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Preparation and reactions of 3,4-bisstannyl-2(5*H*)furanones

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Abstract—Bistributylstannyl-2(5*H*)-furanone **4a** has been prepared from 3-(tetrahydropyran-2-yl)oxy but-2-ynoate and shown to exhibit good selectivity in its Stille reactions with a range of halogenated compounds, leading to 4-substituted-3-stannyl-2(5*H*)-furanones, in generally moderate yield. Under certain reaction conditions, doubly substituted products were also isolated from the reactions. The 3,4-bistrimethylstannyl furanone, **4b**, corresponding to **4a** was prepared, but decomposed during all attempts to execute Stille reactions upon it.

1. Introduction

Many natural and bioactive compounds contain the 2(5*H*)-furanone subunit;[1] consequently, we have attempted to develop methodology to allow synthesis of such compounds via palladium-catalyzed cross-coupling of 3- and 4-tributylstannyl 2(5*H*)-furanones **1** and **2** (Fig. 1) with aryl iodides.[2] Furthermore, 3,4-diaryl-2(5*H*)-furanones (such as VIOXX™, **3**[3]) have been demonstrated to be orally-active, potent and selective inhibitors of cyclooxygenase-2 ('COX-2') enzymes, thereby offering much promise as therapeutic moieties.[4] We here report in detail[5] the first preparation of 3,4-bistributyl- and 3,4-bistrimethylstannyl 2(5*H*)-furanone **4a** and **4b**, respectively, and describe how compound **4a** was shown to undergo regiospecific palladium-catalyzed cross-coupling reactions ('Stille reactions') with halides; we also describe here the details of optimization studies aimed at improving the efficiency of the latter reaction.

2. Results and discussion

In our previous work, monostannylfuranones **1** and **2** displayed differing reactivities in Stille couplings with a variety of aryl iodides: in all cases, stannane **1** reacted more efficiently.[2] We reasoned, therefore, that bisstannane **4a** might exhibit regioselectivity in its reactions with coupling partners and, we predicted, that if selectivity was exhibited, the C4–Sn bond would be more reactive than the neighbouring C3–Sn bond. Thus, it was anticipated that **4a** would react with 1 equiv. of a suitable coupling partner to give a 4-substituted 3-tributylstannylfuranone **5**, rather than a 3-substituted 4-tributylstannylfuranone **6** (Scheme 1).

2.1. Synthesis of 3,4-bisstannyl-2(5*H*)furanone

Our first synthetic targets were (*Z*)-2,3-bistributylstannyl-butenoates **7a** and **7b**, which we anticipated would give easy access to **4a**. Thus, butynoates **8a** and **8b**[6] reacted with

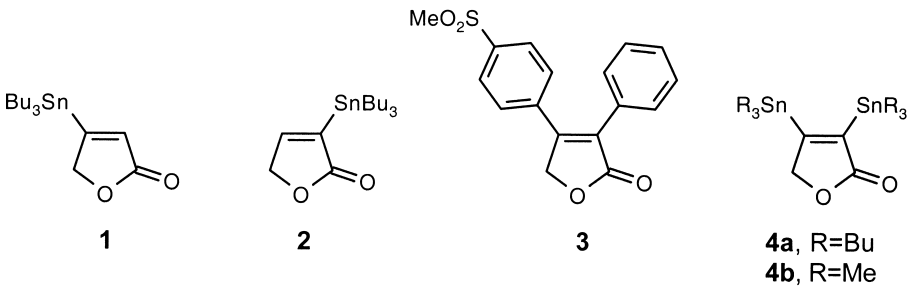

Figure 1.

Keywords: furanones; Stille reactions; nucleophilic.

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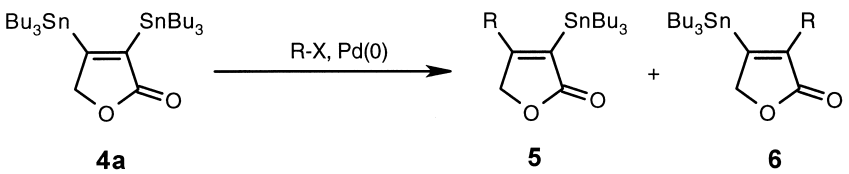
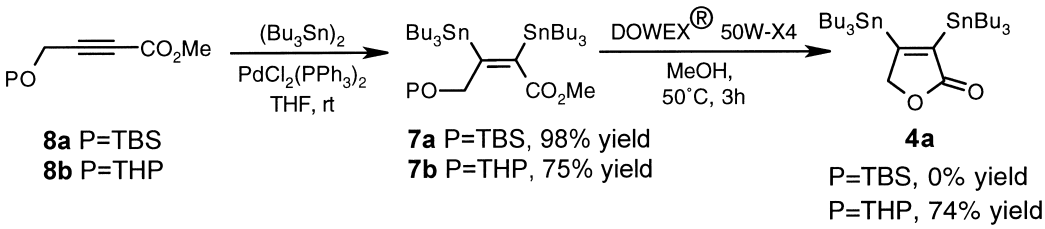


Scheme 1.



Scheme 2.

hexabutylditin in the presence of $PdCl_2(PPh_3)_2$[7] to give these enoates in 75 and 98% yield, respectively (Scheme 2). Using an acid-mediated cyclization protocol, only **7b** gave lactone **4a** as a colourless liquid, in 74% yield. Under a range of reaction conditions, the TBS-protected 3-hydroxymethyl-2,3-bisstannylacrylate **7a** underwent decomposition to give products whose structure could not be determined.

2.2. Cross-coupling reactions of 3,4-bistributylstannyl-2(5*H*)furanone

Thus, we were poised to examine the selectivity, if any, shown by **4a** in its coupling reactions. We expected that **4a** would, upon reaction with iodobenzene in the presence of Pd_2dba_3, triphenylarsine and Cu(I)I in THF, would give 3-tributylstannyl-4-phenyl-2(5*H*)-furanone **5a**, as the major product of the reaction. It was gratifying to see that only one compound was produced in the reaction, in 37% yield. But how could we determine the structure of the product? Using the data already available, and that we had already gleaned from our earlier studies,[1] we predicted the ^{13}C NMR resonances of **5a** and **6a** to be those shown in Diagram 1.

As can be see from Scheme 3, the predicted ^{13}C NMR data for **5a** closely matched the values observed whereas that predicted for **6a** was quite different; chemical correlation (via protodestannylation, to give **9a**[1]) confirmed that the product of Stille coupling was indeed **5a**. Thus, our prediction that the difference in reactivity of the C3–Sn and C4–Sn bond could be exploited had been borne out in practice.

The selectivity shown in the coupling reaction proved to be general: a range of aryl iodides reacted under typical conditions to give products of cross-coupling, albeit in moderate yield (Table 1). Reaction with allyl and benzyl bromide, benzoyl chloride and β-bromostyrene proceeded with similar regiocontrol and yields. These reactions did not produce any trace of product in which two couplings had occurred (i.e. where both C3– and C4–Sn bonds had reacted with the coupling partner) or any product in which coupling had occurred selectively at position 3 of the furanone. Protodestannylation confirmed the regioselectivity of the reactions (Table 1).

2.3. Optimization of the cross-coupling reaction

Having demonstrated the validity of our synthetic proposal, we next turned our attention to a thorough examination of

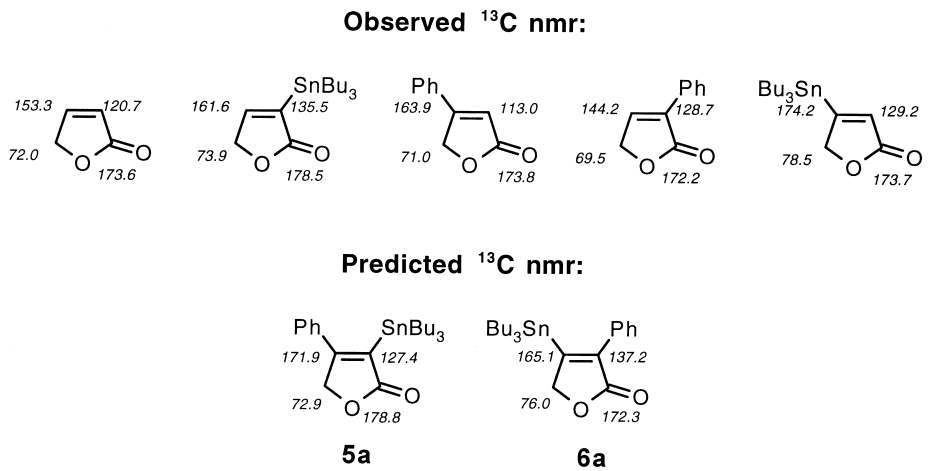
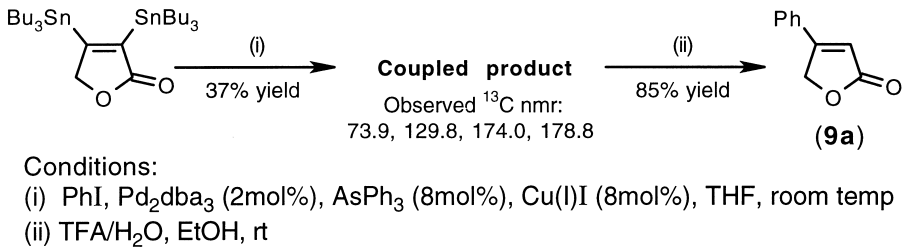


Diagram 1.

