), 2.47 (1 H, m, Bu_3SnCH), 1.6–0.8 (27 H, m, Bu); $\delta_C(CDCl_3)$ 175.8, 133.0, 132.5, 129.1, 128.3, 72.4, 49.8, 29.3, 29.1, 27.3, 13.6, 10.5; 2nd isomer: 7.6–7.2 (5 H, m, Ph), 4.57 (1 H, dd, *J* 9, 9, C*H*$_2$O), 4.20 (1 H, dd, *J* 9, 9, C*H*$_2$O), 3.70 (1 H, d, *J* 10.4, PhSC*H*), 1.99 (1 H, m, Bu_3SnCH), 1.6–0.8 (27 H, m, Bu).

3-Phenylsulfinylfuran-2(5*H*)-one 8[5]

To a solution of 3-phenylsulfanylfuran-2(5*H*)-one (1.00 g, 5.21 mmol) in dichloromethane (20 ml) was added at −15 °C a solution of *m*-chloroperoxybenzoic acid (MCPBA) (0.90 g, 5.21 mmol) in dichloromethane (40 ml) and the reaction mixture stirred for 1 h. A further 40 ml CH_2Cl_2 was added along with 5% aqueous $NaHCO_3$ (50 ml) and the layers separated. The organic phase was washed with 5% aqueous $NaHCO_3$ (50 ml) and brine (50 ml), dried ($MgSO_4$) and evaporated to give *furanone* **8** as a white solid (791 mg, 73%), mp 84–85 °C (lit.,[5] 83–85, 86–88 °C); $\delta_H(CDCl_3)$ 8.1 (1 H, br s, vinylic), 7.9–7.5 (5 H, m, Ph), 5.05 (1 H, d, *J* 20, CH_2O), 4.95 (1 H, d, *J* 20, CH_2O).

3,3-Bis(phenylselanyl)-γ-butyrolactone 9

To a solution of diisopropylamine (1.41 g, 13.94 mmol) in THF (30 ml) under nitrogen at 0 °C was added butyllithium (2.5 M solution; 5.58 ml, 13.9 mmol). The reaction mixture was stirred for 5 min at this temperature before cooling to −78 °C. γ-Butyrolactone (500 mg, 5.81 mmol) was added and the reaction warmed to 0 °C. The clear solution was recooled to −78 °C and phenylselanyl chloride (2.66 g, 13.9 mmol) in THF (20 ml) was added and the reaction mixture gradually warmed to room temperature. Water and diethyl ether (1:1, 100 ml) were added, the layers separated and the aqueous phase extracted with diethyl ether (50 ml). The combined organic phases were washed with water (100 ml) and brine (100 ml), dried ($MgSO_4$) and evaporated. Column chromatography using diethyl ether–light petroleum (1:3, then 1:1) as eluent afforded *lactone* **9** as a white crystalline solid, (1.24 g, 54%) (Found: C, 48.49; H, 3.62. $C_{16}H_{14}O_2Se_2$ requires: C, 48.50; H, 3.56%); *m*/*z* 396 (M^+, 13.9%), 241 (100), 239 (50), 195 (38), 157 (94), 77 (91); $\nu_{max}(CCl_4)/cm^{-1}$ 3061, 2908, 1778 (C=O), 1476, 1438, 1150; $\delta_H(CDCl_3)$ 7.75–7.69, 746–7.31 (10 H, m, Ph), 4.03 (2 H, t, *J* 6.8, CH_2O), 2.44 (2 H, t, *J* 6.8, CH_2); $\delta_C(CDCl_3)$ 174.0, 137.2, 130.0, 129.3, 127.5, 65.5, 44.8, 37.1.

3-Phenylselanylfuran-2(5*H*)-one 10

To a solution of 3,3-bis(phenylselanyl)-γ-butyrolactone (250 mg, 0.631 mmol) in dichloromethane (10 ml) was added 'wet' alumina (790 mg) and OXONE® (430 mg, 0.694 mmol). The reaction mixture was stirred at room temperature for 18 h then filtered through Celite and the solvent evaporated. Column chromatography of the residue gave *furanone* **10** as a colourless oil (66.2 mg, 44%) along with unchanged starting material (50 mg, 20%); $\delta_H(CDCl_3)$ 7.66–7.63, 7.43–7.33 (5 H, m, Ph), 6.81 (1 H, t, *J* 2.02, vinylic), 4.77 (2 H, d, *J* 2.02, CH_2O); $\delta_C(CDCl_3)$ 171.6, 145.2, 135.6, 129.9, 129.3, 127.6, 125.5, 72.6; the relative instability of **10** precluded further characterization.

