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Regiospecific Synthesis of 3,4-Disubstituted Furans and 3-Substituted Furans Using 3,4-Bis(tri-*n*-butylstannyl)furan and 3-(Tri-*n*-butylstannyl)furan as Building Blocks[1,2,3]

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Abstract: 3,4-Bis(tri-*n*-butylstannyl)furan and 3-(tri-*n*-butylstannyl)furan have been prepared and used successfully as building blocks to lead to various 3,4-disubstituted furans and 3-substituted furans, respectively.

INTRODUCTION

Furan nucleus abounds in naturally occurring oxygen-containing compounds.[5] They are divided according to their structural features into furanosesquiterpenes, furanocembranolides and furanoid fatty acids, etc. Many of these furan natural products have interesting biological activities, such as cytotoxic and antitumor properties,[6,7] antispasmodic,[8] antifeeding,[9] and several other potentially useful activities. More natural furan-containing compounds continue to be found at a rapid pace.[10]

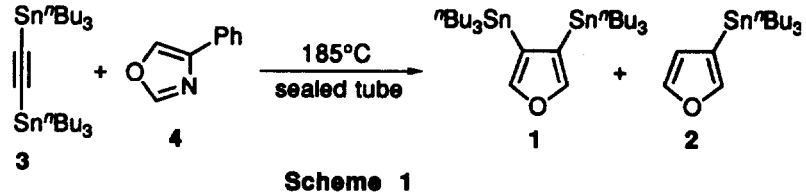
In addition to being important building blocks found in natural molecules with pharmaceutical implications, polysubstituted furans[11] appear also especially worthy of study because they can serve as starting materials for the syntheses of natural and non-natural products.[12] Nevertheless, the tendency of furans to undergo both lithiation and electrophilic substitution at C-2 or C-5[13] makes the synthesis of 3,4-disubstituted furans an exceedingly challenging task. To evade this, several special methods have been blueprinted.[14] We would like to report herein the preparation of 3,4-bis(tri-*n*-butylstannyl)furan (**1**) and its pivotal role as a prominent building block for 3,4-disubstituted furan. Recent works on the conversion of trialkylstannylfurans[15] to 3-substituted furans also prompted us to disclose our own results on the preparation of similar compounds utilizing 3-(tri-*n*-butylstannyl)furan (**2**), which was unexpectedly isolated as a side product in our preparation of **1**.

RESULTS AND DISCUSSION

(a) Preparation of 3,4-bis(tri-*n*-butylstannyl)furan (1) and 3-(tri-*n*-butylstannyl)furan (2)

Due to the large kinetic β-effect exhibited by stannyl groups,[16] it was expected that **1** and **2** would lead efficiently to 3,4-disubstituted and 3-substituted furans, respectively. The preparation of **1** and the side product **2** is shown in Scheme 1. The strategy to be employed for the preparation of **1** was the alkyne-oxazole Diels-

Alder cycloaddition and cycloreversion. Thus, a solution of bis(tri-*n*-butylstannyl)acetylene (3) and 4-phenyloxazole (4)[17] was thermolyzed in a sealed tube at 185°C for 10 days to give a separable mixture of 1 and the known 2[15c] in 22% and 10%, respectively. The formation of 2 was likely due to the decomposition of 1. Higher reaction temperatures were also tried but these only resulted in extensive decomposition, because of the weakness of the C-Sn bond. While at lower temperatures the reaction was much slower. One of the major reasons for the low yield was that the tri-*n*-butylstannyl group is very bulky, thus resulting in greater steric congestion in the addition product. A compromise between the two contradicting thermal factors therefore gave a lower yield of 1 as well as generated the undesired 2. Another factor for the low yield of 1 might be attributed to the inverse electronic demands of the Diels-Alder reaction,[18] with the electron-rich dienophile being 3 and the electron-deficient diene being 4.



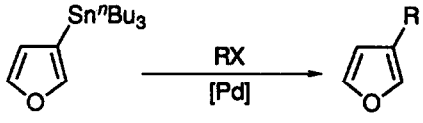
3 4 1 2

Scheme 1

All efforts to recover the unreacted 3 from the reaction mixture by either chromatography or distillation were met with failure. On silica gel columns, severe destannylation of the unreacted 3 as well as the products occurred, whereas the low resolution capacity of neutral alumina rendered the separation of 3 from 1 and 2 impractical. Distillation of organostannanes usually required high temperatures at or above 200°C, even under a high vacuum of 0.01 mmHg, and hence could not be used because this would destroy 1. Because of the above difficulties, 3 was eventually destroyed by absorbing on activated alumina. Furan 2, nevertheless, was separated from 1 by distillation, b.p. 80°C (0.01 mmHg), leaving 1 as a high boiling residue which was further purified by chromatography on a short column of neutral alumina.

(b) Palladium-catalyzed coupling reactions of 3-(tri-*n*-butylstannyl)furan (2)[19,20]

With an aim to solidify the role of 2 as a versatile precursor for the syntheses of 3-substituted furans,[15b,c,e,f] a systematic study of 2 was carried out, in which both palladium-catalyzed coupling reaction as well as palladium-catalyzed carbonylation reaction were executed. Table 1 lists the reaction conditions and yields of the 3-substituted furans 5 from the reactions between 2 and various electrophiles RX (Scheme 2).



2 5

Scheme 2

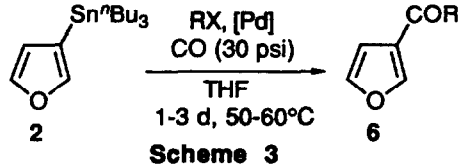
As can be seen in Table 1 and in the Experimental Section, the smooth reaction of 2 with benzoyl chloride catalyzed by $Pd(PPh_3)_2Cl_2$ was in agreement with a previous report (Entry 1).[15f] As an entry to ketones, this reaction has several advantages over the traditional methods. For example, it could tolerate functional groups while the method using lithium derivatives could not.[21a] In addition, it would be devoid of the

over-addition problem which hinders the use of other organometallic reagents such as cadmium, zinc and magnesium.[21] Catalyzed either by $Ph(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ or $Pd(MeCN)_2Cl_2$, **2** coupled also with aryl halides (Entries 2, 3 and 4), vinyl halides (Entries 5, 6, 7, 8 and 9), and an allyl bromide (Entry 10), respectively (Table 1).

Table 1. Palladium-catalyzed coupling reaction of 2 with RX

Entry	RX	[Pd] / solvent	Temperature / time	5 (yield)
1	PhCOCl	$Pd(PPh_3)_2Cl_2$ / THF	60°C / 2 h	**5a** (80%)
2	PhI	$Pd(PPh_3)_2Cl_2$ / DMF	70°C / 2 h	**5b** (75%)
3	*p*-MeC_6H_4I	$Pd(PPh_3)_2Cl_2$-CuI / DMF	r.t. / 2 h	**5c** (72%)
4	PhBr	$Pd(PPh_3)_4$ / DMF	70°C / 1.5 h	**5b** (80%)
5	*trans*-PhCH=CHBr	$Pd(PPh_3)_4$ / HMPA	60°C / 23 h	**5d** (80%)
6	(*Z*)-MeCOCH=C(Me)Br	$Pd(PPh_3)_2Cl_2$ / DMF	70°C / 6 h	**5e** (77%)
7	(*E*)-MeCOCH=C(Me)Br	$Pd(PPh_3)_2Cl_2$ / DMF	70°C / 6 h	**5f** (70%)
8	*trans*-PhCH=CHI	$Pd(PPh_3)_2Cl_2$ / DMF	60°C / 1 h	**5d** (71%)
9	*trans*-*n*-C_5H_{11}CH=CHI	$Pd(PPh_3)_2Cl_2$-CuI / DMF	60°C / 1 d	**5g** (71%)
10	*trans*-EtO_2CCH=$CHCH_2Br$	$Pd(MeCN)_2Cl_2$ / DMF	60°C / 2 h	**5h** (60%)

The palladium-catalyzed carbon monoxide insertion reaction[19,22] is an alternative way to synthesize ketones, especially when the palladium-catalyzed coupling of acid halides with organostannanes could not be employed either because of the difficult access to the starting acid halides or the presence of certain interfering functionalities such as hydroxy and amino groups. The mechanism of the carbonylative coupling has been discussed,[22] in which the transmetallation step is generally believed to be preceded by an CO insertion. However, the direct coupling of RX is still able to compete with the carbonylation, depending upon the relative rate for the reaction of the intermediate $RPdXL_2$ with CO (insertion) and with organostannane (transmetallation). Consequently, the insertion reaction is probably the slow step when the CO pressure is low. Indeed, a carbonylation product will be the sole product when CO pressure is sufficiently high, because the reactivity of the intermediate after an insertion, namely $RCOPdXL_2$ is higher than that of $RPdXL_2$ towards organostannanes.[22] All organohalides that take part in direct coupling reactions are also suitable for carbonylation. Carbonylation can even be performed with organohalides containing a β-hydrogen.[23] The palladium catalysts used and the yield of the 3-acyl furans **6** through the carbonylation reaction of **2** with various RX (Scheme 3) are summarized in Table 2.

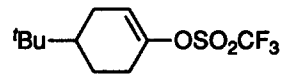


2 **6**

Scheme 3

As shown in Table 2, benzyl bromide underwent the palladium-catalyzed carbonylation with **2** to give good yield of benzyl furan-3-yl ketone (**6a**) (Entry 1), while *trans*-β-iodostyrene and *trans*-1-iodohept-1-ene gave only moderate yields of the corresponding ketones (Entries 2 and 3). The formation of **6b** (Entry 2) was accompanied by 20% yield of a by-product, namely bis(furan-3-yl)ketone (**6i**). In fact, **6i** was obtained as a by-product in all our low yield carbonylation reactions. This implies that **2** might possibly participate in an oxidative-addition-like reaction with palladium in the presence of CO. In the case of 4-*tert*-butyl-cyclohex-1-enyl triflate, it was found that when 2 mol% $Pd_2(dba)_3$ in the presence of 3 mol% tris(furan-2-yl)phosphine in DMF was used, the reaction was fast and gave **6d** in 44% yield after 3 days at 55-60°C (Entry 4).[24] Aryl iodides and 2 coupled without difficulty to give fair yields of ketones (Entries 5 and 6). In particular, methyl *o*-iodobenzoate gave ketone **6e** in 85% yield despite the steric hindrance due to *ortho*-substitution. With ethyl *trans*-4-bromocrotonate, **2** gave poor yield of a mixture of two isomers **6g** and **6h**, the ratio of which being 22:28 (Entry 8). However, egomaketone (**6f**) was generated from 1-bromo-3-methyl-2-butene in 66% yield without suffering from double bond migration (Entry 7) (Table 2).

Table 2. Palladium-catalyzed carbonylation of 2 with RX

Entry	RX	[Pd]	6 (yield)
1	$PhCH_2Br$	$Pd(PPh_3)_2Cl_2$	**6a** (82%)
2	*trans*-PhCH=CHI	$Pd(PPh_3)_4$	**6b** (40%)
3	*trans*-$C_5H_{11}CH$=CHI	$Pd(PPh_3)_2Cl_2$	**6c** (52%)
4*		$Pd_2(dba)_3$ (furan-2-yl)$_3$P	**6d** (44%)
5	*o*-$MeO_2CC_6H_4I$	$Pd(PPh_3)_2Cl_2$	**6e** (85%)
6	PhI	$Pd(PPh_3)_2Cl_2$	**5a** (60%)
7	Me_2C=$CHCH_2Br$	$Pd(PPh_3)_4$	**6f** (66%) **6g** (22%)
8	*trans*-EtO_2CCH=$CHCH_2Br$	$Pd(PPh_3)_2Cl_2$	R = *trans*-CH_2CH=$CHCO_2Et$ **6h** (28%) R = *trans*-CH=$CHCH_2CO_2Et$

* DMF as solvent

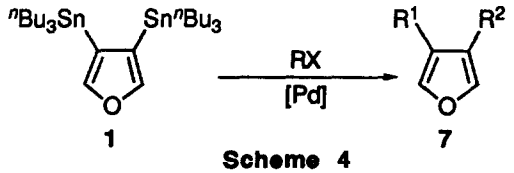
(c) Palladium-catalyzed coupling reactions of 3,4-bis(tri-*n*-butylstannyl)furan (1)[19,20]

By virtue of the incorporation of two tri-*n*-butylstannyl groups, furan **1** appeared to be an ideal precursor for the realization of 3,4-disubstituted furans, which are widely regarded as challenging targets.[14] In light of the fact that **2** could be converted to a number of 3-substituted furans via palladium-catalyzed coupling reactions, **1** was likewise allowed to undergo similar conversions. Up to now, the Stille reaction of bis-stannyl compounds is rare and sporadic,[25] and no regioselectivity of these compounds has been recorded in the literature. For this reason, we initiated a program to investigate the use of **1** for the synthesis of symmetrical as well as unsymmetrical 3,4-disubstituted furans. The palladium-catalyzed coupling reactions of **1** with acid