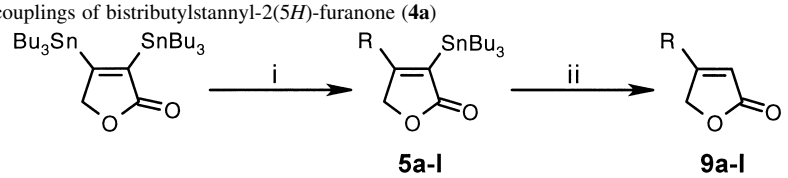


Scheme 3.

the reaction conditions of the initial cross-coupling process, with a view to improving the yields of 4-substituted-3-tributylstannylfuranones obtained. The reaction of iodobenzene with **4a** was examined under a wide range of conditions, as detailed in Table 2, but the overall effect upon the efficiency of the selective coupling process was, except in a few cases, slight. A number of facts can be deduced from these investigations: firstly, use of an excess of either iodobenzene (entry 9) or bisstannane (entry 10) did not improve the yield of **5a**; it is noteworthy, however, that even under these conditions the doubly-coupled product was not seen in the crude product. The optimum temperature for the process seems to be in the range 50–70°C. Furthermore, the polarity of the reaction solvent exerts a strong effect upon the yield and selectivity of the process. Thus, when CH_2Cl_2 (entry 22), THF, DME (entry 20) or NMP (entry 21) was employed, a single product, **5a**, was usually obtained in a maximum of 44% yield (entry 28); when DMF was used (entries 16–18), the yield of **5a** was lower (≤29%) and the selectivity of the reaction was altered, because the product of double coupling, 3,4-diphenyl-2(5*H*)-furanone **10**, was also obtained (in 28–36% yield) (entries 16–18 and Table 3). A similar observation was made when methanol was used as solvent (entry 19). A mixture of singly and doubly-substituted furanones (27 and 39% yield, respectively) was also obtained in THF solvent when $Pd(dppb)_2$ was the coupling catalyst (entry 7), although use of the lower homologue, $Pd(dppp)_2$, did not furnish any coupled products. Intriguingly, reaction of **4a** with excess iodobenzene under the conditions which gave doubly-coupled material did not give **10** as a single product: the yields of **5a** and **10** remained the same, allowing for experimental error. Other than these latter data, the choice of catalyst seems to have little effect, with Pd_2dba_3, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$ and $PdCl_2(PhCN)_2$ all providing roughly similar yields of singly-coupled furanone upon reaction in THF; variation of catalyst stoichiometry (entries 23–25) led to diminished yields of singly-coupled product and no double-coupling was observed. In our hands, Cu(I) did not catalyze coupling (entry 37). The nature of the additives present in the reaction has a pronounced effect upon the yield, but not the selectivity of the reaction. Thus, Cu(I)I alone (entry 30) is a more effective additive than $AsPh_3$ alone (entry 29) and the nature of the Cu(I) species seems unimportant (compare entries 30–32 and 34). The use of phenyl triflate rather than iodobenzene was unproductive (entry 36). Addition of further catalyst after an initial reaction period (entry 14) did not enhance the yield sufficiently for the process to be deemed necessary, and slow addition of stannane to the reaction mixture (entry 35) had only a slight (and detrimental) effect upon the yield of the reaction.

Given the bulk of the tributylstannyl group, it might be reasonable to suggest that there is a steric inhibition of the

Table 1. Regioselective Stille couplings of bistributylstannyl-2(5*H*)-furanone (**4a**)



R	Conditions[a]	Product (yield (%))	Product (yield (%))
Ph	A	**5a** (37)	**9a** (85)
2-Naphthyl	B	**5b** (40)	**9b** (80)
2-MeC_6H_4	A	**5c** (49)	**9c** (95)
3-$CF_3C_6H_4$	A	**5d** (27)	**9d** (91)
2-$MeOC_6H_4$	A	**5e** (40)	**9e** (88)
2-$O_2NCC_6H_4$	B	**5f** (47)	**9f** (82)
2-$MeO_2CC_6H_4$	A	**5g** (51)	**9g** (89)
2-Thienyl	A	**5h** (22)	**9h** (88)
Bn	A	**5i** (9)	**9i** (86)
CH_2=$CHCH_2$	A	**5j** (23)	**9j** (73)
PhCO	C	**5k** (33)	**9k** (90)
PhCH=CH	D	**5l** (35)[b]	**9l** (92)

[a] A: R-I (1 equiv.), Pd_2dba_3 (2 mol%), $AsPh_3$ (8 mol%), Cu(I)I (8 mol%), THF; Method B: $PdCl_2(PPh_3)_2$ (2 mol%), $AsPh_3$ (8 mol%), Cu(I)I (8 mol%), THF, 50°C; Method C: PhCOCl, $BnClPd(PPh_3)_2$ (2 mol%), CO, DMF, 50°C; Method D: PhCH=CHBr, Pd_2dba_3 (2 mol%), DMF, 50°C.

[b] Only *E*-isomer obtained.

Table 2. Optimization of the reaction of **4a** with iodobenzene (1 equiv.)

Entry	Catalyst (mol%)	Additives (mol%)	Reaction conditions	Yield (%) **5a**
1	Pd_2dba_3 (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	35
2	Pd_2dba_3 (2)	CuI (8), $(2\text{-furyl})_3P$ (8)	THF, 50°C, 18–24 h	31
3	$Pd(PPh_3)_4$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	24
4	$PdCl_2(MeCN)_2$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	32
5	$PdCl_2(PhCN)_2$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	33
6	$Pd(dppp)_2$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	No reaction
7[a]	$Pd(dppb)_2$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	27
8	$PdCl_2(PPh_3)_2$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	38
9[b]	$PdCl_2(PPh_3)_2$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	37
10[c]	$PdCl_2(PPh_3)_2$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	26
11	$PdCl_2(PPh_3)_2$ (1)	None	THF, 50°C, 18–24 h	no reaction
12	$PdCl_2(PPh_3)_2$ (2)	None	THF, 50°C, 18–24 h	No reaction
13	$PdCl_2(PPh_3)_2$ (2)	CuI (8), $(2\text{-furyl})_3P$ (8)	THF, 50°C, 18–24 h	24
14[d]	$PdCl_2(PPh_3)_2$ (4)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 36–48 h	42
15	$PdCl_2(PPh_3)_2$ (4)	CuI (8), $AsPh_3$ (8)	THF, rt, 7 days	18
16[e]	$PdCl_2(PPh_3)_2$ (4)	CuI (8), $AsPh_3$ (8)	DMF, 50°C, 18–24 h	29
17[f]	$PdCl_2(PPh_3)_2$ (4)	CuI (8), $AsPh_3$ (8)	DMF, 70°C, 18–24 h	28
18[g]	$PdCl_2(PPh_3)_2$ (4)	CuI (8), $AsPh_3$ (8)	DMF, 90°C, 18–24 h	25
19[h]	$PdCl_2(PPh_3)_2$ (4)	CuI (8), $AsPh_3$ (8)	MeOH, 50°C, 18–24 h	12
20	$PdCl_2(PPh_3)_2$ (4)	CuI (8), $AsPh_3$ (8)	1,2-DME, 50°C, 18–24 h	30
21	$PdCl_2(PPh_3)_2$ (4)	CuI (8), $AsPh_3$ (8)	NMP, 50°C, 18–24 h	25
22	$PdCl_2(PPh_3)_2$ (4)	CuI (8), PPh_3 (8)	CH_2Cl_2, rt, 3 days	27
23	$PdCl_2(PPh_3)_2$ (5)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	37
24	$PdCl_2(PPh_3)_2$ (10)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	29
25	$PdCl_2(PPh_3)_2$ (15)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	11
26	$PdCl_2(PPh_3)_2$ (2)	CuI (8), $AsPh_3$ (20)	THF, 50°C, 18–24 h	39
27	$PdCl_2(PPh_3)_2$ (2)	CuI (50), $AsPh_3$ (8)	THF, 50°C, 18–24 h	29
28	$PdCl_2(PPh_3)_2$ (2)	CuI (200), $AsPh_3$ (8)	THF, 50°C, 18–24 h	44
29	$PdCl_2(PPh_3)_2$ (2)	$AsPh_3$ (8)	THF, 50°C, 18–24 h	18
30	$PdCl_2(PPh_3)_2$ (2)	CuI (8)	THF, 50°C, 18–24 h	39
31	$PdCl_2(PPh_3)_2$ (2)	CuCN (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	36
32	$PdCl_2(PPh_3)_2$ (2)	CuCl (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	27
33[i]	$PdCl_2(PPh_3)_2$ (2)	CuO_2CAr[j] (130), $AsPh_3$ (8)	NMP, rt–50°C, 36–48 h	No reaction
34	$PdCl_2(PPh_3)_2$ (2)	CuO_2CAr (8), $AsPh_3$ (8)	THF, 50°C, 18–24 h	41
35[k]	$PdCl_2(PPh_3)_2$ (2)	CuI (8), $AsPh_3$ (8)	THF, 50°C, 8 h	27
36[l]	$PdCl_2(PPh_3)_2$ (2)	LiCl (300), $AsPh_3$ (8)	NMP, 35°C, 18–24 h	No reaction
37	CuI (10)	NaCl (300)	NMP, 90°C, 6 h	No reaction
38	$PdCl_2(PPh_3)_2$ (2)	LiCl (300)	THF/DMF 1:1, 80°C, 18–24 h	No reaction