3-Phenylsulfanyl-γ-butyrolactone 14

To a solution of thiophenol (1.10 g, 10.0 mmol) in THF (10 ml) at −50 °C under nitrogen was added butyllithium (2.5 M; 4 ml, 10.0 mmol) dropwise. After stirring for 15 min at this temperature, a mixture of furan-2(5*H*)-one (841 mg, 10.0 mmol) and phenol (940 mg, 10.0 mmol) in THF (10 ml) was added over 10 min. The reaction mixture was stirred at −50 °C for 1 h before being allowed to warm to room temperature and stirred for a further 1 h. The solution was washed with saturated aqueous $NaHCO_3$ (2 × 20 ml) and the aqueous washings extracted with Et_2O (3 × 10 ml). The combined organic phases were dried ($MgSO_4$) and the solvent evaporated to give a yellow oil. Purification by column chromatography using diethyl ether–light petroleum (2:3) as eluent afforded *lactone* **14** as a pale yellow oil (1.67 g, 86%); $\delta_H(CDCl_3)$ 7.35 (m, 5 H, Ph), 4.53 (1 H, dd, *J* 6.59, 9.77, CH_2O), 4.21 (1 H, dd, *J* 9.77, 5.37, CH_2O), 4.00 (1 H, m, CHSPh), 2.89 (1 H, dd, *J* 17.82, 8.06, $OCCH_2$), 2.53 (1 H, dd, *J* 17.82, 6.10, $OCCH_2$); $\delta_C(CDCl_3)$ 174.9, 132.7, 132.1, 129.4, 128.3, 72.5, 41.5, 35.0; the relative instability of **14** precluded further characterization.

4-Phenylsulfanylfuran-2(5*H*)-one 16[18]

To a solution of 3-phenylsulfanyl-γ-butyrolactone (7.0 g, 36.1 mmol) in dichloromethane under a nitrogen atmosphere was added *N*-chlorosuccinimide (5.06 g, 37.9 mmol) in one portion. The resultant slightly cloudy solution was stirred in the dark for 16 h by which time TLC indicated completion of the reaction. The solvent was removed *in vacuo* and carbon tetrachloride (125 ml) added to the residue. The insoluble succinimide was removed by filtration and the solvent evaporated to give an orange oil. Column chromatography with diethyl ether–light petroleum (1:1) as eluent furnished *furanone* **16** as a white crystalline solid (6.23 g, 90%); mp 47–48 °C; $\delta_H(CDCl_3)$ 7.60–7.37 (5 H, m, Ph), 5.46 (1 H, t, *J* 1.46, vinylic), 4.71 (2 H, d, *J* 1.46, CH_2O); $\delta_C(CDCl_3)$ 172.0, 168.5, 135.1, 134.5, 130.5, 130.0, 110.8, 71.6.

4-(Tributylstannyl)furan-2(5*H*)-one 2

From 2-phenylsulfanyl-3-tributylstannyl-γ-butyrolactone. To a solution of 2-phenylsulfanyl-3-tributylstannyl-γ-butyrolactone **4** (45 mg, 0.09 mmol) cooled to −20 °C in CH_2Cl_2 (0.5 ml) was added MCPBA (16 mg, 0.09 mmol). The reaction mixture was stirred for 1 h and then concentrated *in vacuo* to yield an off-white solid residue. This residue was dissolved in benzene and the resulting solution heated to reflux for 18 h. The reaction vessel was cooled and the crude product obtained by removal of the solvent *in vacuo*. This product was purified by flash chromatography using gradient elution [light petroleum followed by diethyl ether–light petroleum (1:3)] to give *furanone* **2** as a colourless oil (8 mg, 23%); ν_{max}(neat)/cm^{-1} 2956, 2923, 2853, 1776 (C=O), 1745 (C=O), 1463, 1159, 1037; $\delta_H(CDCl_3)$ 6.15 (1 H, t, *J* 2, vinylic), 4.93 (2 H, d, *J* 2, CH_2O), 1.57–0.82 (27 H, m, Bu); $\delta_C(CDCl_3)$ 174.2, 173.7, 129.2, 78.5, 28.9, 27.1, 13.5, 9.8 [HRMS: found (M − Bu)$^+$, 313.0562.