Table 3. Palladium-catalyzed coupling reaction of 1 with RX

Entry	RX	[Pd] / solvent	Temperature time	7 (yield %)
1	MeCOCl	$Pd(PPh_3)_2Cl_2$ THF	80°C 24 h	**7a** $R^1 = Sn^nBu_3$ (59) $R^2 = COMe$
2	^nBuCOCl	$Pd(PPh_3)_2Cl_2$ THF	65°C 10 h	**7b** $R^1 = Sn^nBu_3$ (57) $R^2 = CO^nBu$
3	PhCOCl	$Pd(PPh_3)_2Cl_2$ THF	65°C 8 h	**7c** $R^1 = Sn^nBu_3$ (95) $R^2 = COPh$
4	PhBr	$Pd(PPh_3)_4$ HMPA or DMF	65°C 10 h	**7d** $R^1 = Ph$ (54) $R^2 = Ph$
5	*p*-$MeCOC_6H_4Br$	$Pd(PPh_3)_4$ HMPA or DMF	80°C 20 h	**7e** $R^1 = C_6H_4COMe$-*p* (45) $R^2 = C_6H_4COMe$-*p*
6	*p*-$NO_2C_6H_4Br$	$Pd(PPh_3)_4$ HMPA or DMF	80°C 24 h	**7f** $R^1 = C_6H_4NO_2$-*p* (85) $R^2 = C_6H_4NO_2$-*p*
7	PhI	$Pd(PPh_3)_2Cl_2$ HMPA or DMF	65°C 24 h	**7d** $R^1 = Ph$ (12) $R^2 = Ph$
8	PhI	$Pd(PPh_3)_4$ HMPA or DMF	65°C 24 h	**7d** $R^1 = Ph$ (12) $R^2 = Ph$
9	PhI	$Pd(PPh_3)_2Cl_2$ CuI, DMF	65°C 10 h	**7d** $R^1 = Ph$ (55) $R^2 = Ph$
10	*p*-MeC_6H_4I	$Pd(PPh_3)_2Cl_2$ CuI, DMF	65°C 10 h	**7g** $R^1 = C_6H_4Me$-*p* (45) $R^2 = C_6H_4Me$-*p*
11	PhI	$[(C_3H_5)PdCl]_2$ DMF	65°C 2 h	**7d** $R^1 = Ph$ (65) $R^2 = Ph$
12	*trans*-PhCH=CHBr	$[(C_3H_5)PdCl]_2$ HMPA	r.t. 1 h	**7h** $R^1 =$ *trans*-CH=CHPh (69) $R^2 =$ *trans*-CH=CHPh
13	(*Z*)-MeCOCH=C(Me)Br	$[(C_3H_5)PdCl]_2$ DMF	70°C 1 h	**7i** $R^1 =$ (*Z*)-CH(Me)=CHCOMe (79) $R^2 =$ (*Z*)-CH(Me)=CHCOMe
14	*trans*-PhCH=CHI	$[(C_3H_5)PdCl]_2$ DMF	70°C 10 h	**7h** $R^1 =$ *trans*-CH=CHPh (47) $R^2 =$ *trans*-CH=CHPh
15	*trans*-$EtO_2CCH=CHCH_2Br$	$Pd(MeCN)_2Cl_2$ PPh_3, DMF	70°C 2 h	**7j** $R^1 = CH_2CH^{\dagger}{=}CHCO_2Et$ (67) $R^2 = CH_2CH^{\dagger}{=}CHCO_2Et$
16	$PhCH_2Br$	$Pd(PPh_3)_4$ DMF	70°C 10 h	**7k** $R^1 = CH_2Ph$ (45) $R^2 = CH_2Ph$
17	$PhCH_2Cl$	$Pd(PPh_3)_4$ DMF	100°C 12 h	**7k** $R^1 = CH_2Ph$ (70) $R^2 = CH_2Ph$

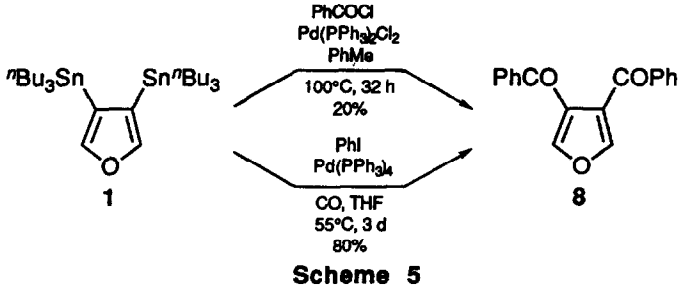
chlorides, aryl halides, vinyl halides, benzyl halides and an allyl bromide were carried out (Scheme 4). The catalysts used, solvents, reaction conditions and the yields of the 3,4-disubstituted furans **7** are illustrated in Table 3.



1 **7**

Scheme 4

Furan **1** reacted with one equivalent of acid chlorides to furnish moderate to good yields of mono-acylated products **7a**, **7b** and **7c** (Table 3, Entries 1, 2 and 3). It is noteworthy that the yields with aliphatic acid chlorides were inferior to that of benzoyl chloride. Somewhat surprisingly, reaction of **1** with two equivalents or more of the acid chlorides only afforded mono-acylated products, without any detectable amount of bis-acylated compounds. Under forcing conditions in toluene at 100°C, 3,4-dibenzoylfuran **8** was formed, but in very low yield, and the reaction was not complete after 32 hours (Scheme 5). There has been an example to show that the rate-determining step in the coupling of organostannanes and acid halides was in nature an S_E2 reaction, in which the palladium complex resulted from an oxidative addition was the electrophile.[26] Based on this mechanistic consideration, a rationalization can be made to support the mono-acylation behavior of **1**. Due to the fact that the transmetallation step is rate-controlling, differentiation would be possible if the reactivities of **1** and **7c** should be largely different. Furan **7c**, with an benzoyl group adjacent to the stannyl group, was electron-deficient and, as a result, would be less willing to undergo S_E2 transmetallation reaction with the electron-seeking palladium complex PhCOPdL$_2$Cl formed from an oxidative addition of PhCOCl to PdL$_2$. This argument, however, cannot be extended to other coupling reactions unless they have a slow transmetallation step. It is not, for instance, applicable to the coupling of aryl halides with organostannanes, which is believed to proceed through a slow oxidative addition.[27] Experimentally, with the exception of acid halides, for the coupling reactions of all the other organohalides discussed below, the competition from the mono-substituted-mono-stannylfurans was very effective, and the coupling reactions could not be stopped at the mono-substitution stage.



1 **8**

Scheme 5

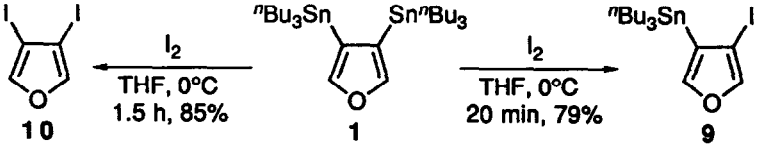
In the cases of aryl bromides, fair yields of bis-arylated furans were obtained when Pd(PPh$_3$)$_4$ was used as catalyst (Table 3, Entries 4, 5 and 6). While with aryl iodides, the conversion was however quite low. For example, only 12% yield of 3,4-diphenylfuran (**7d**) was isolated from the reaction of iodobenzene with **1**

(Entries 7 and 8). The same problem had also been encountered by Liebeskind and Fengl in their effort to couple vinyl stannanes and vinyl iodides.[28] Such situation was improved by using CuI as a co-catalyst to $PhCH_2Pd(PPh_3)_2Cl$. As a result, moderate to good yields of cross-coupled products were produced.[28] In this manner, we found that the use of $Pd(PPh_3)_2Cl_2$ and CuI under nitrogen was very effective (Entries 9 and 10). The active allylpalladium chloride dimer also catalyzed a similar reaction with a good yield of **7d** (Entry 11).

Allylpalladium chloride dimer was found to be the catalyst of choice when vinyl bromides were used (Table 3, Entries 12 and 13). For *trans*-β-iodostyrene, the use of $[(C_3H_5)PdCl]_2$ afforded the desired **7h**, albeit in only 47% yield (Entry 14). On the other hand, the reaction of **1** with ethyl *trans*-4-bromocrotonate utilizing $Pd(MeCN)_2Cl_2$ gave a better yield of **7j** (Entry 15). Finally, with $Pd(PPh_3)_4$, **1** coupled smoothly with benzyl bromide or benzyl chloride to give 3,4-dibenzylfuran (**7k**) (Entries 16 and 17). It has been established that the reaction with benzyl halides should involve the oxidative addition of the palladium catalyst to the C-X bond in an S_N2-type reaction.[27,29] As such, it can be seen that higher temperature was needed for benzyl chloride (Entry 17) because chloride ion is a weaker leaving group.[30] Nevertheless, benzyl chloride also gave a better yield because it is much more stable than benzyl bromide towards heat and moisture.

That the cross-coupling occurred in an *ipso*-fashion was best proved by the chemical shifts of the α-protons in their ^{1}H-NMR spectra (see Experimental Section). Consequently, the chemical shifts of the α-protons on furans are invariably larger than δ 7.00, while those of the β-protons are between δ 6.00-7.00.[31]

Iodination of **1** occurred readily at 0°C in a stepwise manner to give in 79% yield 3-iodo-4-(tri-*n*-butylstannyl)furan (**9**) with one equivalent of iodine, and, with two equivalents of which, 3,4-diiodofuran (**10**) was provided in 85% yield (Scheme 6). It is interesting to note that our method should be better than a 1970 report[32] in which a tedious synthesis and isolation of **10** were noted.

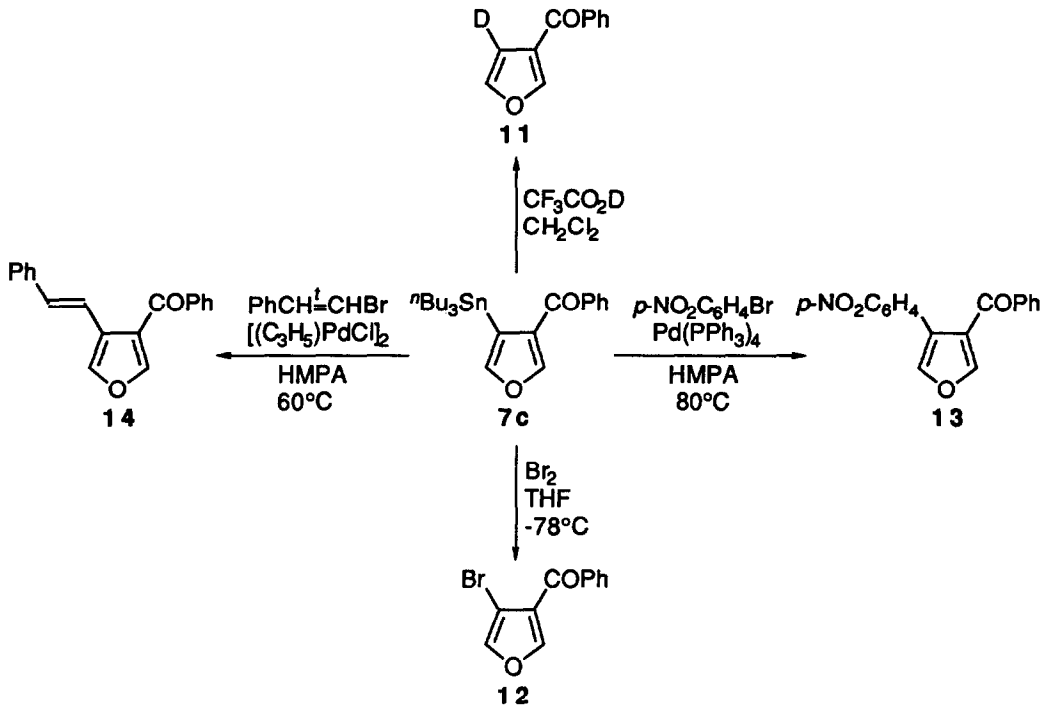


Scheme 6

The carbonylation of furan **1** was also attempted. Thus, a mixture of iodobenzene and **1** was allowed to react under 30 psi of CO catalyzed by $Ph(PPh_3)_4$ in THF. The reaction was complete in 3 days and gave good yield of 3,4-dibenzoylfuran (**8**) (Scheme 5). This is in sharp contrast to the palladium-catalyzed coupling reaction between **1** and benzoyl chloride (Scheme 5). The exact reason for the good yield is yet unknown. It is possible that CO could stabilize the palladium species $RCOPdL_2X$, so that the second carbonylation reaction could proceed to afford **8** even if the reaction is slow.

Upon treatment with either CF_3CO_2D,[33] or bromine,[25b] the remaining tri-*n*-butylstannyl group of **7c** was regiospecifically replaced accordingly with a deuterium atom or a bromine atom, furnishing **11** (approximately 45% deuterium content due presumably to the acid used) and **12** in 96 and 83% yield, respectively (Scheme 7). Noteworthy is that **12** in principle can be converted further into various 3,4-disubstituted furans by employing palladium-catalyzed reactions,[34] thereby enriching the variety of furans as well as enlarging the scope of our synthetic strategy. Moreover, **7c** was also converted through palladium-catalyzed reactions[19] to afford 4-(*p*-nitrophenyl)furan-3-yl phenyl ketone (**13**) and 3-benzoyl-4-(*trans*-

styryl)furan (**14**) in 81 and 82% yield, respectively (Scheme 7).