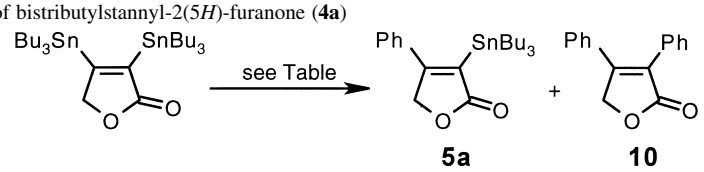
[a] Reaction afforded 3,4-bis-(phenyl)furan-2(5*H*)-one (**9a**), (39%).
[b] Reaction performed with 2 equiv. of iodobenzene.
[c] Reaction performed with 2 equiv. of stannane.
[d] Reaction performed in 2 mol% catalyst for 18–24 h then, a further 2 mol% added for additional 18–24 h.
[e] Reaction afforded 3,4-bis-(phenyl)furan-2(5*H*)-one (**9a**) (28%).
[f] Reaction afforded 3,4-bis-(phenyl)furan-2(5*H*)-one (**9a**) (28%).
[g] Reaction afforded 3,4-bis-(phenyl)furan-2(5*H*)-one (**9a**) (36%).
[h] Reaction afforded 3,4-bis-(phenyl)furan-2(5*H*)-one (**9a**) (27%).
[i] Reaction stirred for 18–24 h at ambient temperature, followed by 18–24 h at 50°C.
[j] Ar=2-thienyl.
[k] Stannane added by syringe pump over 8 h.
[l] Reaction using phenyl triflate as coupling partner.

reaction, leading to the moderate yields obtained in the selective coupling process. To address this point, we prepared the bistrimethylstannylfuranone, **4b**, using a similar route to that detailed above. If a steric phenomenon were at the heart of the problem, one might reasonably expect a smaller tin substituent to ameliorate the difficulties. Thus, butynoate **8b** reacted this time with hexamethylditin to give the bistrimethylstannylacrylate, **11**, in excellent yield (Scheme 4). When reacted under the conditions which had previously been used for the synthesis of the higher stannane, **11** was converted into two compounds, the desired bisstannylfuranone, **4b**, and (*Z*)-methyl-3-(tetrahydropyran-2-yl)oxymethyl-3-bis(trimethylstannyl)propenoate **12**, in an overall yield of 55%, with **4b**, the desired furanone, present in five times excess in the product ratio (**4b/12**=5:1).

These compounds, both low-melting solids, were separable using flash chromatography and were stable indefinitely at −20°C; bisstannane **4b** was however, unstable at temperatures greater than ambient, unless kept under a ruthlessly-purged, oxygen-free environment. Given this fragility, it was perhaps not surprising that **4b** reacted with iodobenzene to give unidentifiable products under a broad range of experimental rubrics; no trace of furanone product or starting material was identified from either the crude reaction mixture or samples analyzed by flash chromatography. Thus, it would seem that, at present, we are unable to examine the influence of steric compromise upon the yield of the selective couplings of bisstannylfuranones.

It is clear from the data presented in Tables 1 and 2 that the

Table 3. Double-coupling reaction of bistributylstannyl-2(5*H*)-furanone (**4a**)



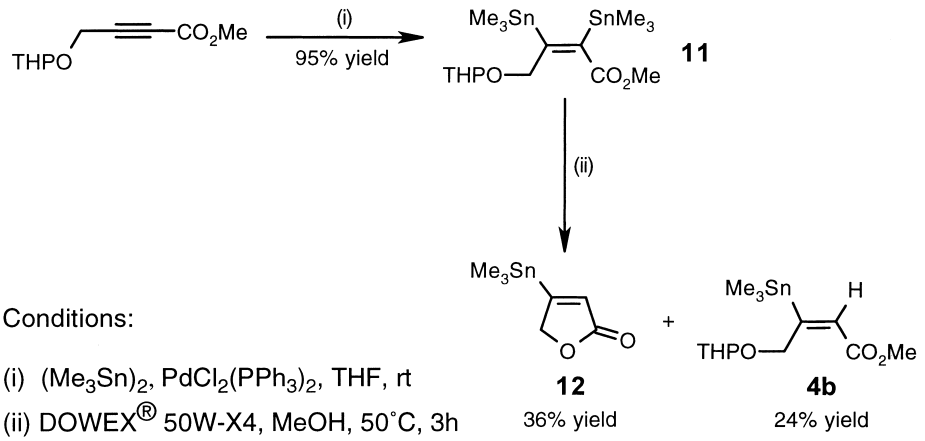
Conditions	Yield **5a** (%)	Yield **10** (%)
THF, 50°C[a]	27	39
DMF, 50°C[b]	29	28
DMF, 70°C[b]	28	28
DMF, 90°C[b]	25	36
MeOH, 50°C[b]	12	27

[a] $Pd(dppb)_2$ (2 mol%), iodobenzene (1 equiv.), CuI (8 mol%), $AsPh_3$ (8 mol%).
[b] $PdCl_2(PPh_3)_2$ (2 mol%), iodobenzene (1 equiv.), CuI (8 mol%), $AsPh_3$ (8 mol%).

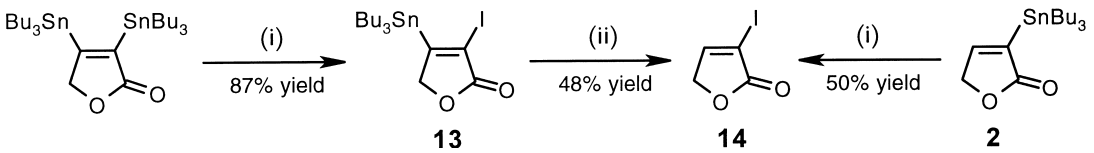
C4–Sn bond reacts preferentially in palladium-catalyzed cross-coupling reactions with substrates. We note that there are two obvious controlling factors in these reactions, an electronic factor and a steric one. One might rationalize these observations by noting that the polarization of the C=C bond of the stannylfuranone diminishes the strength of the C4–Sn bond (Fig. 2), thereby enhancing the rate of transmetallation and favouring coupling at C4, but we have little data which provide a piercing mechanistic insight at this time.

One piece of evidence which perhaps supports this assertion is the observation that bisstannane **4a** reacts with a single equivalent of elemental iodine at the C3–Sn bond (Scheme 5), to give iodostannane **13**, as shown by chemical correlation via protodestannylation to iodofuranone **14** (prepared unambiguously from monostannylfuranone **2**).

Thus, the C3–Sn bond is the more nucleophilic of the two. When 2 equiv. of iodine were used in the reaction, diiodofuranone, **15**, was obtained in 76% yield



Scheme 4.



Scheme 5. *Conditions*: (i) I_2 (2 equiv.), CH_2Cl_2, rt, 18 h; (ii) 50% TFA (aq), EtOH, rt, 48%.

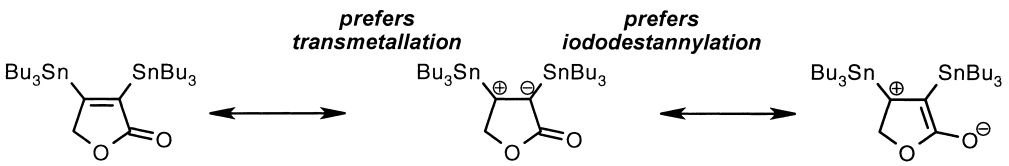
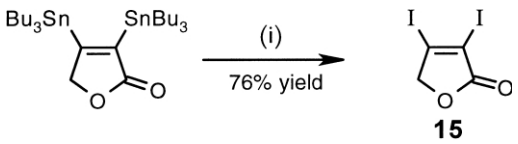


Figure 2.



Scheme 6. *Conditions*: I_2 (2 equiv.), CH_2Cl_2, rt, 120 h.

(Scheme 6); it is noteworthy that the reaction now required almost five times as long as did the conversion of **4a** to **13**, again implying that the C3–Sn bond is the more nucleophilic of the two. Detailed investigation of the mechanistic nuances responsible for these observations are underway in our laboratory.

3. Conclusions

We have prepared, for the first time, bisstannylfuranones **4a** and **4b** and, in the case of **4a**, shown that a selective Stille coupling is possible. The C4–Sn bond is consistently substituted in such processes, except when polar solvents or chelating phosphine ligands are used in the reaction. In contrast, the C3–Sn bond is shown to be the more nucleophilic of the chalcogenic bonds by its selective reaction with iodine. We are currently pursuing zealously the underlying principles responsible for this unusual selectivity.

4. Experimental

4.1. General techniques

Throughout the text, the term 'petrol' refers to the fraction of petroleum ether with the boiling range 40–60°C and 'ether' refers to diethyl ether. Diethyl ether and THF were distilled from sodium benzophenone ketyl, methanol from magnesium methoxide.

Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected. Infra-red spectra were recorded on a Perkin–Elmer 881 or Paragon 1000 spectrophotometer. Mass spectra were recorded on a Fisons Autospec spectrometer. NMR spectra were recorded on a Bruker DPX-250, or Bruker AX-400 spectrometer. Unless otherwise stated, deuterochloroform was used as solvent and TMS was used as the internal standard. Chemical shifts in ^1H NMR spectra are expressed as ppm downfield from TMS, 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 or moisture were conducted under a nitrogen or argon atmosphere in oven or flame-dried apparatus. Column chromatography was performed using Merck Kieselgel 60 or Fluka Kieselgel 60 silica gel. Analytical thin-layer chromatography was performed using either precoated Merck Kieselgel 60 F_{254} glass-backed plates, or precoated Merck Kieselgel 60 F_{254} aluminium backed plates and were visualised under U.V. at 254 nm and by staining with iodine and/or an acidic ammonium molybdate dip.