$C_{12}H_{21}SnO_2$ requires (M − Bu), 313.0564]; m/z 317, 315, 261, 259, 257, 205, 203, 201.

A similar reaction on the same scale, using OXONE® and wet alumina [13] as oxidant gave **2** in 23% yield.

From 4-phenylsulfanylfuran-2(5*H*)-one. To a solution of 4-phenylsulfanylfuran-2(5*H*)-one (2.95 g, 15.4 mmol) in toluene (150 ml) under a nitrogen atmosphere was added 2.05 equiv. of tributyltin hydride (8.47 ml, 31.5 mmol) and AIBN (140 mg, 0.8 mmol). The mixture was brought to reflux for 16 h after which time TLC indicated that some starting material still remained. Addition of a further portion of AIBN (140 mg) and subsequent reflux for 5 h was sufficient for completion of the reaction according to TLC. Removal of solvent from the clear colourless solution left a grey oil. Purification by column chromatography afforded *furanone* **2** as a clear colourless oil (3.27 g, 57%) (Found: C, 51.03; H, 7.99. $C_{16}H_{30}SnO_2$ requires C, 51.32; H, 8.08%). Other physical data as above.

3-Tributylstannylfuran-2(5*H*)-one 1

To a solution of 3-phenylsulfanylfuran-2(5*H*)-one (156 mg, 0.813 mmol) in dry benzene (10 ml) under a nitrogen atmosphere was added 2 equiv. of tributyltin hydride (0.44 ml, 1.625 mmol) and AIBN (13 mg, 0.08 mmol). The mixture was brought to reflux for 5 h after which time TLC indicated that all the starting material had been consumed. Evaporation of the solvent gave a clear oil which was purified by column chromatography using first light petroleum and then diethyl ether–light petroleum (1:3) as eluent. *Furanone* **1** was obtained as a clear colourless oil (250 mg, 82%) (Found: C, 51.20; H, 7.89. $C_{16}H_{30}SnO_2$ requires C, 51.32; H, 8.08); ν_{max}(neat)/cm^{-1} 2956, 2926, 2870, 2853, 1736 (C=O), 1580 (C=C), 1463, 1141, 1050; δ_H($CDCl_3$) 7.55, (1 H, m, vinylic), 4.81 (2 H, m, CH_2O), 1.6–0.75 (27 H, m, Bu); δ_C($CDCl_3$) 178.5, 161.6, 135.1, 73.9, 28.8, 27.1, 13.5, 9.5 [HRMS: found (M − Bu)$^+$, 317.0564. $C_{12}H_{21}SnO_2$ requires (M − Bu), 317.0562]; m/z 361, 359, 357, 317, 315, 203, 201, 199.

General procedure for coupling of stannanes 1 and 2 with aryl iodides

To a flame-dried nitrogen-flushed 10 ml round-bottomed flask fitted with a reflux condenser and stirrer bar was added stannane (100 mg, 0.268 mmol), iodide (0.402 mmol, 1.5 equiv.) and toluene (distilled, 5 ml). Dichlorobis(triphenylphosphine)palladium(II) (1–2 mol%) was then quickly added, stirring was commenced and the mixture was heated to reflux. Reflux was continued until all the stannane starting material had been consumed (as evinced by thin layer chromatography). The mixture was then poured into a separating funnel and washed with aqueous potassium fluoride (8 M; 2 × 5 ml); the organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to yield crude furanone. Flash chromatography furnished 3- and 4-substituted furan-2(5*H*)-ones in analytically pure form.

3-Phenylfuran-2(5*H*)-one 18.[20] Reaction of 3-tributylstannylfuran-2(5*H*)-one (103 mg, 0.276 mmol) with iodobenzene (85 mg, 0.414 mmol) gave *furanone* **18** as white crystals (19.9 mg, 45%); mp 76–78 °C; ν_{max}(CCl_4)/cm^{-1} 2929, 2868, 1770 (C=O), 1606 (C=C), 1345, 1112, 1064; δ_H($CDCl_3$) 7.86–7.82, 7.48–7.36 (5 H, m, Ph), 7.64 (1 H, t, J 1.95, vinylic), 4.92 (2 H, d, J 1.95, CH_2O); δ_C($CDCl_3$) 172.2, 144.2, 131.7, 129.5, 129.3, 128.7, 126.9, 69.5 (HRMS: found M$^+$, 160.0536. $C_{10}H_8O_2$ requires M, 160.0524); m/z 160 (M$^+$, 59%), 132 (21), 131 (17), 103 (100), 77 (18).