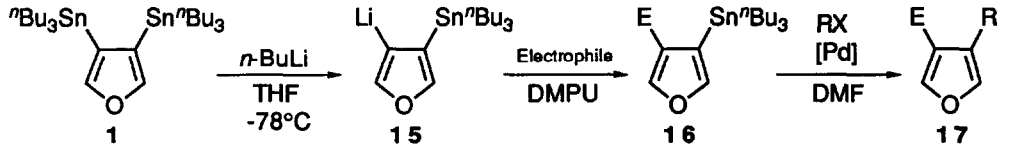


Scheme 7

Another route in which 3,4-disubstituted furans could be obtained from **1** was by utilizing lithiation as the pivotal step. Lithiation of organostannanes with alkyllithium was first discovered and studied by Seyferth in the sixties.[35] This method has since attracted considerable attention and examples of their application in organic synthesis have been abundant.[36] The side product of this reaction was the hydrocarbon-like tetra-*n*-butyltin[35] which was unreactive under the reaction conditions, and was also easily removed by chromatography.[36] This is very advantageous compared with the traditional method by reaction of organohalides with *n*-butyllithium, because the side product *n*-butyl halide usually causes workup and purification problems especially when the product is volatile.[37] Another strong point of the tin-lithium exchange is that it is usually very fast, while the halide-lithium exchange often requires long reaction time at low temperature. Furthermore, the tin-lithium exchange reaction can be conveniently monitored by TLC with the appearance of tetra-*n*-butyltin. While for halide-lithium exchange reactions, the detection methods such as deuteration, NMR spectral technique are inconvenient.[13a] Since tin-lithium exchange has the aforementioned merits, it was applied in our quest for selective, stepwise preparations of unsymmetrical 3,4-disubstituted furans.

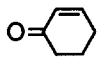
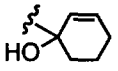
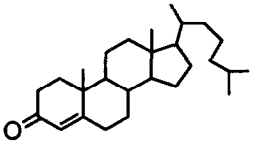
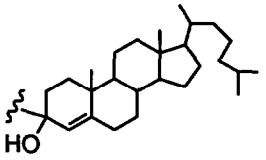
Inspired by Fleming's syntheis of 3-furoic acid from **2**,[15c] we attempted the lithiation of **1** with various amounts of *n*-butyllithium and found that approximately 2 equivalents of *n*-butyllithium were needed to achieve a complete exchange of one tri-*n*-butylstannyl group, generating **15** (Scheme 8). Smaller amounts of *n*-

butyllithium only led to imcomplete conversion, while larger amounts (up to 4 equivalents) gave no sign of exchange with the remaining tri-*n*-butylstannyl group. It came as no surprise because this kind of difficulty in connection with the simultaneous replacement of two stannyl groups has been well-documented in bis-stannylalkenes[38] and bis-stannylarenes.[39] Such a seemingly unfavorable restriction, nonetheless, led to our successful unsymmetrical 3,4-disubstituted furan syntheses.



Scheme 8

Table 4. Conversion of 15 to 16 by addition of electrophiles

Entry	Electrophile	E	16 (yield)
1	Me_2SO_4	Me	**16a**(65%)
2[a]	Me_2SO_4	Me	**16a**(36%)
3[a]	$HCONMe_2$	CHO	**16b**(58%)
4[b]	$HCONMe_2$	CHO	**16b**(69%)
5	$HCONMe_2$	CHO	**16b**(86%)
6	$EtCONMe_2$	COEt	**16c**(63%)
7	Me_2CO	$C(OH)Me_2$	**16d**(60%)
8	PhCHO	CH(OH)Ph	**16e**(75%)
9	Ph_2CO	$C(OH)Ph_2$	**16f**(79%)
10	MeI	Me	**16a**(28%)
11	H_2CO	CH_2OH	**16g**(19%)
12			**16h**(63%)
13			**16i**(44%)

[a]Electrophile added alone. [b]TMEDA added together with *n*-butyllithium.

The regiospecific conversions of **15** to **16** are depicted by examples as outlined in Table 4. As can be seen, the yields of **16a** and **16b** were unsatisfactory (Entries 2 and 3) when Me_2SO_4 and DMF respectively were added alone, but were improved significantly when the electrophiles were added together with 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (Entries 1, 4 and 5). Indeed, DMPU was found to

be the best solvent for these lithiation reactions. In one of the formylation reactions (Entry 4), TMEDA was also added in order to increase the reactivity of furyllithium. Reaction of *N,N*-dimethylpropanamide with **15** gave **16c** in 63% yield (Entry 6). Carbonyl compounds reacted likewise with **15** to give the corresponding addition products **16d**, **16e**, **16f** and **16g** (Entries 7, 8, 9 and 11). With α,β-unsaturated ketones, only 1,2-addition was observed (Entries 12 and 13). To obtain good yields, reactive electrophiles such as dimethyl sulfate and carbonyl compounds should be used. With formaldehyde and less reactive electrophiles such as iodomethane, yields were rather inferior. (Entries 10 and 11). In practice, compounds **16** could be readily isolated from the reaction mixture by chromatography on neutral alumina since the R_f values of the products and side products differ substantially.

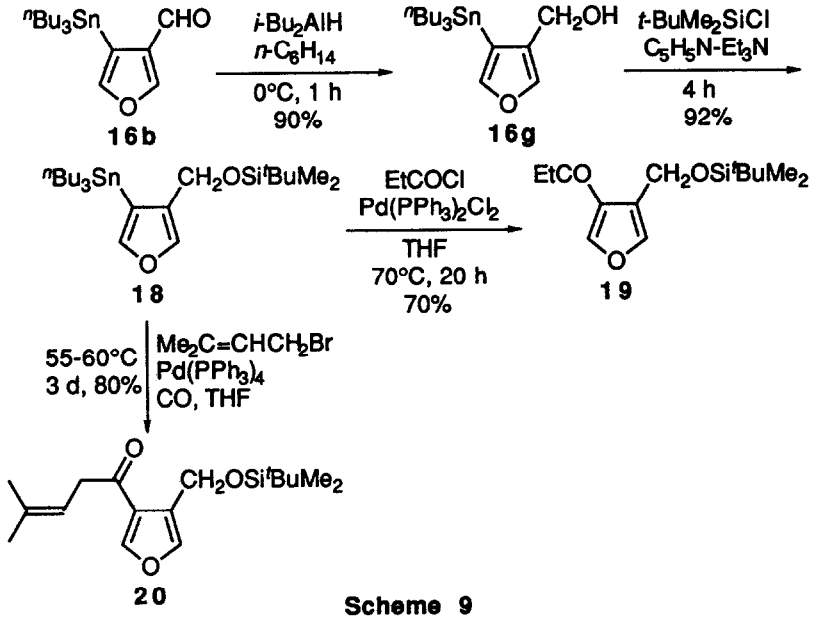
Having achieved the synthesis of **16**, their further transformation into unsymmetrical 3,4-disubstituted furans **17** was sought. Again, palladium-catalyzed coupling reactions were utilized and the results are shown in Table 5. The coupling of 9-bromophenanthrene with **16a** merely gave **17a** in low yield (Entry 1), despite many catalysts had been tried. A possible explanation might be the steric hindrance caused by the bulkiness of the phenanthrene ring. However, it appeared that the steric congestion on **16f** rendered by the two phenyl groups was not so detrimental to the yield of **17d** (Entry 4). (*Z*)-4-Bromo-3-penten-2-one was used to couple with **16d** to afford **17b** (Entry 2). The benzylic hydroxy group did not interfere with the reaction, which was carried out at room temperature to avoid dehydration. The conversion of **16e** into **17c** was quite facile (Entry 3) and this reaction seems to have potential applications in lignan synthesis.[40] The reaction of **16h** with *trans*-β-bromostyrene was unexpectedly not smooth. The reaction was very slow in DMF, and was not complete even after three days. Heating was also not employed because of possible dehydration. Eventually, it was discovered that the reaction took 24 hours to complete at room temperture in a mixture of DMF and HMPA (10:1) as solvents (Entry 5).

Table 5. Palladium-catalyzed coupling of 16 to form 17

Entry	16	RX	[Pd]	Temperature time	17 (yield)
1	**16a**	9-bromophenanthrene	$Pd(PPh_3)_4$	80°C 8 h	**17a**(35%) E = Me R = 9-phenanthryl
2	**16d**	(*Z*)-MeCOCH=C(Me)Br	$[(C_3H_5)PdCl]_2$	r.t. 24 h	**17b**(66%) E = $C(OH)Me_2$ R = (*Z*)-C(Me)=CHCOMe
3	**16e**	$PhCH_2Br$	$Pd(MeCN)_2Cl_2$	60°C 2 h	**17c**(70%) E = CH(OH)Ph R = CH_2Ph
4	**16f**	*p*-$MeCOC_6H_4Br$	$Pd(PPh_3)_4$	75°C 24 h	**17d**(61%) E = $C(OH)Ph_2$ R = C_6H_4COMe-*p*
5*	**16h**	*trans*-PhCH=CHBr	$[(C_3H_5)PdCl]_2$	r.t. 24 h	**17e**(76%) E = 1-hydroxy-1-cyclohexyl R = *trans*-CH=CHPh

* Solvent : DMF / HMPA (10:1)

The conciseness and effectiveness of the combined use of a lithiation reaction plus a palladium-catalyzed coupling reaction are aptly demonstrated by the synthesis of two unsymmetrical 3,4-disubstituted furans **19** and **20** as depicted in Scheme 9. In view of the low yield in the direct preparation of **16g** (Table 4, Entry 11), **16b** (Table 4, Entry 5) was reduced by DIBAL to give a good yield of **16g**. Protection of the primary alcohol of **16g** with dihydropyran in the presence of pyridinium *p*-toluenesulfonate resulted in a gradual protodestannylation. Therefore, the hydroxy group was protected instead as a silyl ether, giving a key intermediate **18**. The palladium-catalyzed coupling reaction of **18** with propanoyl chloride generated furan **19**, which might serve as a key precursor in Corey's synthesis of (20*S*)-camptothecin.[41] Thus, a TBS-protected 3-hydroxymethyl-4-propanoylfuran **19** was synthesized in four steps from **1** in an overall yield of 50%. Alternatively, the palladium-catalyzed carbonylation of **18** afforded **20**, which bears some skeletal resemblance to a naturally occurring furan lactaral.[42]



Scheme 9

EXPERIMENTAL SECTION

General. All solvents were reagent grade. Further purifications and drying by standard methods were employed when necessary. All evaporation of organic solvents was carried out with a rotary evaporator in conjunction with a water aspirator. Melting points were recorded on a Peichert apparatus and are uncorrected. NMR spectra were recorded on a Bruker Cryospec WM 250 spectrometer (250 MHz for ^1H and 62.5 MHz for ^{13}C). All NMR measurements were carried out at room temperature in $CDCl_3$ solution unless otherwise stated. Chemical shifts are reported as parts per million (ppm) in δ unit on the scale downfield from tetramethylsilane (TMS) or relative to the resonance of $CHCl_3$ (7.26 ppm in the ^1H, 77.0 ppm for the central line of the triplet in the ^{13}C modes, respectively). Coupling constants (*J*) are reported in hertz (Hz). Splitting patterns are described as "s" (singlet); "d" (doublet); "t" (triplet); "q" (quartet); "m" (multiplet). ^1H NMR data are reported in this

order: chemical shifts; multiplicity; coupling constant(s); number(s) of proton. Mass spectra were obtained on a VG 7070F mass spectrometer, and recorded at an ionization energy of 70 ev for ordinary compounds and 20 ev for stannyl compounds. TLC was performed on silica gel $60F_{254}$ precoated on aluminum. Column chromatography was performed on silica gel (230-400 mesh) unless otherwise stated. Reverse-phase TLC plates were purchased from Whatman. Elemental analyses were carried out at Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences.

Materials. Reagents were purchased from commercial suppliers and were used without further purification. (Z)-4-Bromo-3-penten-2-one,[43] (*E*)-4-bromo-3-penten-2-one,[43] *trans*-β-iodostyrene,[44-46] *trans*-1-iodo-1-heptene,[44] 4-*tert*-butyl-cyclohex-1-enyl triflate[47] and *N*,*N*-dimethylpropanamide[48,49] were prepared according to the literature.

Bis(tri-*n*-butylstannyl)acetylene (3).[50] Dry acetylene gas was bubbled into a solution of 1.5 M *n*-BuLi (500 mL, 0.75 mol) in THF (50 mL) under nitrogen at -30℃ for 1 h, during which time a thick white suspension was formed. The mixture was then refluxed for 2 h, followed by addition of a solution of *n*-Bu_3SnCl (203 mL, 0.75 mol) in THF (100 mL) at 0℃. The resulting mixture was refluxed for 3 h, then cooled to 0℃ and quenched with icy saturated NH_4Cl solution (200 mL). The aqueous layer was extracted with hexanes (200 mL). The organic layer was dried over $MgSO_4$ and evaporated. Vacuum distillation gave **3** (200 g, 70%) as a colorless liquid: bp: 159-160℃ / 0.01 mmHg (lit.[51] bp 159℃ / 0.01 mmHg); MS *m/z* 604 (M^+); ^1H NMR ($CDCl_3$) δ 0.89 (br. quintet, J = 7.3, 7.3, 7.3, 7.3 Hz, 30H), 1.32 (br. sextet, J = 7.3, 7.3, 7.3, 7.3, 7.3 Hz, 12H), 1.56 (br. quintet, J = 7.3, 7.3, 7.3, 7.3 Hz, 12H); ^{13}C NMR ($CDCl_3$) δ 11.24, 13.57, 26.93, 28.91, 116.35.