4.1.1. 3,4-Bis(tributylstannyl)furan-2(5*H*)-one (4a). (*Z*)-Methyl-3-(tetrahydropyran-2-yl)oxymethyl-2,3-bis(tributyl stannyl)propenoate (**7b**) (20.0 g, 25.7 mmol) and Dowex® 50W-X4 ion exchange resin (20.0 g) were combined in dry methanol (250 mL) and the solution was stirred at 50°C for 3 h. The mixture was allowed to cool to ambient temperature and the resin removed by filtration through Celite® and washed with ether (100 mL). The reaction mixture was concentrated in vacuo and purification by column chromatography (R_f 0.32, ether/petrol, 1:9) afforded furanone (**4a**) as a clear colourless liquid (12.6 g, 74%). ν_{max} 1735, 1539, 1464; δ_H ($CDCl_3$) 0.80–1.50 (54H, m), 4.83 (2H, s, $^{119}Sn/^{117}Sn$ coupling J=4.5 Hz); δ_C ($CDCl_3$) 10.2, 10.4, 13.5, 13.6, 27.3, 29.1, 81.2, 144.4, 178.3, 183.7; *m/z* (EI) Found $(M-Bu)^+$, 605.1589 (69%), $C_{24}H_{47}O_2Sn_2$ requires 605.1620, 560 (15), 291 (25), 235 (48), 177 (100).

4.1.2. (*Z*)-Methyl 4-*tert*-butyldimethylsilyloxy-2,3-bis (tributylstannyl)but-2-enoate (7a). Hexabutylditin (0.72 g, 1.17 mmol) and methyl 4-(*tert*-butyldimethylsilyloxy)but-2-ynoate (**8a**) (0.25 g, 1.17 mmol) were combined in dry deoxygenated THF (7.5 mL). Dichlorobis(triphenylphosphine)palladium(II) (10 mg, 0.002 mmol) was added, and the mixture stirred at room temperature for 18 h. A further portion of catalyst (247 mg, 0.035 mmol) was then added, and the mixture stirred for a further 24 h. The reaction mixture was concentrated in vacuo and purification by column chromatography (R_f 0.51, ether/petrol, 1:19) furnished bisstannane (**7a**) as a clear colourless liquid (0.95 g, 98%). ν_{max} 1708, 1549, 1465; δ_H ($CDCl_3$) 0.05 (6H, s), 0.78–1.48 (54H, m), 0.84 (9H, br. s), 3.60 (3H, s), 4.23 (2H, s); δ_C ($CDCl_3$) 11.5, 11.7, 13.6, 19.2, 25.4, 27.3, 27.6, 28.9, 29.2, 30.4, 98.0, 149.8, 161.1 172.8; *m/z* (EI) Found $(M-Bu)^+$, 751.2762 (6%), $C_{31}H_{65}O_3SiSn_2$ requires 751.2747, 463 (14), 347 (17), 291 (42).

4.1.3. (*Z*)-Methyl 4-[(tetrahydropyran-2-yl)oxy]-2,3-bis(-tributylstannyl)but-2-enoate (7b). Hexabutylditin (20.5 g, 35.3 mmol) and methyl 4-[(tetrahydropyran-2-yl)oxy]but-2-ynoate (**8b**)[6] (7.0 g, 35.3 mmol) were combined in dry deoxygenated THF (500 mL). Dichlorobis(triphenylphosphine)palladium (II) (247 mg, 0.035 mmol) was added, and the mixture stirred at ambient temperature for 18 h. A further portion of catalyst (247 mg, 0.035 mmol) was then added, and the mixture stirred for a further 24 h. The reaction mixture was concentrated in vacuo and the residue placed under high vacuum (0.1 mm Hg) for 4 h to give a brown oil. Purification by column chromatography (R_f 0.18, ether/petrol, 1:9) gave bisstannane (**7b**) as a clear colourless liquid (20.6 g, 75%). ν_{max} 1707, 1547, 1463; δ_H ($CDCl_3$) 0.89–1.39 (54H, m), 1.45–1.92 (6H, m), 3.49–3.50 (1H, m), 3.67 (3H, s), 3.80–3.85 (1H, m), 4.03 (1H, d, J=12.5 Hz), 4.39 (1H, d, J=12.5 Hz), 4.59–4.61 (1H, m); δ_C ($CDCl_3$) 11.6,11.9, 14.0, 19.8, 25.9, 27.7, 27.9, 28.3, 29.5, 29.7, 31.0, 50.9, 61.7, 72.5, 98.0, 149.8, 161.1, 172.8; *m/z* (CI, NH_3) Found $(M-Bu)^+$, 723.2414 (100%), $C_{30}H_{59}O_4Sn_2$ requires 723.2457, 679 (15), 637 (15), 433 (45), 373 (45), 335 (50), 269 (80), 177 (10), 138 (25), 85 (100).

4.1.4. Methyl 4-(*tert*-butyldimethylsilyloxy)but-2-ynoate (8a). Methyl 4-hydroxybut-2-ynoate (0.5 g, 4.38 mmol), *tert*-butyldimethylsilylchloride (0.73 g, 4.8 mmol), DMAP

(54 mg, 0.438 mmol) and triethylamine (0.67 mL, 4.38 mmol) were combined in dichloromethane (10 mL) under argon. The mixture was stirred at ambient temperature for 18 h. The solvent was removed in vacuo and purification by column chromatography (R_f 0.48, ether/petrol 1:9) yielded butynoate (**8a**) as a clear colourless liquid (0.47 g, 79%). ν_{max} 2240, 1720; δ_H ($CDCl_3$) 0.13 (6H, s), 0.90 (9H, s), 3.77 (3H, s), 4.43 (2H, s); *m/z* (EI) Found $(MNH_4)^+$, 246.1533 (10%), $C_{11}H_{24}NO_3Si$ requires 246.1526.

4.1.5. (*Z*)-Methyl-3-(tetrahydropyran-2-yl)oxymethyl-2,3-bistrimethylstannyl propenoate (11). Hexamethylditin (1.0 g, 3.05 mmol) and methyl 4-[(tetrahydropyran-2-yl)oxy]but-2-ynoate (**8b**) (0.66 g, 3.33 mmol) were combined in dry deoxygenated THF (15 mL). Dichlorobis(triphenylphosphine)palladium (II) (4.2 mg, 0.03 mmol) was added, and the mixture stirred at ambient temperature for 24 h. The solvent was removed in vacuo and purification by column chromatography (R_f 0.4, ether/petrol, 1:4) afforded bisstannane **11** as a clear colourless liquid (1.5 g, 95%). ν_{max} 2948, 1707, 1557, 1455; δ_H ($CDCl_3$) 0.22 (9H, s), 0.27 (9H, s), 1.52–1.83 (6H, m), 3.35–3.45 (1H, m), 3.70 (3H, s), 3.80–3.85 (1H, m), 4.06–4.12 (1H, m), 4.44–4.38 (1H, m), 4.52 (1H, t, J=3.3 Hz); δ_C ($CDCl_3$) −6.7, −6.4, 19.3, 25.3, 30.3, 50.9, 61.5, 72.0, 97.8, 149.5, 162.2, 171.9; *m/z* (EI) Found $(M-Me)^+$, 511.0125 (23%), $C_{15}H_{29}O_4Sn_2$ requires 511.0120, 427 (7), 328 (7), 246 (87), 165 (100).

4.1.6. 3,4-Bistrimethylstannylfuran-2(5*H*)-one (4b) and (*Z*)-methyl-3-(tetrahydropyran-2-yl)oxymethyl-3-bis-(trimethylstannyl)propenoate (12). (*Z*)-Methyl-3-(tetrahydropyran-2-yl)oxymethyl-2,3-bistrimethylstannylpropenoate (**11**) (690 mg, 1.307 mmol) and Dowex® 50W-X4 ion-exchange resin (1.38 g) were combined in dry methanol (10 mL) and stirred at 50°C for 3 h. The resin was removed by gravity filtration, washed with ether (25 mL) and the solvent removed in vacuo. Purification by column chromatography (R_f 0.28, ether/petrol, 1:4) yielded bisstannane (**4b**) as a semi-solid (245 mg, 46%). ν_{max} ($CHBr_3$) 1726, 1536, 1441, 1330; δ_H ($CDCl_3$) 0.30 (9H, s, coupling to $^{119}Sn/^{117}Sn$ J=22.0, 228.0 Hz), 0.32 (9H, s, coupling to $^{119}Sn/^{117}Sn$ J=22.0, 28.0 Hz), 4.90 (2H, s, coupling to $^{119}Sn/^{117}Sn$ J=5.0 Hz); δ_C ($CDCl_3$) −7.6, −7.4, 80.5, 144.9, 178.9, 184.6; *m/z* (EI) Found $(M-Me)^+$, 394.9272 (72%), $C_9H_{17}O_2Sn_2$ requires 394.9270, 351 (45), 165 (100); and (*Z*)-Methyl-3-(tetrahydropyran-2-yl)-oxymethyl-3-trimethylstannylpropenoate (**12**) (R_f 0.60, ether/petrol, 2:3) as a colourless oil (42 mg, 9%). ν_{max} ($CHCl_3$) 2945, 1715, 1606; δ_H ($CDCl_3$) 0.25 (9H, s, coupling to $^{119}Sn/^{117}Sn$ J=27.5 Hz), 1.50–1.80 (6H, m), 3.48–3.53 (1H, m), 3.70 (3H, s), 3.81–3.84 (1H, m), 4.56 (1H, dd, J=2.7, 17.4 Hz), 4.70 (1H, m), 5.07 (1H, dd, J=2.7, 17.4 Hz), 5.96 (1H, s, coupling to $^{119}Sn/^{117}Sn$ J=2.8 Hz); δ_C (CDCl3) −8.9, 18.4, 24.3, 29.4, 50.1, 60.9, 70.9, 97.6, 122.8, 163.8, 173.5; *m/z* (CI, NH_3) Found $(M-Me)^+$, 349.0472 (24%), $C_{12}H_{21}O_4Sn$ requires 349.0462, 263 (55), 165 (27), 85 (100).