4-Phenylfuran-2(5*H*)-one 19.[21] Reaction of 4-tributylstannylfuran-2(5*H*)-one (50 mg, 0.134 mmol) with iodobenzene (40 mg, 0.196 mmol) gave *furanone* **19** as white crystals (14 mg, 65%), mp 91–93 °C; ν_{max}(CCl_4)/cm^{-1} 2930, 2868, 1783 (C=O), 1758 (C=O), 1628 (C=C), 1597, 1451, 1512, 1056; δ_H($CDCl_3$) 7.54–744 (5 H, m, Ph), 6.37 (1 H, t, J 1.83, vinylic), 5.22 (2 H, d, J 1.83, CH_2O); δ_C($CDCl_3$) 173.8, 163.9, 131.8, 129.6, 129.3, 126.4, 113.0, 71.0 (HRMS: found M$^+$, 160.0513. $C_{10}H_8O_2$ requires M, 160.0524); m/z 160 (M$^+$, 70.3%), 131 (100), 103 (47), 102 (42), 77 (18), 51 (18).

3-(2-Methoxycarbonylphenyl)furan-2(5*H*)-one 20. Reaction of 3-tributylstannylfuran-2(5*H*)-one (118 mg, 0.316 mmol) with methyl 2-iodobenzoate (124 mg, 0.475 mmol) gave *furanone* **20** as orange crystals (44.7 mg, 65%), mp 71–72 °C (Found: C, 65.82; H, 4.44. $C_{12}H_{10}O_4$ requires C, 66.04; H, 4.62%); ν_{max}(CCl_4)/cm^{-1} 2952, 1776 (C=O), 1731 (C=O), 1601 (C=C), 1278, 1118; δ_H($CDCl_3$) 7.96 (1 H, dd, J 1.5, 7.5, aromatic), 7.54 (1 H, ddd, J 1.5, 7.3, 7.5, aromatic), 7.46 (1 H, ddd, J 1.5, 7.5, 7.7, aromatic), 7.32 (1 H, dd, J 1.5, 7.5, aromatic), 7.42 (1 H, t, J 1.84, vinylic), 4.97 (2 H, d, J 1.64, CH_2O), 3.84 (3 H, s, OMe); δ_C($CDCl_3$) 172.1, 167.3, 148.4, 144.6, 134.9, 132.0, 131.0, 130.5, 130.4, 129.1, 70.3, 52.3 (HRMS: found M$^+$, 218.0586. $C_{12}H_{10}O_4$ requires M, 218.0579); m/z 218 (M$^+$, 47%), 189 (55), 187 (44), 186 (100), 161 (58), 129 (40), 57 (28).

4-(2-Methoxycarbonylphenyl)furan-2(5*H*)-one 21. Reaction of 4-tributylstannylfuran-2(5*H*)-one (100 mg, 0.268 mmol) with methyl 2-iodobenzoate (105 mg, 0.402 mmol) gave *furanone* **21** as white crystals (42.1 mg, 72%), mp 90–91 °C (Found: C, 65.58; H, 4.55. $C_{12}H_{10}O_4$ requires C, 66.05; H, 4.62%); ν_{max}(CCl_4)/cm^{-1} 2953, 1783 (C=O), 1755 (C=O), 1732 (C=O), 1599, 1272, 1087; δ_H($CDCl_3$) 7.99 (1 H, dd, J 1.46, 7.33, aromatic), 7.60 (1 H, ddd, J 1.46, 7.33, 7.69, aromatic), 7.52 (1 H, ddd, J 1.46, 7.69, 7.69, aromatic), 7.29 (1 H, dd, J 1.46, 7.69, aromatic), 6.04 (1 H, t, J 1.83, vinylic), 5.07 (2 H, d, J 1.46, CH_2O), 3.87 (3 H, s, OMe); δ_C($CDCl_3$) 173.4, 167.5, 166.6, 132.6, 132.5, 130.9, 130.0, 129.1, 117.2, 73.5, 52.6 (HRMS: found M$^+$, 218.0591. $C_{12}H_{10}O_4$ requires M, 218.0579); m/z 218 (M$^+$, 27.4%), 186 (100), 158 (53), 129 (30), 91 (34).