3,4-Bis(tri-*n*-butylstannyl)furan (1) and 3-(tri-*n*-butyl-stannyl)furan (2). A mixture of **3** (200 g, 331 mmol) and 4-phenyloxazole (**4**)[17] (55 g, 0.38 mol) in a sealed tube was heated in an oil bath at 180-185℃ for 10 days. It was then opened and the resulting benzonitrile was removed under vacuum. The residue was chromatographed on neutral alumina (grade II, 5 kg, hexanes) to give a mixture of compound **1**, **2** and unreacted **4**. Alkyne **4** was removed from the mixture by adsorbing on a bed of alumina (700g, Merck 1085 aluminum oxide for TLC, activated by heating in an oven at 120℃ for 4 h and stored in a desiccator) for 1 h and was washed subsequently with hexanes to give a mixture of **1** and **2**. Vacuum distillation (bath temperature not exceeding 190℃) gave **2** (12 g, 10%) as a colorless liquid: bp 80℃ / 0.01 mmHg (lit.[15c] bp 109-111℃ / 0.6 mmHg); MS *m/z* 357 (M^+); ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.2, 7.2 Hz, 9H), 1.01 (t, J = 8.0, 8.0 Hz, 6H), 1.32 (sextet, J = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.47-1.57 (m, 6H), 6.36 (dd, J = 0.6, 1.6 Hz, 1H), 7.24 (t, J = 1.3, 1.3 Hz, 1H), 7.57 (t, J = 1.4, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.92, 13.59, 27.26, 29.16, 113.73, 114.98, 142.55, 147.17. Compound **1** that remained as non-volatile residue was further purified on a short neutral alumina column (grade II-III, 200 g, hexanes) to give pure **1** (47 g, 22%) as a colorless liquid: MS *m/z* 589 ($M^+ - C_4H_8$); ^1H NMR ($CDCl_3$) δ 0.79 (t, J = 7.3, 7.3 Hz, 18H), 0.91 (t, J = 7.5, 7.5 Hz, 12H), 1.23 (sextet, J = 7.3, 7.3, 7.3, 7.3, 7.3 Hz, 12H), 1.34-1.47 (m, 12H), 7.36 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 10.09, 13.57, 27.38, 29.23, 119.32, 148.09. Anal. Calcd. for $C_{28}H_{56}OSn_2$: C, 52.05; H, 8.74. Found: C, 52.40; H, 9.04.

3-Benzoylfuran (5a). Furan **2** (356 mg, 1.0 mmol), THF (1 mL), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), and freshly distilled benzoyl chloride (120 μL, 0.1 mmol) were added sequentially to a sealed tube under nitrogen.

The tube was sealed and heated on an oil bath at 60℃ for 2 h. After being cooled to room temperature, the mixture was diluted with Et_2O (20 mL) and filtered through celite. Removal of solvent and chromatography on silica gel (20 g, hexanes : EtOAc 30:1) gave **5a** (138 mg, 80%) as a colorless solid: mp 38-39℃ (lit.[15f] mp 39-40℃); ^1H NMR ($CDCl_3$) δ 6.91 (d, J = 1.9 Hz, 1H), 7.45-7.51 (m, 3H), 7.58 (tt, J = 1.7, 1.7, 7.3 Hz, 1H), 7.83-7.67 (m, 2H), 7.92 (t, J = 0.6, 0.6 Hz, 1H).

General Procedure for the Preparation of 5b-5h

(a) **3-Phenylfuran (5b).** To a mixture of compound **2** (100 mg, 0.28 mmol), iodobenzene (57 mg 0.28 mmol) in DMF (0.3 mL) was added $Pd(PPh_3)_2Cl_2$ (8 mg, 0.01 mmol). The resulting mixture was heated at 70℃ for 2 h, then diluted with Et_2O (20 mL), washed with water (5 mL), and dried over $MgSO_4$. Evaporation and chromatograhpy on silica gel (20 g, hexanes) gave **5b** (30 mg, 75%) as a colorless solid: mp 57-58℃ (lit.[52] mp 58.5-59.5℃). MS *m/z* 144 (M^+); ^1H NMR ($CDCl_3$) δ 6.71 (dd, J = 0.7, 1.8 Hz, 1H), 7.26 (tt, J = 1.2, 1.2, 7.2, 7.2 Hz, 1H), 7.37 (br. t, J = 6.3, 6.3 Hz, 2H), 7.50 (dt, J = 1.7, 1.7, 8.8 Hz, 3H), 7.74 (dd, J = 0.7, 1.3 Hz, 1H).

(b) **3-(*p*-Tolyl)furan (5c)** was prepared from **2** (356 mg, 1.0 mmol), *p*-iodotoluene (240 mg, 1.1 mmol), CuI (15 mg, 0.08 mmol) and $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) in DMF (1.0 mL) after stirring at room temperature for 2 h. Chromatography on silica gel (20 g, hexanes) afforded **5c** as a colorless solid (114 mg, 72%): mp 65-66℃; MS *m/z* 158 (M^+); ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 6.68 (dd, J = 0.8, 1.7 Hz, 1H), 7.18 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 1.7, 1.7 Hz, 1H), 7.70 (t, J = 1.0, 1.0 Hz, 1H); high resolution MS: 158.0701, $C_{11}H_{10}O$ Calcd. 158.0729.

(c) **3-Phenylfuran (5b)** was prepared from **2** (100 mg, 0.28 mmol), bromobenzene (29 mg, 0.3 mmol) and $Pd(PPh_3)_4$ (14 mg, 0.01 mmol) in DMF (0.5 mL) after heating at 70℃ for 1.5 h. Furan **5b**, obtained as a colorless solid (32 mg, 80%), was identical spectrometrically to an authentic sample prepared previously.

(d) **3-(*trans*-Styryl)furan (5d)** was prepared from **2** (200 mg, 0.56 mmol), *trans*-β-bromostyrene (112 mg, 0.6 mmol) and $Pd(PPh_3)_4$ (26 mg, 0.02 mmol) in HMPA (0.5 mL) after heating at 60℃ for 23 h. Chromatography on silica gel (20 g, hexanes) gave **5d** as a colorless solid (76 mg, 80%): mp 88-90℃; MS *m/z* 170 (M^+); ^1H NMR ($CDCl_3$) δ 6.66 (d, J = 1.7 Hz, 1H), 6.81 (d, J = 16.2 Hz, 1H), 6.97 (d, J = 16.2 Hz, 1H), 7.23 (tt, J = 1.8, 1.8, 7.1, 7.1 Hz, 1H), 7.33 (dt, J = 1.5, 1.5, 7.6 Hz, 2H), 7.40-7.46 (m, 3H), 7.52 (br. s, 1H). Anal. Calcd. for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.62; H, 5.72.

(e) **(Z)-2-(Furan-3-yl)-2-penten-4-one (5e)** was prepared from **2** (100 mg, 0.28 mmol), (Z)-4-bromo-3-penten-2-one (50 mg, 0.31 mmol) and $Pd(PPh_3)_2Cl_2$ (8 mg, 0.01 mmol) in DMF (0.5 mL) after heating at 70℃ for 6 h. Chromatography on silica gel (20 g, hexanes : EtOAc 30:1) gave **5e** as a colorless oil (32 mg, 77%). MS *m/z* 150 (M^+); ^1H NMR ($CDCl_3$) δ 2.19(s, 3H), 2.44 (d, J = 1.2 Hz, 3H), 6.46 (s, 1H), 6.60 (m, 1H), 7.43 (s, 1H), 7.69 (s, 1H). Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.83; H, 6.69.

(f) **(*E*)-2-(Furan-3-yl)-2-penten-4-one (5f)** was prepared from **2** (100 mg, 0.28 mmol), (*E*)-4-bromo-3-penten-2-one (50 mg, 0.31 mmol) and $Pd(PPh_3)_2Cl_2$ (8 mg, 0.01 mmol) in DMF (0.5 mL) after heating at 70℃ for 6 h. Furan **5f** was obtained as a colorless oil (29 mg, 70%). MS *m/z* 150 (M^+); ^1H NMR ($CDCl_3$) δ 2.27 (s, 3H), 2.44 (d, J = 1.1 Hz, 3H), 6.46 (s, 1H), 6.60 (dd, J = 1.0, 2.0 Hz, 1H), 7.43 (dd, J = 1.5, 2.0 Hz, 1H), 7.69 (s, 1H). Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.90; H, 6.73.

(g) **3-(*trans*-Styryl)furan (5d)** was prepared from **2** (200 mg, 0.56 mmol), *trans*-β-iodostyrene (142 mg, 0.62 mmol) and $Pd(PPh_3)_2Cl_2$ (16 mg, 0.02 mmol) in DMF (0.5 mL) after heating under nitrogen at 60℃ for 1 h. Furan **5d**, obtained as a colorless solid (68 mg, 71%), was identical spectrometrically to an authentic sample prepared previously.

(h) **3-(*trans*-1-Heptenyl)furan (5g)** was prepared from **2** (200 mg, 0.56 mmol), *trans*-1-iodo-1-heptene (100 mg, 0.62 mmol), $Pd(PPh_3)_2Cl_2$ (16 mg, 0.02 mmol) and CuI (8 mg, 0.05 mmol) in DMF (0.5 mL) after heating at 60°C for 24 h under nitrogen. Chromatography on silica gel (20 g, hexanes) gave **5g** as a colorless oil (65 mg, 71%). MS *m/z* 164 (M^+); ^1H NMR ($CDCl_3$) δ 0.87-0.92 (m, 3H), 1.26-1.47 (m, 6H), 2.14 (q, *J* = 7.1, 7.1, 7.1 Hz, 2H), 5.94 (dt, *J* = 6.9, 6.9, 15.8 Hz, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.50 (t, *J* = 1.4, 1.4 Hz, 1H), 7.33 (t, *J* = 1.4, 1.4 Hz, 2H); high resolution MS: 164.1194, $C_{11}H_{16}O$ Calcd. 164.1197.

(i) **Ethyl 4-(furan-3-yl)-2-butenoate (5h)** was prepared from **2** (200 mg, 0.56 mmol), ethyl *trans*-4-bromocrotonate (118 mg, 0.62 mmol), $Pd(MeCN)_2Cl_2$(6 mg, 0.02 mmol) and PPh_3 (3 mg, 0.01 mmol) in DMF (0.5 mL) after heating at 60°C for 2 h. Chromatography on silica gel (20 g, hexanes : EtOAc 30:1) gave **5h** as a light yellowish oil (60 mg, 60%). MS *m/z* 180 (M^+); ^1H NMR ($CDCl_3$) δ 1.28 (t, *J* = 7.0, 7.0 Hz, 3H), 3.33 (d, *J* = 6.5 Hz, 2H), 4.18 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 5.84 (dt, *J* = 1.7, 1.7, 15.5 Hz, 1H), 6.27 (d, *J* = 0.7 Hz, 1H), 7.03 (dt, *J* = 7.0, 7.0, 15.5 Hz), 7.26 (dd, *J* = 0.7, 1.4 Hz, 1H), 7.39 (t, *J* = 1.6, 1.6 Hz, 1H); high resolution MS: 180.0768, $C_9H_{12}O_3$ Calcd. 180.0783.

General Procedure for the Carbonylation Reactions

(a) **Benzyl furan-3-yl ketone (6a)**. A mixture of **2** (100 mg, 0.28 mmol), benzyl bromide (49 mg, 0.29 mmol) and $Pd(PPh_3)_2Cl_2$ (8 mg, 0.01 mmol) in THF (2 mL) was placed in a Schlenk tube under CO atmosphere and then pressurized to 30 psi. The mixture was heated at 50°C for 2 d. The remaining CO was released and the mixture was diluted with Et_2O, stirred vigorously with 50% aqueous KF solution for 15 min. The water layer was extracted with Et_2O (2×20 mL). The combined organic layer was dried ($MgSO_4$), evaporated and chromatographed on silica gel (20 g, hexanes : EtOAc 10:1) to give **6a** (42 mg, 82%) as a colorless solid: mp 49-51°C; MS *m/z* 186 (M^+); ^1H NMR ($CDCl_3$) δ 1.68 (s, 2H), 6.76 (t, *J* = 0.7, 0.7 Hz, 1H), 7.24-7.32 (m, 5 H), 7.40 (s, 1H), 8.00 (d, *J* = 0.73 Hz, 1H). Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.31; H, 5.35.

(b) **Furan-3-yl *trans*-styryl ketone (6b) and bis(furan-3-yl) ketone (6i)** was prepared from **2** (100 mg, 0.28 mmol), *trans*-β-iodostyrene (60 mg, 0.26 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.02 mmol) in THF (2 mL) after heating at 50°C under CO (30 psi) for 1 d. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) gave a mixture of **6b** (16 mg, 40 %) and **6i** (12 mg, 20%). They were separated by sublimation. Compound **6i** sublimed at 56°C / 0.01 mmHg to give colorless flakes: mp 132-134°C; MS *m/z* 162 (M^+); ^1H NMR ($CDCl_3$) δ 6.88 (dt, *J* = 0.6, 0.6, 1.0 Hz, 1H), 7.51 (t, *J* = 1.6, 1.6 Hz, 1H), 8.03 (s, 1H). Anal. Calcd. for $C_9H_6O_3$: C, 66.66; H, 3.73. Found: C, 66.76; H, 3.97. Compound **6b** sublimed at 100°C / 0.01 mmHg to give colorless crystals: mp 102-104°C; MS *m/z* 198 (M^+); ^1H NMR ($CDCl_3$) δ 6.91 (dd, *J* = 0.8, 1.0 Hz, 1H), 7.17 (d, *J* = 15.6 Hz, 1H), 7.40-7.43 (m, 3 H), 7.50 (br. t, *J* = 1.2, 1.2 Hz, 1H), 7.61-7.63 (m, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 8.16 (s, 1H). Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.77; H, 5.08. Found: C, 78.39; H, 5.10.