4.1.7. Synthesis of 4-aryl-3-tributylstannylfuran-2(5*H*)-ones. Two methods were generally employed:

Method A. To a stirred solution of aryl iodide (0.755 mmol, 1.0 equiv.) in dry deoxygenated THF (5 mL) was added copper(I) iodide (11.4 mg, 0.08 equiv.) and triphenylarsine (18.4 mg, 0.08 equiv.) under an argon atmosphere. 3,4-Bis(tributylstannyl)furan-2(5*H*)-one (**4a**) (500 mg, 0.755 mmol) was added in deoxygenated THF (5 mL) and the mixture stirred at ambient temperature. Tris(dibenzylideneacetone)dipalladium(0) (13.7 mg, 0.02 equiv.) was added to give a purple solution which became lime green in colour over 10 min. The reaction mixture was then heated to 50°C for 18–24 h, by which time the reaction was judged complete by tlc. The reaction mixture was concentrated in vacuo and the residue purified by column chromatography.

4.1.8. 4-Phenyl-3-tributylstannylfuran-2(5*H*)-one (5a). Reaction of 3,4-bis(tributylstannyl)furan-2(5*H*)-one (**4a**) (500 mg, 0.755 mmol) and iodobenzene (154 mg, 0.755 mmol) gave furanone (**5a**) after purification by column chromatography (R_f 0.28, ether/petrol, 1:4) as a clear colourless oil (127 mg, 37%). ν_{max} 1734, 1620, 1590; δ_H ($CDCl_3$) 0.81–1.48 (27H, m), 5.08 (2H, t, J=3.5 Hz), 7.33–7.36 (2H, m), 7.43–7.47 (3H, m); δ_C ($CDCl_3$) 10.4, 13.6, 27.1, 28.9, 73.9, 126.8, 128.8, 129.8, 130.2, 133.9, 174.0, 178.8; *m/z* (CI, NH_3) Found $(M-Bu)^+$, 393.0879 (24%), $C_{18}H_{25}O_2Sn$ requires 393.0877, 235 (34), 161 (100), 131 (45), 104 (27).

4.1.9. 4-(2-Methylphenyl)-3-tributylstannylfuran-2(5*H*)-one (5c). Reaction of 3,4-bis(tributylstannyl)furan-2(5*H*)-one (**4a**) (500 mg, 0.755 mmol) and 2-iodotoluene (165 mg, 0.755 mmol) gave furanone (**5c**) after purification by column chromatography (R_f 0.38, ether/petrol, 1:4) as a clear colourless oil (171 mg, 49%). ν_{max} 1741, 1620, 1597; δ_H ($CDCl_3$) 0.74–1.44 (27H, m), 2.27 (3H, s), 4.92 (2H, t, J=3.5 Hz), 7.05–7.33 (4H, m); δ_C ($CDCl_3$) 9.5, 13.5, 19.6, 27.1, 28.8, 75.2, 125.8, 127.7, 129.1, 130.3, 132.2, 134.1, 134.5, 176.1, 178.4; *m/z* (EI) Found $(M-Bu)^+$, 407.1041 (100%), $C_{19}H_{27}O_2Sn$ requires 407.1033, 292 (45), 129 (21).

4.1.10. 4-(3-Trifluromethylphenyl)-3-tributylstannylfuran-2(5*H*)-one (5d). Reaction of 3,4-bis(tributylstannyl)-furan-2(5*H*)-one (**4a**) (500 mg, 0.755 mmol) and 3-iodotrifluoromethylbenzene (205 mg, 0.755 mmol) gave furanone (**5d**) after purification by column chromatography (R_f 0.38, ether/petrol, 1:4) as a clear colourless oil (106 mg, 27%). ν_{max} 1743, 1620, 1583; δ_H ($CDCl_3$) 0.80–1.50 (27H, m), 5.10 (2H, t, J=3.5 Hz), 7.52–7.74 (4H, m); δ_C ($CDCl_3$) 10.7, 13.8, 27.4, 29.1, 74.0, 124.2 (q, J=3.5 Hz), 127.0 (q, J=3.7 Hz), 129.8, 130.3, 131.6 (q, J=33 Hz), 132.6, 135.1, 172.4, 178.5; *m/z* (EI) Found $(M-Bu)^+$, 461.0748 (34%), $C_{19}H_{24}F_3O_2Sn$ requires 461.0750, 347 (19), 131 (100).

4.1.11. 4-(2-Methoxycarbonylphenyl)-3-tributylstannylfuran-2(5*H*)-one (5g). Reaction of 3,4-bis(tributylstannyl)-furan-2(5*H*)-one (**4a**) (500 mg, 0.755 mmol) and methyl-2-iodobenzoate (135 mg, 0.755 mmol) gave furanone (**5g**) after purification by column chromatography (R_f 0.21, ether/petrol, 1:3) as a clear colourless oil (195 mg, 51%). ν_{max} 1726, 1619, 1594; δ_H ($CDCl_3$) 0.77–1.55 (27H, m), 3.86 (3H, s), 5.03 (2H, t, J=3.5 Hz), 7.23 (1H, dd, J=1.0, 7.5 Hz), 7.55 (1H, ddd, J=1.5, 7.5, 7.4 Hz), 7.63 (1H, ddd, J=1.5, 7.5, 7.5 Hz), 8.10 (1H, dd, J=1.0, 7.5 Hz); δ_C ($CDCl_3$) 9.4, 13.4, 27.0, 28.6, 52.0, 74.6, 128.6, 129.0, 130.2, 130.7, 132.2, 136.2, 165.9, 176.7, 178.3; *m/z* (EI) Found $(M-Bu)^+$, 451.0953 (9%), $C_{20}H_{27}O_4Sn$ requires 451.0931, 313 (40), 253 (19), 211 (79), 186 (24), 131 (12).

4.1.12. 4-(2-Thienyl)-3-tributylstannylfuran-2(5*H*)-one (5h). Reaction of 3,4-bis(tributylstannyl)furan-2(5*H*)-one (**4a**) (500 mg, 0.755 mmol) and 2-iodothiophene (158 mg, 0.755 mmol) gave furanone (**5h**) after purification by column chromatogaphy (R_f 0.31, ether/petrol, 1:4) as a clear colourless oil (75 mg, 22%). ν_{max} 1736, 1610, 1580; δ_H ($CDCl_3$) 0.84–1.55 (27H, m), 5.08 (2H, t, J=3.0 Hz), 7.15 (1H, dd, J=3.5, 5.0 Hz), 7.23 (1H, dd, J=1.0, 3.5 Hz), 7.52 (1H, dd, J=1.0, 5.0 Hz); δ_C ($CDCl_3$) 10.8, 13.6, 27.2, 29.0, 73.1, 127.5, 127.7, 128.1, 129.0, 135.7, 165.3, 178.7; *m/z* (EI) Found $(M-Bu)^+$, 399.0439 (100%), $C_{16}H_{23}O_2SSn$ requires 399.04407, 285 (56), 121 (10).

Method B. To a stirred solution of organohalide in dry deoxygenated THF (typically 3–5 mL) under an argon atmosphere, was added $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%) and copper(I) iodide (8 mol%). After 10 min at ambient temperature, the mixture was heated to 50°C and (**4a**), as a solution in THF (3–5 mL), was added by syringe. After 18–24 h at 50°C, the product mixture was gravity filtered and the solvent removed in vacuo to produce a yellow/brown oil. Purification by flash chromatography on silica gel (ether/petrol 1:19 to 2:3), afforded (**5b**, **5e** and **5f**) in varying yield as clear colourless oils.

4.1.13. 3-Tributylstannyl-4-(1-naphthyl)furan-2(5*H*)-one (5b). Reaction of 1-iodonaphthalene (0.15 g, 0.60 mmol, 88 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.40 g, 0.60 mmol) in THF (10 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel (R_f 0.48 ether/petrol, 2:3), afforded (**5b**), (0.12 g, 0.24 mmol, 40%). ν_{max} 2956, 1740, 1589; δ_H ($CDCl_3$), 0.65–1.34 (m, 27H), 5.10 (s), 7.30–7.94 (m, 7H); δ_C ($CDCl_3$) 10.0, 13.9, 27.5, 29.3, 76.5, 125.1, 125.3, 125.4, 127.0, 127.4, 129.0, 129.9, 131.1, 132.6, 133.9, 134.8, 174.8, 178.9; *m/z* (CI, NH_3) Found 443.1028 $(M-n\text{-}Bu)^+$, 25, $C_{22}H_{27}SnO_2$ requires 443.1033; 269 (15), 211 (100), 181 (10), 153 (20).

4.1.14. 3-Tributylstannyl-4-(*o*-methoxyphenyl)furan-2(5*H*)-one (5e). Reaction of *o*-iodomethoxybenzene (28 mg, 0.12 mmol, 16 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (80 mg, 0.12 mmol) in THF (2 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel (R_f 0.40, ether/petrol 2:3), afforded (**5e**), (23 mg, 0.05 mmol, 40%). ν_{max} 2956, 1736, 1592; δ_H ($CDCl_3$) δ 0.80–1.62 (27H, m), 3.83 (3H, s), 5.09 (1H, s), 6.93–7.41 (4H, m); δ_C ($CDCl_3$) 10.3, 13.9, 27.5, 29.1, 55.6, 75.2, 111.1, 120.8, 123.6, 129.7, 131.4, 131.5, 156.8, 173.7, 179.1. *m/z* (CI, NH_3) Found 423.0968 $(M-n\text{-}Bu)^+$, 20, $C_{19}H_{27}SnO_3$ requires 423.0982; 269 (10), 191 (100).