3-(3-Trifluoromethylphenyl)furan-2(5*H*)-one 22. Reaction of 3-tributylstannylfuran-2(5*H*)-one (123 mg, 0.330 mmol) with 1-iodo-3-trifluoromethylbenzene (135 mg, 0.495 mmol) gave *furanone* **22** as a tan oil (17.5 mg, 23%) (Found: C, 57.49; H, 2.99; $C_{11}H_7O_2F_3$ requires C, 57.88; H, 3.09%); ν_{max}(CCl_4)/cm^{-1} 2930, 2869, 1775 (C=O), 1609, 1332, 1135; δ_H($CDCl_3$) 8.12–8.05, 7.68–7.51 (4 H, m, aromatic), 7.76 (1 H, t, J 2.01, vinylic), 4.97 (2 H, d, J 2.01, CH_2O); δ_C($CDCl_3$) 171.6, 145.6, 131.2 (q, J 33), 130.6, 130.2, 129.3, 128.7, 126.0 (q, J 4), 123.8 (q, J 272), 123.8 (q, J 4), 69.6 (HRMS: found M$^+$, 228.0405. $C_{11}H_7O_2F_3$ requires M, 228.0398); m/z 228 (M$^+$, 44%), 200 (15), 173 (36), 171 (100), 151 (27).

4-(3-Trifluoromethylphenyl)furan-2(5*H*)-one 23. Reaction of 4-tributylstannylfuran-2(5*H*)-one (98 mg, 0.263 mmol) with 1-iodo-3-trifluoromethylbenzene (107 mg, 0.394 mmol) gave *furanone* **23** as colourless crystals (36.6 mg, 61%), mp 106–112 °C (Found: C, 57.38; H, 3.00. $C_{11}H_7O_2F_3$ requires C, 57.88; H, 3.09%); ν_{max}(CH_2Cl_2)/cm^{-1} 1787 (C=O), 1752 (C=O), 1630 (C=C), 1333, 1133, 1055; δ_H($CDCl_3$) 7.77–7.59 (4 H, m, C_6H_4), 6.47 (1 H, t, J 1.83, 3-H), 5.24 (2 H, d, J 1.83, 5-H); δ_C($CDCl_3$) 173.1, 162.1, 131.9 (q, J 33), 130.4, 130.0, 129.6, 128.2 (q, J 3), 123.4 (q, J 272), 123.1 (q, J 4.6), 114.9, 70.8 (HRMS: found M$^+$, 228.0413. $C_{11}H_7O_2F_3$ requires M, 228.0398); m/z 228 (M$^+$, 48.5%), 119 (100), 171 (31), 170 (29), 151 (25).

3-(2-Methylphenyl)furan-2(5*H*)-one 24. Reaction of 3-tributylstannylfuran-2(5*H*)-one (121 mg, 0.324 mmol) with 2-iodotoluene (105 mg, 0.482 mmol) gave *furanone* **24** as a colourless oil (20.3 mg, 36%) (Found: C, 75.40; H, 5.62. $C_{11}H_{10}O_2$ requires C, 75.83; H, 5.79%); ν_{max}(CCl_4)/cm^{-1} 3065, 2929, 1777 (C=O), 1605, 1344, 1127, 1100; δ_H($CDCl_3$) 7.44 (1 H, t, J 1.84, vinylic), 7.4–7.2 (4 H, m, aromatic), 4.98 (2 H, d, J 1.84, CH_2O), 2.34 (3 H, s, Me); δ_C($CDCl_3$) 172.6, 147.7, 136.5, 133.5, 130.6, 129.5, 129.0, 127.0, 125.8, 70.0, 20.4 (HRMS: found M$^+$, 174.0694. $C_{11}H_{10}O_2$ requires M, 174.0681); m/z 174 (M$^+$, 44%), 129 (100), 128 (26), 117 (32), 115 (36), 91 (13), 51 (11).