(c) **Furan-3-yl *trans*-hept-1-enyl ketone (6c)** was prepared from **2** (100 mg, 0.28 mmol), *trans*-1-iodo-1-heptene (63 mg, 0.28 mmol) and $Pd(PPh_3)_2Cl_2$ (8 mg, 0.01 mmol) in THF (2 mL) after heating at 55-60°C under CO (30 psi) for 1.5 d. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) gave **6c** (28 mg, 52%) as a colorless oil: MS *m/z* 192 (M^+); ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 6.7, 6.7 Hz, 3 H), 1.29-1.36 (m, 4H), 1.51 (quintet, *J* = 7.1, 7.1, 7.1, 7.1 Hz, 2H), 2.27 (dq, *J* = 1.4, 7.1, 7.1, 7.1 Hz, 2H), 6.55 (dt, *J* = 1.5, 1.5, 15.3 Hz, 1H), 6.84 (d, *J* = 1.6 Hz, 1H), 7.06 (dt, *J* = 7.0, 7.0, 15.3 Hz, 1H), 7.45 (t, *J* = 1.6, 1.6 Hz, 1H), 8.05 (s, 1H); high resolution MS: 192.1148, $C_{12}H_{16}O_2$ Calcd. 192.1146.

(d) **Furan-3-yl 4-*tert*-butyl-cyclohex-1-enyl ketone (6d)** was prepared from **2** (140 mg, 0.39 mmol), 4-*tert*-butylcyclohex-1-enyl triflate (94 mg, 0.39 mmol), $Pd_2(dba)_3$ (3 mg, 0.003 mmol) and tris(furan-2-yl)phosphine (3 mg, 0.01 mmol) in DMF (2 mL) after heating at 60°C under CO (30 psi) for 3 d. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) gave **6d** (40 mg, 44%) as a colorless solid: mp 69-71°C; MS *m/z* 232 (M^+); ^1H NMR ($CDCl_3$) δ 0.91 (s, 9 H), 1.19 (td, *J* = 4.9, 12.0, 12.0 Hz, 1H), 1.34 (tdd, *J* = 1.9, 4.9, 12.0, 12.0 Hz, 1H) 1.93-2.30 (m, 4H), 2.66 (dt, *J* = 2.5, 2.5, 15.0 Hz, 1H), 6.76 (dd, *J* = 0.6, 1.6 Hz, 1H), 6.81 (q, *J* = 2.5, 2.5, 2.5 Hz, 1H), 7.43 (t, *J* = 1.6, 1.6 Hz, 1H), 7.82 (dd, *J* = 0.6, 1.6 Hz, 1H). Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.73; H, 8.89.

(e) **Methyl *o*-(3-furyl)benzoate (6e)** was prepared from **2** (200 mg, 0.56 mmol), methyl *o*-iodo-benzoate (158 mg, 0.6 mmol) and $Pd(PPh_3)_2Cl_2$ (16 mg, 0.023 mmol) in THF (4 mL) after heating at 55°C under CO (30 psi) for 3 d. Chromatography on silica gel (20 g, hexanes : EtOAc 6:1) gave **6e** (106 mg, 85%) as a colorless solid: mp 33-33.5°C; MS *m/z* 230 (M^+); ^1H NMR ($CDCl_3$) δ 3.73 (s, 3 H), 6.85 (dd, *J* = 0.7, 1.8 Hz, 1H), 7.42-7.62 (m, 5H), 7.98 (dd, *J* = 1.3, 8.8 Hz, 1H). Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.66; H, 4.11.

(f) **3-Furyl phenyl ketone (5a)** was prepared from **2** (200 mg, 0.56 mmol), iodobenzene (122 mg, 0.60 mmol) and $Pd(PPh_3)_2Cl_2$ (16 mg, 0.023 mmol) in THF (4 mL) after heating at 55°C under CO for 3 d. Compound **5a**, obtained as a colorless solid (58 mg, 60%), was identical spectrometrically to an authentic sample prepared previously.

(g) **3-Furyl 3-methyl-but-2-enyl ketone (egomaketone) (6f)**[53] was prepared from **2** (0.102 g, 0.29 mmol), 4-bromo-2-methyl-2-butene (45 mg, 0.30 mmol) and $Pd(PPh_3)_4$ (14 mg, 0.01 mmol) in THF (2 mL) after heating at 55°C under CO (30 psi) for 1.5 d. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) gave **6f** (31 mg, 66%) as a colorless oil (lit.[53] bp 122-126°C / 20 mmHg): MS *m/z* 164 (M^+); ^1H NMR ($CDCl_3$) δ 1.68 (s, 3H), 1.76 (d, *J* = 1.1 Hz, 3H), 3.46 (d, *J* = 7.1 Hz, 2H), 5.38 (t of quintet, *J* = 1.4, 1.4, 1.4, 1.4, 7.1, 7.1 Hz, 1H), 6.75 (dd, *J* = 0.7, 1.8 Hz, 1H), 7.42 (t, *J* = 1.6, 1.6 Hz, 1H), 8.04 (dd, *J* = 0.7, 1.3 Hz, 1H).

(h) **Ethyl *trans*-4-(3-furyl)-but-2-enoate (6g) and ethyl *trans*-4-(3-furyl)-but-3-enoate (6h)** were prepared from **2** (100 mg, 0.28 mmol), ethyl *trans*-4-bromocrotonate (56 mg, 0.29 mmol) and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) in THF (2 mL) after heating at 60°C under CO (30 psi) for 1 d. An inseparable isomeric mixture of **6g** and **6h** (18 mg, 50%) in a ratio of 1 to 1.3 was obtained after chromatography on silica gel (20 g, hexanes : EtOAc 8:1) as a colorless oil: MS *m/z* 208 (M^+); ^1H NMR ($CDCl_3$) **6g**: δ 1.28 (t, *J* = 7.0, 7.0 Hz, 3H), 3.67 (dd, *J* = 1.5, 7 Hz, 2H), 4.20 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 5.97 (d, *J* = 15.7 Hz, 1H), 6.84 (dd, *J* = 0.7, 1.8 Hz, 1H), 7.07 (dt, *J* = 7.0, 7.0, 15.7 Hz, 1H), 7.46 (t, *J* = 1.7, 1.7 Hz, 1H), 8.08 (d, *J* = 1.1 Hz, 1H). **6h**: δ 1.28 (t, *J* = 7.0, 7.0 Hz, 3H), 3.31 (dd, *J* = 1.5, 7.2 Hz, 2H), 4.20 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 6.64 (d, *J* = 15.4 Hz, 1H), 6.78 (dd, *J* = 0.8, 1.9 Hz, 1H), 7.22 (dt, *J* = 7.25, 7.25, 15.4 Hz, 1H), 7.46 (t, *J* = 1.7, 1.7 Hz, 1H), 8.07 (d, *J* = 0.7 Hz, 1H); high resolution MS: 208.0712, $C_{11}H_{12}O_4$ Calcd. 208.0732.

General Procedure for the Preparation of 7a-7c

(a) **4-(Tri-*n*-butylstannyl)furan-3-yl methyl ketone (7a)**. In a sealed tube equipped with a magnetic stirring bar were added $Pd(PPh_3)_2Cl_2$ (20 mg, 0.03 mmol), **1** (458 mg, 0.71 mmol), acetyl chloride (110 μL, 1.6 mmol) and THF (2 mL). The mixture was then heated at 80°C for 24 h. After being cooled to room temperature, the mixture was concentrated *in vacuo* and the residue was chromatographed on neutral alumina (grade II-III, 30 g, hexanes : EtOAc 20:1) to give **7a** (168 mg, 59%) as a colorless oil: MS *m/z* 343 (M^+-C_4H_8); ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.4, 7.4 Hz, 9H), 1.00 (t, *J* = 8.1, 8.1 Hz, 6H), 1.3 (sextet, *J* = 7.4, 7.4,

7.4, 7.4, 7.4 Hz, 6H), 1.47 (quintet, J = 8.1, 8.1, 8.1, 8.1 Hz, 6H), 2.42 (s, 3H), 7.18 (d, J = 1.3 Hz, 1H), 8.13 (d, J = 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.47, 13.56, 27.18, 29.15, 115.46, 132.70, 148.50, 148.98, 192.84. Anal. Calcd. for $C_{18}H_{32}O_2Sn$: C, 54.16; H, 8.08. Found: C, 54.07; H, 8.29.

(b) **4-(Tri-*n*-butylstannyl)furan-3-yl butyl ketone (7b)** was prepared from **1** (313 mg, 0.48 mmol), pentanoyl chloride (60 μL, 0.5 mmol) and $Pd(PPh_3)_2Cl_2$ (17 mg, 0.02 mmol) in THF (2 mL) after heating at 65℃ for 10 h. Chromatography on neutral alumina (grade II-III, 30 g, hexanes : EtOAc 20:1) gave **7b** (122 mg, 57%) as a colorless oil: MS *m/z* 441 (M^+), ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2, 7.2 Hz, 9H), 0.93 (t, J = 8.0, 8.0 Hz, 3H), 1.04 (t, J = 8.0, 8.0 Hz, 6H), 1.30 (sextet, J = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 8H), 1.49 (quintet, J = 8.4, 8.4, 8.4, 8.4 Hz, 6H), 1.69 (m, 2H), 2.73 (t, J = 7.4, 7.4 Hz, 2H), 7.17 (d, J = 1.2 Hz, 1H), 8.13 (d, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.48, 13.57, 13.75, 22.48, 27.22, 29.01, 29.19, 39.83, 115.61, 132.37, 147.84, 148.87, 195.98. Anal. Calcd. for $C_{21}H_{38}O_2Sn$: C, 57.16; H, 8.68. Found: C, 56.63; H, 8.88.

(c) **4-(Tri-*n*-butylstannyl)furan-3-yl phenyl ketone (7c)** was prepared from **1** (3.98 g, 6 mmol), benzoyl chloride (0.7 mL, 6 mmol) and $Pd(PPh_3)_2Cl_2$ (169 mg, 0.24 mmol) in THF (5 mL) after heating at 65℃ for 8 h. Chromatography on neutral alumina (grade II-III, 30 g, hexanes : EtOAc 20:1) gave **7c** (263 mg, 95%) as a colorless oil: MS *m/z* 461 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.2, 7.2 Hz, 9H), 1.11 (t, J = 8.1, 8.1 Hz, 6H), 1.32 (sextet, J = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.48-1.61 (m, 6H), 7.26 (s, 1H), 7.42-7.54 (m, 3H), 7.81 (d, J = 7.0 Hz, 2H), 7.95 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 10.56, 13.59, 27.19, 29.19, 116.93, 128.42, 128.62, 131.08, 131.94, 139.61, 148.71, 149.66, 190.45. Anal. Calcd. for $C_{23}H_{34}O_2Sn$: C, 59.90; H, 7.43. Found: C, 59.92; H, 7.35.

General Procedure for the Preparation of 7d-7k

(a) **3,4-Diphenylfuran (7d)**. A mixture of **1** (200 mg, 0.3 mmol), bromobenzene (109 mg, 0.69 mmol) and $Pd(PPh_3)_4$ (32 mg, 0.03 mmol) in HMPA (0.3 mL) was heated at 65℃ for 10 h. After being cooled to room temperature, the mixture was diluted with Et_2O (30 mL) and stirred vigorously with 50% aqueous KF solution for 15 min. The water layer was extracted with Et_2O (2×20 mL). The combined ethereal layer was washed with water (10 mL), dried over $MgSO_4$ and evaporated. Flash chromatography on silica gel (20 g, hexanes) gave **7d** (37 mg, 54%) as a colorless solid. Recrystallization from MeOH gave colorless crystals: mp 107-111℃ (lit.[14e] mp 111-112℃); MS *m/z* 220 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.20-7.30 (m, 10H), 7.54 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 126.10, 127.01, 128.36, 128.58, 132.20, 140.70.

(b) **3,4-Bis(*p*-acetylphenyl)furan (7e)** was prepared from **1** (200 mg, 0.3 mmol), *p*-acetylphenyl bromide (123 mg, 0.62 mmol) and $Pd(PPh_3)_4$ (22 mg, 0.02 mmol) in HMPA (0.3 mL) after heating at 80℃ for 20 h. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) gave solid **7e** contaminated with *n*-Bu_3SnBr. Washing with hexanes and recrystallization from *n*-hexane gave pure **7e** (42 mg, 45%) as colorless needles: mp 133-134℃; MS *m/z* 304 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 6H), 7.31 (d, J = 8.3 Hz, 4H), 7.66 (s, 2H), 7.90 (d, J = 8.3 Hz, 4H); ^{13}C NMR δ 26.36, 125.20, 128.55, 128.61, 136.19, 136.67, 141.70, 197.25. Anal. Calcd. for $C_{20}H_{16}O_3$: C, 79.93; H, 5.30. Found: C, 79.80; H, 5.04.

(c) **3,4-Bis(*p*-nitrophenyl)furan (7f)** was prepared from **1** (200 mg, 0.3 mmol), *p*-nitrophenyl bromide (178 mg, 0.68 mmol) and $Pd(PPh_3)_4$ (28 mg, 0.02 mmol) in HMPA (0.2 mL) after heating at 80℃ for 24 h. Chromatography on silica gel (20 g, hexanes : EtOAc 6:1) gave **7f** as a colorless solid contaminated with *n*-Bu_3SnBr. Washing with hexanes and recrystallization from MeOH gave pure **7f** (82 mg, 85%) as colorless crystals: mp 191-193℃; MS *m/z* 310 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 4H), 7.73 (s, 2H), 8.19

(d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 124.07, 127.97, 129.10, 138.18, 142.48, 147.43. Anal. Calcd. for $C_{16}H_{10}O_5N_2$: C, 61.94; H, 3.25; N, 9.03. Found: C, 61.69; H, 3.25; N, 8.70.

(d) **3,4-Diphenylfuran (7d)** was prepared from **1** (200 mg, 0.3 mmol), iodobenzene (138 mg, 0.68 mmol) and $Pd(PPh_3)_2Cl_2$ (17 mg, 0.02 mmol) in DMF (0.2 mL) after heating at 65℃ for 24 h. Flash chromatography on silica gel (20 g, hexanes) afforded **7d** (8 mg, 12%) which was identical spectrometrically to an authentic sample prepared previously.