4.1.15. 3-Tributylstannyl-4-(*o*-nitrophenyl)furan-2(5*H*)-one (5f). Reaction of *o*-iodonitrobenzene (75 mg, 0.30 mmol), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel (R_f 0.27, ether/petrol, 2:3), afforded (**5f**), (68 mg, 0.14 mmol, 47%). ν_{max} 2956, 1740, 1594; δ_H ($CDCl_3$), 0.76–1.65 (27H, m), 5.02 (2H, s), 7.30–8.23 (4H, m); δ_C ($CDCl_3$) 10.1, 13.9, 27.5, 29.2, 75.6, 125.5, 130.7, 130.8, 131.0, 133.3, 134.1, 147.6, 172.6, 178.2. *m/z* (CI, NH_3) Found 438.0703 $(M-n\text{-}Bu)^+$, 100, $C_{18}H_{24}SnO_4N$ requires 438.0727; 361 (65), 270 (45), 206 (40), 138 (25).

4.1.16. 3-Tributylstannyl-4-benzylfuran-2(5*H*)-one (5i). Reaction of benzyl bromide (55 mg, 0.32 mmol, 38 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.21 g, 0.32 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel (R_f 0.54, ether/petrol 2:3), afforded (**5i**), (14 mg, 0.03 mmol, 9%). ν_{max} 2961, 1741, 1611; δ_H ($CDCl_3$), 0.87–1.68 (27H, m), 3.80 (2H, s), 4.58 (2H, s), 7.13–7.16 (2H, m), 7.28–7.38 (3H, m); δ_C ($CDCl_3$) 10.4, 12.2, 27.7, 29.6, 37.4, 74.5, 127.7, 128.8, 129.4, 129.8, 137.0, 176.3, 179.2. *m/z* (CI, NH_3) Found 407.1041 $(M-n\text{-}Bu)^+$, 60, $C_{19}H_{27}SnO_2$ requires 407.1033; 175 (100), 91 (35).

4.1.17. 3-Tributylstannyl-4-(prop-2-enyl)furan-2(5*H*)-one (5j). Reaction of allyl bromide (36 mg, 0.30 mmol, 26 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel (R_f 0.43, ether/petrol 2:3), afforded (**5j**), (29 mg, 0.07 mmol, 23%). ν_{max} 2956, 1740, 1578; δ_H ($CDCl_3$), 0.83–1.64 (27H, m), 3.21 (2H, d, J=6.5 Hz), 4.72 (2H, s), 5.11–5.20 (2H, m), 5.71–5.84 (1H, m); δ_C ($CDCl_3$) 10.3, 14.1, 27.9, 29.4, 35.4, 74.5, 118.8, 129.5, 133.4, 175.8, 179.3. *m/z* $(EI)^+$ Found $(M-Bu)^+$, 357.0855 (100%), $C_{15}H_{25}O_2Sn$ requires 357.0877, 328 (15). 291 (70), 253 (55), 211 (17), 152 (15), 125 (45), 66 (32).

4.1.18. 4-Benzoyl-3-tributylstannylfuran-2(5*H*)-one (5k). 3,4-Bis(tributylstannyl)furan-2(5*H*)-one (**4a**) (500 mg, 0.755 mmol) and benzoyl chloride (106 mg, 0.755 mmol) were combined under a carbon monoxide atmosphere with benzylchlorobistriphenylphosphinepalladium(II) in chloroform (10 mL). The mixture was heated to 55°C under an atmospheric pressure of carbon monoxide for 18 h, by which time the reaction mixture was black in colour. The reaction mixture was concentrated in vacuo and purification by column chromatography (R_f 0.28, ether/petrol 1:3) yielded furanone (**5k**) as an orange oil (120 mg, 33%). ν_{max} 1751, 1700, 1663; δ_H ($CDCl_3$) 0.81–1.40 (27H, m), 5.10 (2H, t, J=4.0 Hz), 7.52–7.90 (5H, m); δ_C ($CDCl_3$) 10.3, 13.6, 27.1, 28.8, 73.8, 129.1, 129.6, 129.8, 134.7, 135.8, 139.4, 170.4, 177.5, 193.2; *m/z* (EI) Found $(M-Bu)^+$, 421.0837 (100%), $C_{19}H_{25}O_3Sn$ requires 421.0825, 307 (21), 329 (15), 149 (19), 105 (99).

4.1.19. 4-(*E*)-(2-Phenylethenyl)-3-tributylstannylfuran-2(5*H*)-one (5l). β-Bromostyrene (138 mg, 0.755 mmol) and triphenylarsine (18.4 mg, 0.08 equiv.) were combined in dry deoxygenated DMF (5 mL). 3,4-Bis(tributylstannyl)-furan-2(5*H*)-one (**4b**) (500 mg, 0.755 mmol) was added in deoxygenated DMF (5 mL). Tris(dibenzylideneacetone)-dipalladium(II) (13.7 mg, 0.02 equiv.) was added to give a purple solution which changed to lime green in colour over 10 min. The reaction mixture was stirred under an argon atmosphere at 50°C for 18 h. The reaction mixture was concentrated in vacuo and purification by column

chromatography (R_f 0.32, ether/petrol, 1:3) gave furanone (**5l**) as a clear colourless oil (126 mg, 35%). ν_{max} 1743, 1727, 1624; δ_H ($CDCl_3$) 0.88–1.61 (27H, m), 5.08 (2H, br.s), 6.80 (1H, d, J=16.0 Hz), 7.06 (1H, d, J=16.0 Hz), 7.34–7.47 (5H, m); δ_C ($CDCl_3$) 10.3, 13.7, 27.3, 29.0, 71.8, 121.6, 127.2, 129.1, 129.6, 131.9, 135.5, 135.7, 169.8, 178.9; *m/z* (EI) Found $(M-Bu)^+$, 419.1029 (100%), $C_{20}H_{27}O_2Sn$ requires 419.1033, 305 (44), 259 (11), 141 (90).

4.2. Protodestannylation of stannylfuranones 5a–5l

General procedure. To a stirred solution of 4-aryl-3-stannylfuran-2(5*H*)-one (50–100 mg) in methanol (5 mL) was added a solution of 50% TFA (aq) (1.0 mL). The mixture was stirred at room temperature for 18–24 h. The solvent was removed in vacuo and purification by column chromatography and recrystallisation from petrol yielded 4-arylfuranones as colourless needles.

4.2.1. 4-Phenylfuran-2(5*H*)-one (9a).[1] Reaction of 4-phenyl-3-tributylstannylfuran-2(5*H*)-one (**5a**) (50 mg, 0.11 mmol) and 50% TFA (aq) gave furanone **9a** after purification by column chromatography (R_f 0.25, ether/petrol, 1:1) as colourless needles (15 mg, 85%) mp 95–96°C (from petrol). ν_{max} ($CHBr_3$) 1783, 1746, 1624, 1596; δ_H ($CDCl_3$) 5.21 (2H, d, J=2.0 Hz), 6.36 (1H, t, J=2.0 Hz), 7.43–7.51 (5H, m); δ_C ($CDCl_3$) 71.0, 113.1, 126.4, 129.3, 129.6, 131.8, 163.9, 173.8; *m/z* (EI) Found $(M)^+$, 164.0521 (62%), $C_{10}H_8O_2$ requires 160.0524, 131 (100), 103 (80), 102 (70), 77 (40), 51 (27).

4.2.2. 4-(1-Napthyl)-furan-2(5*H*)-one (9b).[1] Reaction of 4-(1-napthyl)-3-tributylstannylfuran-2(5*H*)-one (**5b**) (60 mg, 0.12 mmol) and 50% TFA (aq) gave furanone **9b** after purification by column chromatography (R_f 0.42, ether/petrol, 1:1) as colourless needles (20 mg, 80%) mp 98–100°C (petrol). ν_{max} 1736, 1685; δ_H ($CDCl_3$) 5.20 (2H, d, J=2.0 Hz), 6.39 (1H, t, J=2.0 Hz), 7.19–7.55 (4H, m), 7.85–8.07 (3H, m); δ_C ($CDCl_3$) 73.6, 119.3, 124.6, 125.4, 125.9, 127.2, 128.1, 128.9, 129.5, 130.7, 131.6, 134.3, 164.3, 174.0; *m/z* (CI, NH_3) Found $(MH)^+$, 211.0751 (100%), $C_{14}H_{11}O_2$ requires 211.0759, 181 (7), 165 (20), 152 (15).

4.2.3. 4-(2-methylphenyl)-furan-2(5*H*)-one (9c).[1] Reaction of 4-(2-methylphenyl)-3-tributylstannylfuran-2(5*H*)-one (**5c**) (50 mg, 0.108 mmol) and 50% TFA (aq) gave furanone **9c** after purification by column chromatography (R_f 0.28, ether/petrol, 1:1) as colourless needles (17 mg, 95%) mp 66–67°C (pentane). ν_{max} ($CHBr_3$) 1780, 1749, 1615, 1571; δ_H ($CDCl_3$) 2.48 (3H, s), 5.19 (2H, d, J=2.0 Hz), 6.27 (1H, t, J=2.0 Hz), 7.26–7.40 (4H, m); δ_C ($CDCl_3$) 22.0, 72.3, 117.2, 126.6, 127.3, 129.7, 130.7, 132.0, 137.3, 163.8, 174.0; *m/z* (EI) Found $(M)^+$, 174.0684 (86%), $C_{11}H_{10}O_2$ requires 174.0680, 145 (100), 117 (44), 116 (52), 115 (85), 91 (17).