4-(2-Methylphenyl)furan-2(5*H*)-one 25. Reaction of 4-tributylstannylfuran-2(5*H*)-one (100 mg, 0.268 mmol) with 2-iodotoluene (88 mg, 0.402 mmol) gave *furanone* **25** as colourless crystals (35.5 mg, 76%), mp 67–69 °C (Found: C, 75.55; H, 5.69. $C_{11}H_{10}O_2$ requires C, 75.83; H, 5.79%); ν_{max}(CCl_4)/cm^{-1} 2963,

1786 (C=O), 1763 (C=O), 1617 (C=C), 1261, 1157, 1060; $\delta_H(CDCl_3)$ 7.33–7.18 (4 H, m, aromatic), 6.20 (1 H, t, *J* 1.83, vinylic), 5.12 (2 H, d, *J* 1.83, CH_2O), 2.41 (3 H, s, Me); $\delta_C(CDCl_3)$ 174.0, 163.7, 137.3, 131.9, 130.7, 129.6, 127.2, 126.5, 117.1, 72.7, 21.9 (HRMS: found M^+, 174.0680. $C_{11}H_{10}O_2$ requires *M*, 174.0681); *m/z* 174 (M^+, 91%), 145 (100), 117 (40), 116 (43), 115 (63), 91 (14), 58 (14).

4-(2-Thienyl)furan-2(5*H*)-one 26. Reaction of 4-tributylstannylfuran-2(5*H*)-one (111 mg, 0.298 mmol) with 2-iodothiophene (94 mg, 0.45 mmol) gave *furanone* **26** as white crystals (29 mg, 58%), mp 94–96 °C (Found: C, 57.62; H, 3.59. $C_8H_6O_2S$ requires C, 57.83; H, 3.64%); $\nu_{max}(CCl_4)/cm^{-1}$ 2931, 1781 (C=O), 1752 (C=O), 1619 (C=C), 1425, 1143, 1045; $\delta_H(CDCl_3)$ 7.56 (1 H, dd, *J* 5.1, 0.92, thienyl 5-H), 7.30 (1 H, br d, *J* 3.7, thienyl 3-H), 7.13 (1 H, dd, *J* 3.7, 5.1, thienyl 4-H), 6.15 (1 H, t, *J* 1.65, 3-H), 5.16 (2 H, d, *J* 1.65, 5-H); $\delta_C(CDCl_3)$ 173.5, 157.1, 132.7, 130.4, 128.4, 128.4, 111.2, 70.8 (HRMS: found M^+, 166.0099. $C_8H_6O_2S$ requires *M*, 166.0088); *m/z* 166 (M^+, 100%), 137 (55), 109 (29), 108 (60), 69 (12).

4-Trimethylsilylfuran-2(5*H*)-one 27

To a solution of 4-tributylstannylfuran-2(5*H*)-one **2** (210 mg, 0.56 mmol) in tetrahydrofuran (5 ml) at −100 °C under nitrogen was added methyllithium (0.44 ml of 1.4 M solution in Et_2O, 0.62 mmol). The reaction mixture was maintained at −100 °C for 20 min before chlorotrimethylsilane (0.10 ml, 0.79 mmol) was added dropwise. The reaction mixture was stirred for a further 20 min at −100 °C, 1 h at −78 °C then warmed to room temperature. The solvent was removed *in vacuo* and the residue purified by column chromatography using diethyl ether–light petroleum (1:3) as eluent furnishing **2** (32 mg, 15%) and *furanone* **27** as a clear colourless oil (14.0 mg, 16%); $\nu_{max}(CCl_4)/cm^{-1}$ 2959, 2861, 1785 (C=O), 1754 (C=O), 1592, 1336, 1256, 1159, 1060; $\delta_H(CDCl_3)$ 6.18 (1 H, t, *J* 2.19, vinylic), 4.90 (2 H, d, *J* 2.19, CH_2O), 0.24 (9 H, s, SiMe); $\delta_C(CDCl_3)$, 174.0, 171.3, 127.9, 75.3, −2.2 (HRMS: found M^+, 156.0610. $C_7H_{12}O_2Si$ requires *M*, 156.0606); *m/z* 156 (M^+, 4.5%), 141 (46), 113 (23), 83 (20), 73 (100), 43 (16).

3-Trimethylsilylfuran-2(5*H*)-one 28[22]

An analogous procedure to that for the 4-silylated compound above was employed using 3-tributylstannylfuran-2(5*H*)-one (229 mg, 0.614 mmol) and chlorotrimethylsilane (0.78 ml, 6.1 mmol). *Furanone* **28** was isolated by preparative thin layer chromatography as a colourless oil (5 mg, 5%); $\delta_H(CDCl_3)$ 7.63 (1 H, t, *J* 1.55, vinylic), 4.83 (2 H, d, *J* 1.55, CH_2O), 0.25 (9 H, s, SiMe); $\delta_C(CDCl_3)$ 176.4, 160.3, 135.0, 72.6, −2.2.

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