(e) **3,4-Diphenylfuran (7d)** was prepared from **1** (200 mg, 0.3 mmol), iodobenzene (138 mg, 0.68 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.02 mmol) in DMF (0.2 mL) after heating at 65℃ for 24 h. Compound **7d** (8 mg, 12%) was identical spectrometrically to an authentic sample prepared previously.

(f) **3,4-Diphenylfuran (7d)** was prepared from **1** (97 mg, 0.15 mmol), iodobenzene (72 mg, 0.35 mmol), $Pd(PPh_3)_2Cl_2$ (8 mg, 0.01 mmol) and CuI (5 mg, 0.03 mmol) in DMF (0.5 mL) after heating at 65℃ for 10 h. Flash chromatography on silica gel (20 g, hexanes) gave **7d** (18 mg, 55%) which was identical spectrometrically to an authentic sample prepared previously.

(g) **3,4-Bis(*p*-tolyl)furan (7g)** was prepared from **1** (200 mg, 0.3 mmol), *p*-iodotoluene (154 mg, 0.71 mmol), CuI (14 mg, 0.068 mmol) and $Pd(PPh_3)_2Cl_2$ (24 mg, 0.03 mmol) in DMF (0.2 mL) after heating at 65℃ for 10 h under nitrogen. Flash chromatography on silica gel (20 g, hexanes) gave **7g** (35 mg, 45%) which was recrystallized from MeOH to afford colorless needles: mp 105-107℃ (lit.[15a] mp 106-107℃); ^1H NMR ($CDCl_3$) δ 2.33 (s, 6H), 7.11 (AX, J = 3.7 Hz, 8H), 7.51 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.11, 125.99, 128.46, 129.09, 129.33, 136.64, 140.45.

(h) **3,4-Diphenylfuran (7d)** was prepared from **1** (100 mg, 0.16 mmol), iodobenzene (73 mg, 0.36 mmol) and $[(C_3H_5)PdCl]_2$ (6.6 mg, 0.02 mmol) in DMF (0.5 mL) after heating at 65℃ for 2 h under nitrogen. Flash chromatography on silica gel (20 g, hexanes) gave **7d** (22 mg, 65%) which was identical spectrometrically to an authentic sample prepared previously.

(i) **3,4-Bis(*trans*-styryl)furan (7h)** was prepared from **1** (190 mg, 0.29 mmol), trans-β-bromostyrene (125 mg, 0.68 mmol) and $[(C_3H_5)PdCl]_2$ (9 mg, 0.01 mmol) in HMPA (0.3 mL) after stirring at room temperature for 1 h. Chromatography on silica gel (20 g, hexanes) gave **7h** (54 mg, 69%) as yellow solids: mp 77-79℃; MS *m/z* 272 (M^+); ^1H NMR ($CDCl_3$) δ 6.88 (d, J = 16.3 Hz, 2H), 6.99 (d, J = 16.3 Hz, 2H), 7.24 (br. tt, J = 1.4, 1.4, 6.2, 6.2 Hz, 2H), 7.34 (br. tt, J = 1.8, 1.8, 7.3, 7.3 Hz, 4H), 7.43-7.48 (m, 4H), 7.58 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 118.11, 123.36, 126.30, 127.58, 128.69, 130.38, 137.41, 140.64; high resolution MS: 272.1161, $C_{20}H_{16}O$ Calcd. 272.1197.

(j) **3,4-Bis[(*Z*)-4-oxo-2-penten-2-yl]furan (7i)** was prepared from **1** (203 mg, 0.31 mmol), (Z)-4-bromo-3-penten-2-one (110 mg, 0.67 mmol) and $[(C_3H_5)PdCl]_2$ (9 mg, 0.01 mmol) in DMF (0.4 mL) after heating at 70℃ for 1 h. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) gave **7i** (60 mg, 79%) as an yellowish oil: MS *m/z* 232 (M^+); ^1H NMR ($CDCl_3$) δ 2.24 (s, 6H), 2.38 (d, J = 1.2 Hz, 6H), 6.31 (d, J = 1.2 Hz, 2H), 7.48 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 19.45, 31.92, 125.45, 127.86, 142.12, 145.25, 198.21. Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.07; H, 6.71.

(k) **3,4-Bis(*trans*-styryl)furan (7h)** was prepared from **1** (190 mg, 0.29 mmol), *trans*-β-iodostyrene (156 mg, 0.68 mmol) and $[(C_3H_5)PdCl]_2$ (9 mg, 0.01 mmol) in DMF (0.3 mL) after heating at 70℃ for 10 h. Chromatography on silica gel (20 g, hexanes) gave **7h** (37 mg, 47%) which was identical spectrometrically to an authentic sample prepared previously.

(l) **3,4-Bis(3-ethoxycarbonyl-*trans*-prop-2-en-1-yl)furan (7j)** was prepared from **1** (208 mg, 0.32 mmol), ethyl *trans*-4-bromocrotonate (133 mg, 0.69 mmol), $Pd(MeCN)_2Cl_2$ (6 mg, 0.02 mmol) and PPh_3 (4

mg, 0.02 mmol) in DMF (0.4 mL) after heating at 70°C for 2 h. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) gave **7j** contaminated with *n*-Bu_3SnBr, which was removed by adding 1.0 M *n*-Bu_4NF solution in THF (1 mL). Further chromatography on silica gel (20 g, hexanes : EtOAc 6:1) gave pure **7j** (45 mg, 67%) as an yellowish oil: MS *m/z* 292 (M^+); ^1H NMR ($CDCl_3$) δ 1.28 (t, *J* = 7.2, 7.2 Hz, 6H), 3.24 (dd, *J* = 1.7, 6.3 Hz, 4H), 4.19 (q, *J* = 7.2, 7.2, 7.2 Hz, 4H), 5.80 (dt, *J* = 1.7, 1.7, 15.6 Hz, 2H), 7.02 (dt, *J* = 6.3, 6.3, 15.6 Hz, 2H), 7.24 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.14, 26.13, 60.22, 120.61, 122.61, 140.69, 145.62, 166.18. Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.44; H, 6.95.

(m) **3,4-Dibenzylfuran (7k)** was prepared from **1** (195 mg, 0.30 mmol), benzyl bromide (113 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (28 mg, 0.02 mmol) in HMPA (0.2 mL) after heating at 75°C for 10 h. Chromatography on silica gel (20 g, hexanes) gave **7k** (35 mg, 45%) as a colorless solid: mp 37-39°C; MS *m/z* 248 (M^+); ^1H NMR ($CDCl_3$) δ 3.58 (s, 4H), 7.10 (s, 2H), 7.12 (dd, *J* = 1.7, 8.3 Hz, 4H), 7.20-7.29 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 29.90, 124.15, 126.12, 128.35, 128.58, 139.75, 140.82. Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.58; H, 6.50.

(n) **3,4-Dibenzylfuran (7k)** was prepared from **1** (195 mg, 0.30 mmol), benzyl chloride (167 mg, 0.66 mmol) and $Pd(PPh_3)_4$ (28 mg, 0.02 mmol) in DMF (0.2 mL) after heating at 100°C for 12 h. Chromatography on silica gel (20 g, hexanes) gave **7k** (52 mg, 70%) which was identical spectrometrically to an authentic sample prepared previously.

3,4-Dibenzoylfuran (8). A suspension of **1** (150 mg, 0.23 mmol), benzoyl chloride (70 μL, 0.46 mmol) and $Pd(PPh_3)_2Cl_2$ (16 mg, 0.02 mmol) in toluene (1 mL) was heated in a sealed tube at 100°C for 32 h. Chromatography on silica gel (20 g, hexanes : EtOAc 4:1) gave **8** (13 mg, 20%) as a colorless solid which was recrystallized from *n*-hexane to give colorless needles: mp 125-126°C (lit.[54] mp 126°C); MS *m/z* 276 (M^+); ^1H NMR ($CDCl_3$) δ 7.40 (br. t, *J* = 7.4, 7.4 Hz, 4H), 7.54 (tt, *J* = 2.1, 2.1, 7.4, 7.4 Hz, 2H), 7.78-7.83 (m, 4H), 7.87 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1126.63, 128.48, 129.04, 132.96, 138.08, 146.81, 188.51.

3,4-Dibenzoylfuran (8). A mixture of **1** (150 mg, 0.23 mmol), iodobenzene (114 mg, 0.56 mmol), $Pd(PPh_3)_2Cl_2$ (16 mg, 0.02 mmol) in THF (1 mL) was placed in a Schlenk tube under CO atmosphere and then pressurized to 30 psi. The mixture was heated at 55°C for 3 d. The remaining CO was released and the mixture was diluted with Et_2O (20 mL), stirred vigorously with 50% aqueous KF solution for 15 min. The water layer was extracted with Et_2O (2×20 mL). The combined organic layer was dried ($MgSO_4$), evaporated and chromatographed on silica gel (20 g, hexanes : EtOAc 4:1) to give **8** (51 mg, 80%) as a colorless solid which was identical spectrometrically to an authentic sample prepared previously.

3-Iodo-4-(tri-*n*-butylstannyl)furan (9). To a solution of **1** (208 mg, 0.32 mmol) in THF (4 mL) was added a solution of iodine (82 mg, 0.32 mmol) in THF (6 mL) over 20 min at room temperature. Instant decoloration was observed at the initial stage and later a yellow color persisted. The mixture was concentrated *in vacuo* and the residue was chromatographed on neutral alumina (grade II, 20 g, hexanes) to give **9** (123 mg, 79%) as a colorless oil: MS *m/z* 483 (M^+); ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2, 7.2 Hz, 9H), 1.11 (t, *J* = 8.1, 8.1 Hz, 6H), 1.37 (sextet, *J* = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.50-1.58 (m, 6H), 7.08 (d, *J* = 1.5 Hz, 1H), 7.55 (d, *J* = 1.5 Hz, 1H). Anal. Calcd. for $C_{16}H_{29}OISn$: C, 39.71; H, 6.25. Found: C, 40.65; H, 6.38.

3,4-Diiodofuran (10). A solution of iodine (243 mg, 0.6 mmol) in THF (6 mL) was added to a solution of **1** (310 mg, 0.48 mmol) in THF (10 mL) at room temperature over 1.5 h. The resulting yellow solution was evaporated and chromatographed on neutral alumina (grade II-III, 20 g, hexanes) to give **10** (132 mg, 85%) as a colorless oil (lit.[32] bp 73°C / 1.5 mmHg): MS *m/z* 320 (M^+); ^1H NMR ($CDCl_3$) δ 7.44 (d, *J* = 0.6 Hz, 2H)

[lit.[32] ^{1}H NMR ($CDCl_3$) δ 7.41]; ^{13}C NMR ($CDCl_3$) δ 77.49, 146.31.

4-Deuteriofuran-3-yl phenyl ketone (11). CF_3CO_2D (0.03 mL, 0.3 mmol) was added dropwise to a stirred solution of **7c** (0.15 g, 0.33 mmol) in CH_2Cl_2 (6 mL) at room temperature. The resulting solution was stirred for 40 min, diluted with CH_2Cl_2 (20 mL), washed with water (5 mL), dried over $MgSO_4$ and evaporated. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) gave **11** (89 mg, 95%) as a colorless solid. MS *m/z* 174 (M^+): 173 (M^+-1) 55:45; ^{1}H NMR ($CDCl_3$) δ 6.91 (dd, *J* = 0.6, 1.2 Hz, 0.54H), 7.46-7.58 (m, 4H), 7.85 (dd, *J* = 1.7, 7.6 Hz, 2H), 7.91 (d, *J* = 1.0 Hz, 1H).

4-Bromofuran-3-yl phenyl ketone (12). Bromine (20 mL, 0.4 mmol) in THF (2 mL) was added dropwise to a stirred solution of **7c** (190 mg, 0.41 mmol) in THF (2 mL) at -78℃ over 0.5 h. The resulting solution was warmed to room temperature over 0.5 h, then diluted with Et_2O (20 mL), washed consecutively with 5% aqueous $Na_2S_2O_3$ solution (5 mL) and brine (5 mL), dried over $MgSO_4$ and evaporated. Chromatography on silica gel (20 g, benzene : EtOAc 10:1) gave **12** (85 mg, 83%) as a colorless oil: MS *m/z* 251 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.47 (br. td, *J* = 1.2, 7.3, 7.3 Hz, 2H), 7.55 (d, *J* = 1.4 Hz, 1H), 7.60 (tt, *J* = 1.4, 1.4, 7.2, 7.2 Hz, 1H), 7.76 (d, *J* = 1.4 Hz, 1H), 7.82-7.86 (dt, *J* = 1.6, 1.6, 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 100.15, 124.79, 128.49, 129.20, 132.90, 138.19, 143.06, 148.43, 187.83. Anal. Calcd. for $C_{11}H_7O_2Br$: C, 52.62; H, 2.81. Found: C, 52.54; H, 2.86.