4.2.4. 4-(3-Trifluromethylphenyl)-furan-2(5*H*)-one (9d).[1] Reaction of 4-(3-trifluromethylphenyl)-3-tributylstannylfuran-2(5*H*)-one (**5d**) (50 mg, 0.096 mmol) and 50% TFA (aq) gave furanone **9d** after purification by column chromatography (R_f 0.19, ether/petrol, 1:1) as colourless needles (20 mg, 91%) mp 127–129°C (petrol). ν_{max} ($CHBr_3$) 1782, 1749, 1628; δ_H ($CDCl_3$) 5.27 (2H, d, J=2.0 Hz), 6.49 (1H, t, J=2.0 Hz) 7.63–7.79 (4H, m); δ_C ($CDCl_3$) 70.8, 114.9,123.1 (q, J=3.7 Hz), 128.2 (q, J=3.7 Hz), 129.6, 130.0, 130.5, 131.8, 162.0, 173.0; *m/z* (EI) Found $(M)^+$, 228.0398 (36%), $C_{11}H_7F_3O_4$ requires 228.0398, 199 (100), 171 (32), 170 (24), 151 (21).

4.2.5. 4-(2-Methoxyphenyl)-furan-2(5*H*)-one (9e).[1] Reaction of 4-(2-methoxyphenyl)-3-tributylstannylfuran-2(5*H*)-one (**5e**) (40 mg, 0.083 mmol) and 50% TFA (aq) gave furanone **9e** after purification by column chromatography (R_f 0.38, ether/petrol, 1:1) as colourless needles (14 mg, 88%) mp 85–86°C (petrol). ν_{max} 3089, 1736, 1681; δ_H ($CDCl_3$) 3.86 (3H, s), 5.20 (2H, d, J=2.0 Hz), 6.49 (1H, t, J=2.0 Hz), 6.92 (2H, m), 7.33–7.39 (3H, m); δ_C ($CDCl_3$) 55.9, 73.2, 112.1, 115.3, 119.2, 121.4, 128.8, 133.3, 158.8, 161.4, 175.1; *m/z* (CI, NH_3) Found $(MH)^+$, 191.0701 (100%), $C_{11}H_{11}O_3$ requires 191.0708, 181 (7), 162 (25).

4.2.6. 4-(2-Nitrophenyl)-furan-2(5*H*)-one (9f).[1] Reaction of 4-(2-nitrophenyl)-3-tributylstannylfuran-2(5*H*)-one (**5f**) (16 mg, 0.03 mmol) and 50% TFA (aq) gave furanone **9f** after purification by column chromatography (R_f 0.32, ether) as colourless needles (5 mg, 82%) mp 181–182°C (petrol). ν_{max} (paraffin) 1751; δ_H (CD_3OD) 5.10 (d, 2H, J=2.0 Hz), 6.18 (t, 1H, J=2.0 Hz), 7.42–7.46 (m, 1H), 7.66–7.80 (m, 2H), 8.14–8.18 (m, 1H); δ_C (CD_3OD) 74.4, 118.8, 126.0, 127.6, 131.5, 132.4, 134.9, 148.8, 166.0, 175.2; *m/z* (CI, NH_3) Found $(MH)^+$, 206.0442 (100%), $C_{10}H_8NO_4$ requires 206.0453, 223 (70), 291 (100), 133 (10).

4.2.7. 4-(2-Methoxycarbonylphenyl)-furan-2(5*H*)-one (9g).[1] Reaction of 4-(2-methoxycarbonylphenyl)-3-tributylstannylfuran-2(5*H*)-one (**5g**) (50 mg, 0.098 mmol) and 50% TFA (aq) gave furanone **9g** after purification by column chromatography (R_f 0.19, ether/petrol, 1:1) as colourless needles (19 mg, 89%) mp 94–95°C (petrol). ν_{max} ($CHBr_3$) 1779, 1748, 1721 1624, 1597; δ_H ($CDCl_3$) 3.89 (3H, s) 5.09 (2H, d, J=2.0 Hz), 7.31 (1H, dd, J=1.0, 7.5 Hz), 7.54 (1H, ddd, J=1.5, 7.5, 7.5 Hz), 7.62 (1H, ddd, J=1.5, 7.5, 7.5 Hz), 8.03 (1H, dd, J=1.0, 7.5 Hz); δ_C ($CDCl_3$) 52.6, 73.5, 117.3, 129.1, 130.0, 130.9, 132.5, 132.6, 166.6, 167.4, 173.4; *m/z* (EI) Found $(M)^+$, 218.0575 (16%), $C_{12}H_{10}O_4$ requires 218.0579, 186 (100), 158 (48), 130 (29), 77 (17).

4.2.8. 4-(2-Thienyl)-furan-2(5*H*)-one (9h).[1] Reaction of 4-(2-thienyl)-3-tributylstannylfuran-2(5*H*)-one (**5h**) (50 mg, 0.110 mmol) and 50% TFA (aq) gave furanone **9h** after purification by column chromatography (R_f 0.32, ether/petrol, 1:1) as colourless needles (16 mg, 88%) mp 96–97°C (petrol). ν_{max} ($CHBr_3$) 1778, 1744, 1616; δ_H ($CDCl_3$) 5.18 (2H, d, J=1.5 Hz), 6.17 (1H, br. s) 7.15 (1H, dd, J=3.5, 5.0 Hz), 7.32 (1H, br. d, J=3.5 Hz), 7.57 (1H, br. s, J=5.0 Hz); δ_C ($CDCl_3$) 70.9,111.3, 128.4, 128.5, 130.5, 132.9, 157.1, 173.5; *m/z* (EI) Found $(M)^+$, 166.0083 (100%), $C_8H_6O_2S$ requires 166.0088, 137 (85), 108 (53), 65 (7), 44 (20).

4.2.9. 4-Benzylfuran-2(5*H*)-one (9i).[1] Reaction of 4-benzyl-3-tributylstannylfuran-2(5*H*)-one (**5i**) (60 mg, 0.173 mmol) and 50% TFA (aq) gave furanone **9i** after purification by column chromatography (R_f 0.33, ether/

petrol, 1:1) as a clear colourless oil (26 mg, 86%). ν_{max} 3031, 1717, 1685; δ_H ($CDCl_3$) 3.67 (2H, s), 4.65 (2H, m), 5.75 (1H, m), 7.10–7.13 (2H, m), 7.22–7.33 (3H, m); δ_C ($CDCl_3$) 35.7, 73.1, 117.1, 127.9, 129.1, 129.5, 135.9, 169.4, 174.1; *m/z* (CI, NH_3) Found $(MH)^+$, 175.0765 (100%), $C_{11}H_{11}O_2$ requires 175.0759, 115 (10), 96 (45), 91 (15).

4.2.10. 4-(Allyl)-furan-2(5*H*)-one (9j). Reaction of 4-(allyl)-3-tributylstannylfuran-2(5*H*)-one (**5j**) (60 mg, 0.145 mmol) and 50% TFA (aq) gave furanone **9j** after purification by column chromatography (R_f 0.32, ether/petrol, 1:1) as a clear colourless oil (13 mg, 73%). ν_{max} 2927, 1748, 1685, 1653; δ_H ($CDCl_3$) 3.11 (2H, m), 4.69 (2H, dt, *J*=1.0, 2.0 Hz), 5.11–5.20 (2H, m), 5.70–5.84 (1H, m); δ_C ($CDCl_3$) 33.3, 73.2, 116.6, 119.7, 131.9, 168.8, 174.2; *m/z* (CI, NH_3) Found $(MH)^+$, 125.0604 (100%), $C_7H_8O_2$ requires 125.0602, 95 (20), 83 (10), 67 (15), 39 (13).

4.2.11. 4-Benzoylfuran-2(5*H*)-one (9k).[8] Reaction of 4-benzoyl-3-tributylstannylfuran-2(5*H*)-one (**5k**) (50 mg, 0.105 mmol) with 50% TFA (aq) gave furanone **9k** after purification by column chromatography (R_f 0.28, ether/petrol, 1:3), as colourless needles (18 mg, 90%) mp 101–102°C (petrol). ν_{max} ($CHBr_3$) 1782, 1750, 1652; δ_H ($CDCl_3$) 5.13 (2H, t, *J*=2.0 Hz) 6.43 (1H, t, *J*=2.0 Hz) 7.47–7.84 (5H, m); δ_C ($CDCl_3$) 72.3, 125.8, 129.7, 135.1, 136.3, 160.2, 172.8, 189.7; *m/z* (EI) Found $(MH)^+$, 189.0546 (100%), $C_{11}H_8O_3$ requires 188.0473, 105 (73), 77 (17), 59 (10).

4.2.12. 4-((*E*)-2-Phenylethenyl)-furan-2(5*H*)-one (9l).[8] 4-((*E*)-2-Phenylethenyl)-3-tributylstannylfuran-2(5*H*)-one (**5l**) (50 mg, 0.105 mmol) was dissolved in methanol (5 mL). A solution of 50% TFA (aq) (1.0 mL) was added, and the mixture stirred at room temperature overnight. The solvent was removed in vacuo and column chromatography (R_f 0.28, diethyl ether/petrol, 1:3) gave the furanone **9l** as colourless needles (18 mg, 92%) mp 118–120°C (from ether/petrol 1:1). ν_{max} ($CHBr_3$) 1778, 1744, 1634, 1590; δ_H ($CDCl_3$) 5.03 (2H, d, *J*=1.0 Hz) 5.96 (1H, br. s), 6.80 (1H, d, *J*=16.5 Hz) 7.00 (1H, d, *J*=16.5 Hz) 7.30–7.44 (5H, m); δ_C ($CDCl_3$) 70.4, 115.6, 118.6, 127.4, 129.0, 130.0, 134.8, 137.2, 161.9, 173.9; *m/z* (EI) Found $(M)^+$, 186.0682 (25%), $C_{12}H_{10}O_2$ requires 186.0681, 141 (100), 128 (52), 102 (10), 77 (11), 51 (20).