4-(*p*-Nitrophenyl)furan-3-yl phenyl ketone (13). A mixture of **7c** (100 mg, 0.2 mmol), *p*-nitrobromobenzene (51 mg, 0.25 mmol), $Pd(PPh_3)_4$ (13 mg, 0.002 mmol) and HMPA (0.5 mL) was heated in a capped flask at 80℃ for 23 h. After being cooled to room temperature, the mixture was diluted with ether (30 mL) and stirred vigorously with 50% aqeous KF solution for 15 min to partially remove the side product *n*-Bu_3SnBr. The water layer was extracted with Et_2O (2×20 mL). The combined ethereal layer was washed with water (10 mL), dried ($MgSO_4$) and evaporated. Chromatography on silica gel (20 g, hexanes : EtOAc 8:1) gave **13** (50 mg, 85%) as colorless crystals from *n*-hexane: mp 106-108℃; MS *m/z* 293 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.47 (br. t, *J* = 7.5, 7.5 Hz, 2H), 7.58 (dt, *J* = 2.1, 2.1, 8.9 Hz, 3H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.86 (d, *J* = 1.6 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 2H), 8.18 (dt, *J* = 2.0, 2.0, 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 123.49, 124.61, 125.75, 128.23, 128.58, 129.33, 133.08, 137.83, 138.49, 142.37, 147.29, 149.83, 189.28. Anal. Calcd. for $C_{17}H_{11}O_4N$: C, 69.62; H, 3.78; N, 4.77. Found: C, 69.34; H, 3.76; N, 4.33.

Phenyl 4-(*trans*-styryl)furan-3-yl ketone (14). A mixture of **7c** (92 mg, 0.2 mmol), *trans*-β-bromostyrene (36 mg, 0.2 mmol), $[(C_3H_5)PdCl]_2$ (5 mg, 0.01 mmol) and HMPA (0.5 mL) was degassed with nitrogen and heated at 60℃ for 2 h. After being cooled to room temperature, the mixture was diluted with Et_2O (30 mL) and stirred vigorously with 50% aqeuous KF solution for 15 min to partially remove the side product *n*-Bu_3SnBr. The water layer was extracted with Et_2O (2×20 mL). The combined ethereal layer was washed with water (10 mL), dried ($MgSO_4$) and evaporated. Chromatography on silica gel (20 g, hexanes : EtOAc 8:1) gave **14** (55 mg, 82%) as a colorless solid. Recrystallization from MeOH gave colorless crystals, mp 72-73℃; MS *m/z* 274 (M^+); ^{1}H NMR ($CDCl_3$) δ 6.98 (d, *J* = 16.6 Hz, 1H), 7.20-7.36 (m, 3H), 7.37 (d, *J* = 16.6 Hz, 1H), 7.50 (br.t, *J* = 7.2, 7.2 Hz, 4H), 7.55-7.65 (tt, *J* = 1.6, 1.6, 7.2, 7.2 Hz, 1H), 7.76-7.80 (m, 2H), 7.84-7.89 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 117.69, 124.51, 124.86, 126.53, 127.63, 128.54, 128.55, 129.07, 131.06, 132.52, 137.29, 139.35, 140.56, 149.80, 190.34. Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 82.82; H, 5.15.

General Procedure for the Preparation of 16a-16i

(a) **3-Methyl-4-(tri-*n*-butylstannyl)furan (16a).** To a solution of **1** (250 mg, 0.39 mmol) in THF (5 mL) was added dropwise 1.5 M *n*-BuLi (0.6 mL, 0.9 mmol). After the addition, the reaction was followed by reverse-phase TLC (CH_2Cl_2 : MeCN 1.75:3) until **1** disappeared. Then a mixture of Me_2SO_4 (0.14 mL, 1.5 mmol) and DMPU (0.12 mL, 0.99 mmol) was added. After 1 h at -78℃, it was warmed to room temperature, quenched with saturated aqueous NH_4Cl (5 mL), extracted with Et_2O (3×20 mL), dried ($MgSO_4$), evaporated and purified by chromatography on neutral alumina (grade II-III, 30 g, hexanes) to give **16a** (93 mg, 65%) as a colorless oil. MS *m/z* 315 (M^+-C_4H_8); ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2, 7.2 Hz, 9H), 1.02 (t, *J* = 8.1, 8.1 Hz, 6H), 1.32 (sextet, *J* = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.48-1.55 (m, 6H), 2.02 (d, *J* = 1.0 Hz, 3H), 7.11 (d, *J* = 1.0 Hz, 1H), 7.29 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.76, 11.53, 13.57, 27.25, 29.20, 117.16, 124.80, 139.25, 147.55. Anal. Calcd. for $C_{17}H_{32}OSn$: C, 55.01; H, 8.69. Found: C, 55.27; H, 8.69.

(b) **3-Methyl-4-(tri-*n*-butylstannyl)furan (16a)** was prepared from **1** (195 mg, 0.30 mmol) in THF (4 mL) with *n*-BuLi (0.48 mL, 0.72 mmol), followed by addition of Me_2SO_4 (0.08 mL, 0.9 mmol) to give **16a** (40 mg, 36%) which was identical spectrometrically to an authentic sample prepared previously.

(c) **4-(Tri-*n*-butylstannyl)furan-3-carbaldehyde (16b)** was prepared from **1** (200 mg, 0.31 mmol) in THF (4 mL) with *n*-BuLi (0.45 mL, 0.68 mmol), followed by addition of DMF (0.06 mL, 0.8 mmol) to give, after chromatography on neutral alumina (grade II-III, 30 g, hexanes : EtOAc 30:1), **16b** (69 mg, 58%) as a colorless oil: MS *m/z* 329 (M^+-C_4H_8); ^1H NMR ($CDCl_3$) δ 0.79 (t, *J* = 7.3, 7.3 Hz, 9H), 1.00 (t, *J* = 8.1, 8.1 Hz, 6H), 1.20 (sextet, *J* = 7.3, 7.3, 7.3, 7.3, 7.3 Hz, 6H), 1.40-1.50 (m, 6H), 7.14 (s, 1H), 8.08 (t, *J* = 0.8, 0.8 Hz, 1H), 9.89 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 10.27, 13.49, 27.12, 29.05, 113.43, 133.75, 149.26, 152.60, 185.11. Anal. Calcd. for $C_{17}H_{30}O_2Sn$: C, 53.02; H, 7.85. Found: C, 53.02; H, 7.77.

(d) **4-(Tri-*n*-butylstannyl)furan-3-carbaldehyde (16b)** was prepared from **1** (230 mg, 0.36 mmol) in THF (4 mL) with added TMEDA (0.12 mL, 0.79 mmol) and *n*-BuLi (0.5 mL, 0.75 mmol), followed by addition of DMF (0.07 mL, 0.9 mmol) to give **16b** (94 mg, 69%) which was identical spectrometrically to an authentic sample prepared previously.

(e) **4-(Tri-*n*-butylstannyl)furan-3-carbaldehyde (16b)** was prepared from **1** (213 mg, 0.33 mmol) in THF (4 mL) with *n*-BuLi (0.5 mL, 0.8 mmol), followed by addition of DMF (0.07 mL, 0.9 mmol) and DMPU (0.09 mL, 0.07 mmol) to give **16b** (109 mg, 86%) which was identical spectrometrically to an authentic sample prepared previously.

(f) **Ethyl 4-(tri-*n*-butylstannyl)furan-3-yl ketone (16c)** was prepared from **1** (198 mg, 0.31 mmol) in THF (4 mL) with *n*-BuLi (0.45 mL, 0.68 mmol), followed by addition of *N*,*N*-dimethylpropanamide (95 mg, 0.94 mmol) and DMPU (0.09 mL, 0.7 mmol). Chromatography on neutral alumina (grade II-III, 30 g, hexanes : EtOAc 30:1) gave **16c** (80 mg, 63%) as a colorless oil: MS *m/z* 357 (M^+-C_4H_8); ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.2, 7.2 Hz, 9H), 1.04 (t, *J* = 8.1, 8.1 Hz, 6H), 1.19 (t, *J* = 7.4, 7.4 Hz, 3H), 1.32 (quintet, *J* = 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.40-1.50 (m, 6H), 2.77 (q, *J* = 7.4, 7.4, 7.4 Hz, 2H), 7.18 (d, *J* = 1.5 Hz, 1H), 8.14 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.80, 10.40, 13.57, 27.18, 29.20, 33.10, 115.50, 131.91, 147.73, 148.81, 196.33. Anal. Calcd. for $C_{19}H_{34}O_2Sn$: C, 55.23; H, 8.29. Found: C, 55.23; H, 8.08.

(g) **3-(1-Methyl-1-hydroxyethyl)-4-(tri-*n*-butylstannyl)furan (16d)** was prepared from **1** (0.62 g, 0.96 mmol) in THF (8 mL) with *n*-BuLi (1.35 mL, 2.0 mmol), followed by addition of acetone (0.5 ml, 7 mmol) and DMPU (0.2 mL, 0.8 mmol) to give, after chromatography on neutral alumina (grade II-III, 30 g, hexanes : EtOAc 10:1), **16d** (234 mg, 60%) as a colorless oil: MS *m/z* 341 (M^+-C_4H_8-H_2O); ^1H NMR

($CDCl_3$) δ 0.87 (t, J = 7.1, 7.1 Hz, 9H), 1.03 (t, J = 8.0, 8.0 Hz, 6H), 1.32 (sextet, J = 7.1, 7.1, 7.1, 7.1, 7.1 Hz, 6H), 1.45-1.56 (m, 12H), 7.13 (d, J = 1.3 Hz, 1H), 7.38 (d, J = 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.77, 13.58, 27.31, 29.13, 31.86, 69.24, 113.83, 137.50, 139.02, 148.20. Anal. Calcd. for $C_{19}H_{36}O_2Sn$: C, 54.97; H, 8.74. Found: C, 55.19; H, 8.59.

(h) **3-(1-Hydroxybenzyl)-4-(tri-*n*-butylstannyl)furan (16e)** was prepared from **1** (0.65 g, 1.0 mmol) in THF (8 mL) with *n*-BuLi (1.40 mL, 2.1 mmol), followed by addition of benzaldehyde (0.5 ml, 4.9 mmol) and DMPU (0.2 mL, 0.8 mmol) to give, after chromatography on neutral alumina (grade II-III, 30 g, hexanes : EtOAc 20:1), **16e** (350 mg, 75%) as a colorless oil: MS *m/z* 407 (M^+-C_4H_8); ^1H NMR ($CDCl_3$) δ 0.88 (q, J = 7.4, 7.4, 7.4 Hz, 15H), 1.25 (sextet, J = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.46 (quintet, J = 7.5, 7.5, 7.5, 7.5 Hz, 6H), 2.03 (br. s, 1H), 5.67 (s, 1H), 7.15 (d, J = 1.3 Hz, 1H), 7.21 (dd, J = 0.7, 1.3 Hz, 1H), 7.23-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 9.98, 13.56, 27.21, 29.09, 70.91, 114.85, 126.84, 127.83, 128.40, 133.97, 140.67, 143.12, 148.36. Anal. Calcd. for $C_{23}H_{36}O_2Sn$: C, 59.64; H, 7.83. Found: C, 59.89; H, 7.72.

(i) **3-(1,1-Diphenyl-1-hydroxymethyl)-4-(tri-*n*-butylstannyl)furan (16f)** was prepared from **1** (200 mg, 0.31 mmol) in THF (4 mL) with *n*-BuLi (0.48 mL, 0.72 mmol), followed by addition of benzophenone (138 mg, 0.76 mmol) and DMPU (0.09 mL, 0.7 mmol) to give, after careful chromatography on neutral alumina (grade II-III, 40 g, hexanes : EtOAc 50:1), **16f** (132 mg, 79%) as a colorless oil: MS *m/z* 483 (M^+-C_4H_8); ^1H NMR ($CDCl_3$) δ 0.64 (t, J = 8.1, 8.1 Hz, 6H), 0.76 (t, J = 7.1, 7.1 Hz, 9H), 1.10-1.30 (m, 12H), 2.52 (s, 1H), 6.75 (d, J = 1.3 Hz, 1H), 7.14 (d, J = 1.3 Hz, 1H), 7.15-7.22 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 10.30, 13.57, 27.24, 29.02, 76.50, 78.09, 115.56, 127.29, 127.91, 137.29, 142.45, 146.80, 148.78. Anal. Calcd. for $C_{29}H_{40}O_2Sn$: C, 64.58; H, 7.48. Found: C, 64.94; H, 7.46.

(j) **3-Methyl-4-(tri-*n*-butylstannyl)furan (16a)** was prepared from **1** (200 mg, 0.31 mmol) in THF (4 mL) with *n*-BuLi (0.48 mL, 0.72 mmol), followed by addition of MeI (0.05 mL, 0.8 mmol) and DMPU (0.09 mL, 0.7 mmol) to give **16a** (32 mg, 28%) as a colorless oil which was identical spectrometrically to an authentic sample prepared previously.

(k) **3-Hydroxymethyl-4-(tri-*n*-butylstannyl)furan (16g)**. After *n*-BuLi (1.2 mL, 1.8 mmol) was added to a solution of **1** (535 mg, 0.83 mmol) in THF (10 mL) at -78℃, the resulting solution was stirred at -78℃ for 1 h. Gaseous formaldehyde, produced by heating solid paraformaldehyde (300 mg, 10 mmol), was introduced into the reaction flask by a slow stream of nitrogen. The solution turned yellow in color and then turned milky. DMPU (0.2 mL, 0.8 mmol) was added and the mixture was stirred at room temperature for 1 h. Workup and chromatography on neural alumina (grade II-III, 30 g, hexanes : EtOAc 6:1) gave **16g** (62 mg, 19%) as a colorless oil: MS *m/z* 387 (M^+); ^1H NMR ($CDCl_3$) δ 0.80 (t, J = 7.2, 7.2 Hz, 9H), 0.96 (t, J = 8.1, 8.1 Hz, 6H), 1.24 (sextet, J = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.38-1.48 (m, 6H), 1.83 (br.s, 1H), 4.40 (d, J = 4.0 Hz, 2H), 7.08 (d, J = 1.1 Hz, 1H), 7.40 (d, J = 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.88, 13.47, 27.63, 29.07, 57.99, 114.96, 130.43, 139.97, 148.11. Anal. Calcd. for $C_{17}H_{32}O_2Sn$: C, 52.74; H, 8.33. Found: C, 52.59; H, 8.39.