4.3. Optimization studies: synthesis of 3-tributylstannyl-4-phenylfuran-2(5*H*)-one (5a)

General method. To a stirred solution of iodobenzene in dry deoxygenated THF, DMF, CH_2Cl_2, MeOH, 1,2-DME or NMP (2–3 mL) were added certain additives. After 10 min at ambient temperature, the mixture was heated to the apposite temperature. Furanone (**4a**) was then added via syringe, as a solution in the appropriate solvent. After the allotted reaction time, the product mixture was filtered and the solvent removed in vacuo to produce the crude product as an oil. Purification by flash chromatography on silica gel afforded (**5a**) in varying yields as a colourless oil. The numbers at the beginning of each paragraph are those associated with the entry in Table 2.

(1) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), Pd_2dba_3 (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (71 mg, 0.16 mmol, 35%).

(2) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), Pd_2dba_3 (2 mol%), tri-(2-furyl)phosphine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (65 mg, 0.14 mmol, 31%).

(3) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $Pd(PPh_3)_4$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50° C, followed by purification by flash chromatography on silica gel afforded (**5a**), (48 mg, 0.11 mmol, 24%).

(4) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(MeCN)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (65 mg, 0.14 mmol, 32%).

(5) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PhCN)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (69 mg, 0.15 mmol, 33%).

(7) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $Pd(dppb)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) were heated in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (55 mg, 0.12 mmol, 27%) and (**10**), (42 mg, 0.18 mmol, 39%).

(8) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (77 mg, 0.17 mmol, 38%).

(9) Reaction of iodobenzene (184 mg, 0.90 mmol, 101 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (75 mg, 0.17 mmol, 37%).

(10) Reaction of iodobenzene (47 mg, 0.23 mmol, 26 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (53 mg, 0.12 mmol, 26%).

(13) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL),

$PdCl_2(PPh_3)_2$ (2 mol%), tri-(2-furyl)phosphine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (48 mg, 0.11 mmol, 24%).

(14) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 18–24 h at 50°C. A second addition of $PdCl_2(PPh_3)_2$ (2 mol%) was made and the reaction mixture stirred at 50°C for a further 18–24 h, followed by purification by flash chromatography on silica gel afforded (**5a**), (85 mg, 0.19 mmol, 42%).

(15) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in THF (6 mL) for 1 week at ambient temperature, followed by purification by flash chromatography on silica gel afforded (**5a**), (36 mg, 0.08 mmol, 18%).

(16) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in DMF (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (59 mg, 0.13 mmol, 29%) and (**10**), (30 mg, 0.13 mmol, 28%).

(17) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in DMF (6 mL) for 18–24 h at 70°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (57 mg, 0.13 mmol, 28%) and (**10**), (30 mg, 0.13 mmol, 28%).

(18) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in DMF (6 mL) for 18–24 h at 90°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (51 mg, 0.11 mmol, 25%) and (**10**), (38 mg, 0.16 mmol, 36%).

(19) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in MeOH (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (24 mg, 0.05 mmol, 12%) and (**10**), (29 mg, 0.12 mmol, 27%).

(20) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in 1,2-DME (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (41 mg, 0.09 mmol, 30%).

(21) Reaction of iodobenzene (92 mg, 0.45 mmol, 50 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.30 g, 0.45 mmol) in NMP (6 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (51 mg, 0.11 mmol, 25%).

(22) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in CH_2Cl_2 (4 mL) for 72 h at ambient temperature, followed by purification by flash chromatography on silica gel afforded (**5a**), (37 mg, 0.08 mmol, 27%).

(23) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (5 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) were heated in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (50 mg, 0.11 mmol, 37%).

(24) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (10 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (39 mg, 0.09 mmol, 29%).

(25) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (15 mol%), triphenylarsine (8 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (15 mg, 0.03 mmol, 11%).

(26) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (20 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (53 mg, 0.12 mmol, 39%).

(27) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (0.5 equiv.) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (39 mg, 0.09 mmol, 29%).

(28) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) iodide (2 equiv.) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (59 mg, 0.13 mmol, 44%).

(29) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (24 mg, 0.05 mmol, 18%).

(30) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), copper(I) iodide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (53 mg, 0.12 mmol, 39%).

(31) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%),

copper(I) cyanide (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (48 mg, 0.11 mmol, 36%).

(32) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) chloride (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (36 mg, 0.08 mmol, 27%).

(34) Reaction of iodobenzene (61 mg, 0.30 mmol, 34 μL), $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%), copper(I) thiophene-2-carboxylate (8 mol%) and (**4a**), (0.20 g, 0.30 mmol) in THF (4 mL) for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (55 mg, 0.12 mmol, 41%).

(35) To a solution of iodobenzene (61 mg, 0.30 mmol, 34 μL) in THF (2 mL) under an argon atmosphere, was added $PdCl_2(PPh_3)_2$ (2 mol%), triphenylarsine (8 mol%) and copper(I) iodide (8 mol%). The mixture was heated to 50°C and (**4a**), (0.20 g, 0.30 mmol) was added in THF (2 ml) by syringe pump over 8 h. The reaction mixture was stirred in total for 18–24 h at 50°C, followed by purification by flash chromatography on silica gel afforded (**5a**), (37 mg, 0.08 mmol, 27%).

4.3.1. 3-Iodo-4-tributylstannylfuran-2(5*H*)-one (13). Iodine (383 mg, 1.51 mmol) and 3,4-bistributylstannylfuran-2(5*H*)-one (**4a**) (1.0 g, 1.51 mmol) were combined in dichloromethane (10 mL) and cooled to 0°C under an argon atmosphere. The flask was wrapped in aluminium foil, the mixture allowed to warm to ambient temperature and stirred for 18 h in the absence of light. Solid potassium fluoride (87 mg, 1.51 mmol) was added and the mixture stirred for 3 h. The mixture was filtered through Celite® and the solvent removed in vacuo. Purification by column chromatography (R_f 0.38, ether/petrol, 1:4) in the absence of light yielded furanone **13** as a clear colourless oil (0.65 g, 87%). ν_{max} 2924, 2871, 2851, 1758, 1556, 1464; δ_H ($CDCl_3$) 0.87–1.56 (27H, m), 4.86 (2H, s); δ_C ($CDCl_3$) 10.1, 13.6, 27.2, 29.0, 80.7, 95.9, 170.6, 180.0; *m/z* (EI) Found $(M-Bu)^+$, 442.9537 (44%), $C_{12}H_{20}O_2SnI$ requires 442.9530, 386 (21), 329 (30), 247 (18), 177 (13), 121 (19).

4.3.2. 3-Iodofuran-2(5*H*)-one (14). *Method A*. To a stirred solution of 3-iodo-4-tributylstannylfuran-2(5*H*)-one (**13**) (100 mg, 0.2 mmol) in methanol (5 mL) cooled to 0°C was added a solution of 50% aqueous TFA (1.0 mL). The flask was wrapped in aluminium foil, the mixture allowed to warm to ambient temperature and stirred in the absence of light for 20 h. The solvent was removed in vacuo and purification by column chromatography (R_f 0.26, ether/petrol, 1:1) in the absence of light furnished the iodide **14** as colourless needles (20 mg, 48%) mp 102–103°C (ether). ν_{max} ($CHBr_3$) 1765, 1594, 1491, 1441; δ_H ($CDCl_3$), 4.82 (2H, d, J=2.0 Hz), 7.78 (1H, t, J=2.0 Hz); δ_C ($CDCl_3$) 74.0, 85.0, 157.5, 170.7; *m/z* (EI) Found $(M)^+$, 209.9140 (100%), $C_4H_2O_2I$ requires 209.9178, 181 (87), 153 (37), 126 (24), 83 (33), 53 (29).

Method B. Iodine (136 mg, 0.54 mmol) and 3-tributylstannyl-furan-2(5*H*)-one (**4a**) (200 mg, 0.54 mmol) were combined in dichloromethane (10 mL) and cooled to 0°C under an argon atmosphere. The mixture was allowed to warm to ambient temperature and stirred for 18 h. Solid KF (31 mg, 0.54 mmol) was added and the mixture stirred for 3 h. The mixture was filtered through Celite® and the solvent removed in vacuo. Purification by column chromatography (R_f 0.26, ether/petrol, 1:1) in the absence of light furnished the iodide **14** as a colourless needles (55 mg, 50%); the physical data associated with this compound exactly matched that of the material obtained using Method A.

4.3.3. 3,4-Bisiodofuran-2(5*H*)-one (15). Iodine (767 mg, 3.0 mmol) and 3,4-bistributylstannylfuran-2(5*H*)-one (**4a**) (1.0 g, 1.51 mmol) were combined in dichloromethane (10 mL) and cooled to 0°C under an argon atmosphere. The mixture was allowed to warm to ambient temperature and stirred for 120 h in the absence of light. Solid potassium fluoride (174 mg, 3.0 mmol) was added and the mixture stirred for 3 h. The mixture was filtered through Celite® and the solvent removed in vacuo. Purification by column chromatography (R_f 0.52, ether/petrol, 1:1) in the absence of light gave furanone **15** as a clear colourless oil (0.38 g, 76%) mp 140–141°C (ether). ν_{max} ($CHBr_3$) 1773, 1748, 1578; δ_H ($CDCl_3$) 4.77 (2H, s); δ_C ($CDCl_3$) 80.3, 99.3, 128.6, 169.0; *m/z* (EI) Found $(M)^+$, 335.8144 (74%), $C_4H_2O_2I_2$ requires 335.8144, 209 (100), 165 (30), 127 (37).

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