(l) **3-(1-Hydroxycyclohex-2-en-1-yl)-4-(tri-*n*-butylstannyl)furan (16h)**was prepared from **1** (225 mg, 0.35 mmol) in THF (4 mL) with *n*-BuLi (0.5 mL, 0.8 mmol), followed by addition of 2-cyclohexenone (0.1 mL, 1 mmol) and DMPU (0.1 mL, 0.8 mmol) to give, after chromatography on neutral alumina (grade II-III, 30 g, hexanes : EtOAc 20:1), **16h** (100 mg, 63%) as a colorless oil: MS *m/z* 435 (M^+-H_2O); ^1H NMR

($CDCl_3$) δ 0.89 (t, J = 7.2, 7.2 Hz, 9H), 1.01 (t, J = 8.1, 8.1 Hz, 6H), 1.32 (sextet, J = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.50 (m, 6H), 1.60-1.90 (m, 5H), 2.05 (br. s, 1H), 5.72 (d, J = 10.0 Hz, 1H), 5.85 (dt, J = 3.5, 3.5, 10.0 Hz, 1H), 7.14 (d, J = 1.4 Hz, 1H), 7.33 (d, J = 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.80, 13.55, 19.16, 24.90, 27.30, 29.12, 38.28, 68.92, 113.71, 129.44, 132.86, 137.26, 139.22, 148.34. Anal. Calcd. for $C_{22}H_{38}O_2Sn$: C, 58.30; H, 8.45. Found: C, 58.56; H, 8.51.

(m) **3-(3-Hydroxy-4-cholesten-3-yl)-4-(tri-*n*-butylstannyl)furan (16i)** was prepared from **1** (224 mg, 0.35 mmol) in THF (4 mL) with *n*-BuLi (0.5 mL, 0.8 mmol), followed by addition of 4-cholesten-3-one (355 mg, 0.92 mmol) and DMPU (0.1 mL, 0.8 mmol) to give, after chromatography on neutral alumina (Grade II, 30 g, hexanes : EtOAc 100:1), **16i** (139 mg, 44%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.60-1.74 (m, 71H), 5.21 (s, 1H), 7.08 (s, 1H), 7.15 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 1.00, 10.80, 12.04, 13.63, 18.72, 21.25, 22.56, 22.78, 23.92, 24.28, 24.28. 27.36, 28.03, 28.23, 29.18, 32.37, 33.50, 34.52, 34.63, 35.83, 36.15, 36.26, 37.41, 39.59, 39.92, 42.60, 54.94, 56.24, 56.36, 70.47, 113.84, 125.16, 136.24, 140.15, 146.90, 148.56. Destannylation of **16i** was carried out by adsorbing **16i** onto silica gel (1 g) followed by column chromatography on silica gel (10 g, hexanes : EtOAc 20:1) to afford destannylated product: high resolution MS: 452.3579, $C_{31}H_{48}O_2$ Calcd. 452.3642.

General Procedure for the Preparation of 17a-17e

(a) **3-Methyl-4-(phenanthr-9-yl)furan (17a).** Compound **16a** (54 mg, 0.15 mmol), 9-bromophenanthrene (39 mg, 0.15 mmol), DMF (1 mL) and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol) were heated at 80°C for 8 h. Then it was diluted with Et_2O (25 mL) and stirred vigorously with 50% aqueous KF solution for 15 min. The water layer was extracted with Et_2O (3×20 mL). The ethereal layer was dried ($MgSO_4$), evaporated and purified by chromatography on silica gel (20 g, hexanes). Recrystallization from MeOH gave **17a** (13 mg, 35%) as colorless leaflets: mp 123-124°C; MS *m/z* 258 (M^+); ^1H NMR ($CDCl_3$) δ 1.87 (d, J = 1.0 Hz, 3H), 7.40 (t, J = 1.0, 1.0 Hz, 1H), 7.53-7.69 (m, 6H), 7.87 (dd, J = 1.4, 6.2 Hz, 2H), 8.73 (td, J = 0.6, 9.0, 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 8.53, 122.58, 122.86, 125.91, 126.61, 126.78, 126.89, 128.54, 139.83, 140.96. Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.39; H, 5.55.

(b) **3-(1-Methyl-1-hydroxyethyl)-4-[(Z)-4-oxo-pent-2-en-2-yl]furan (17b)** was prepared from **16d** (0.18 g, 0.43 mmol), (Z)-4-bromo-3-penten-2-one (78 mg, 0.55 mmol) and $[(C_3H_5)PdCl]_2$ (9 mg, 0.02 mmol) in DMF (1 mL) after stirring at room temperature for 24 h. Chromatography on silica gel (20 g, hexanes : EtOAc 8:1) gave solid **17b** contaminated with a trace of *n*-Bu_3SnBr. Washing with hexanes gave pure **17b** (60 mg, 66%) as yellowish solids: m.p. 65-67°C; MS *m/z* 208 (M^+); ^1H NMR ($CDCl_3$) δ 1.56 (s, 6H), 2.22 (s, 3H), 2.45 (d, J = 1.1 Hz, 3H), 6.74 (s, 1H), 7.33 (d, J = 1.8 Hz, 1H), 7.38 (d, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.04, 30.74, 31.90, 68.69, 127.51, 128.64, 131.67, 139.87, 142.04, 146.92, 198.80. Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.51; H, 7.81.

(c) **3-Benzyl-4-(1-hydroxybenzyl)furan (17c)** was prepared from **16e** (156 mg, 0.38 mmol), benzyl bromide (0.06 mL, 0.5 mmol) and $Pd(MeCN)_2Cl_2$ (4 mg, 0.02 mmol) in DMF (1 mL) after heating at 60°C for 2 h. Chromatography on silica gel (20 g, hexanes : EtOAc 20:1) gave **17c** (69 mg, 70%) as a colorless oil: MS *m/z* 264 (M^+); ^1H NMR ($CDCl_3$) δ 2.02 (br. s, 1H), 3.55 (d, J = 16.0 Hz, 1H), 3.64 (d, J = 16.0 Hz, 1H), 5.53 (s, 1H), 7.08-7.32 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 29.97, 69.01, 123.37, 126.29, 126.60, 127.79, 128.40, 128.64, 139.69, 141.38, 141.45, 142.47. Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.91; H, 6.03.

(d) **3-(*p*-Acetylphenyl)-4-(1,1-diphenyl-1-hydroxymethyl)furan (17d)** was prepared from **16f** (100 mg, 0.19 mmol), *p*-acetylphenyl bromide (50 mg, 0.25 mmol) and $Pd(PPh_3)_4$ (13 mg, 0.012 mmol) in DMF (1 mL) after heating at 75°C for 24 h. Chromatography on silica gel (20 g, hexanes : EtOAc 8:1) gave solid **17d** contaminated with a trace of *n*-Bu_3SnBr. Washing with hexanes yielded pure **17d** (112 mg, 61%) as yellowish solids: mp 138-140°C; MS *m/z* 368 (M^+); ^1H NMR ($CDCl_3$) δ 2.51 (s, 3H), 2.92 (s, 1H), 6.76 (d, *J* = 1.8 Hz, 1H), 7.18-7.33 (m, 12H), 7.52 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.32, 77.50, 125.80, 127.09, 127.38, 127.89, 127.99, 129.49, 131.69, 135.76, 137.52, 142.20, 143.64, 145.93, 197.43; high resolution MS: 368.1420, $C_{25}H_{20}O_3$ Calcd. 368.1407.

(e) **3-(1-Hydroxycyclohex-2-en-1-yl)-4-(*trans*-styryl)-furan (17e)** was prepared from **16h** (93 mg, 0.21 mmol), (*E*)-β-bromostyrene (43 mg, 0.23 mmol) and $[(C_3H_5)PdCl]_2$ (4 mg, 0.01 mmol) in DMF (1 mL) and HMPA (0.1 mL) after stirring at room temperature for 24 h. Chromatography on silica gel (20 g, hexanes : EtOAc 10:1) provided **17e** (42 mg, 76%) as a colorless oil: MS *m/z* 266 (M^+); ^1H NMR ($CDCl_3$) δ 1.60-1.65 (m, 2H), 1.70-1.90 (m, 1H), 1.93-2.13 (m, 4H), 5.84 (d, *J* = 10.0 Hz, 1H), 5.96 (dt, *J* = 3.6, 3.6, 10.0 Hz, 1H), 6.83 (d, *J* = 16.4 Hz, 1H), 7.14 (dd, *J* = 0.7, 16.4 Hz, 1H), 7.17-7.36 (m, 4H), 7.43 (d, *J* = 7.1 Hz, 1H), 7.62 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.07, 25.06, 37.15, 68.74, 119.13, 123.20, 126.32, 127.33, 128.62, 129.28, 130.43, 131.96, 137.75, 140.31, 140.51; high resolution MS: 266.1336, $C_{18}H_{18}O_2$ Calcd. 266.1302.

3-Hydroxymethyl-4-(tri-*n*-butylstannyl)furan (16g). 1.0 M solution of DIBAL in hexanes (5.5 mL, 5.5 mmol) was added dropwise to a stirred solution of **16b** (1.0 g, 2.6 mmol) in *n*-hexane (10 mL) at 0°C over 1h. Wet Et_2O (20 mL) was added gradually, and was followed by addition of saturated aqueous NH_4Cl solution (5 mL). After the white precipitate was removed by suction filtration, the whole mixture was extracted with Et_2O (3×20 mL). The ethereal layer was dried ($MgSO_4$) and evaporated. Chromatography on neutral alumina (grade III, 50 g, hexanes : EtOAc 10:1) gave **16g** (914 mg, 90%) as a colorless oil, which was identical spectrometrically to an authentic sample prepared previously.

3-*tert*-Butyldimethylsiloxymethyl-4-(tri-*n*-butylstannyl)furan (18). To a solution of **16g** (472 mg, 1.22 mmol) in Et_3N (1.0 mL, 7.2 mmol) and pyridine (9 mL) was added *t*-$BuMe_2SiCl$ (276 mg, 1.83 mmol). The resulting solution was stirred at room temperature for 4 h. 5% Aqueous $KHCO_3$ solution (5 mL) was added, and the mixture was extracted with Et_2O (3×25 mL). The organic layer was dried ($MgSO_4$) and evaporated. Column chromatography on neutral alumina (grade III, 30 g, hexanes : EtOAc 30:1) gave **70** (562 mg, 92%) as a colorless oil: MS *m/z* 444 (M^+-C_4H_9); ^1H NMR ($CDCl_3$) δ 0.07 (s, 6H), 0.89 (t, *J* = 7.2, 7.2 Hz, 9H), 0.92 (s, 9H), 1.03 (t, *J* = 8.1, 8.1 Hz, 6H), 1.32 (sextet, *J* = 7.2, 7.2, 7.2, 7.2, 7.2 Hz, 6H), 1.50 (sextet, *J* = 8.0, 8.0, 8.0, 8.0, 8.0 Hz, 6H), 4.55 (s, 2H), 7.13 (d, *J* = 1.0 Hz, 1H), 7.43 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -5.20, 9.89, 13.57, 18.50, 26.04, 27.30, 29.19, 59.21, 114.28, 130.86, 139.80, 147.87. Anal. Calcd. for $C_{23}H_{46}O_2SnSi$: C, 55.10; H, 9.25. Found: C, 55.27; H, 9.20.

3-*tert*-Butyldimethylsiloxymethyl-4-propanoylfuran (19). In a sealed tube equipped with a magnetic stirring bar were added $Pd(PPh_3)_2Cl_2$ (11 mg, 0.02 mmol), **18** (153 mg, 0.31 mmol), propanoyl chloride (40 μL, 0.46 mmol) and THF (1 mL). Then the mixture was heated at 70°C for 20 h. After being cooled to room temperature, the mixture was concentrated *in vacuo* and the residue was chromatographed on silica gel (20 g, hexanes : EtOAc 50:1) to give **19** (57 mg, 70%) as a colorless oil:. MS *m/z* 268 (M^+); ^1H NMR ($CDCl_3$) δ 0.10

(s, 6H), 0.93 (s, 9H), 1.16 (t, J = 7.4, 7.4 Hz, 3H), 2.75 (q, J = 7.4, 7.4, 7.4 Hz, 2H), 4.87 (t, J = 0.7, 0.7 Hz, 2H), 7.40 (dd, J = 0.6, 1.7 Hz, 1H), 7.98 (t, J = 0.9, 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -5.48, 8.08, 18.30, 25.89, 33.42, 58.53, 125.08, 126.97, 141.64, 148.11, 196.36. Anal. Calcd. for $C_{14}H_{24}O_3Si$: C, 62.64; H, 9.01. Found: C, 63.10; H, 8.82.

3-(*tert*-Butyldimethylsiloxymethyl)-4-(4-methylpent-3-en-1-oyl]furan (20). A mixture of **18** (214 mg, 0.42 mmol), 3-bromo-1-methyl-2-butene (74 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.02 mmol) in THF (5 mL) was heated at 55-60°C for 3 d to give, after workup and chromatography on silica gel (20 g, hexanes : EtOAc 30:1), **20** (103 mg, 80%) as a colorless oil: MS *m/z* 308 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 6H), 0.93 (s, 9H), 1.68 (s, 3H), 1.76 (d, J = 1.2 Hz, 3H), 3.44 (dd, J = 0.8, 7.0 Hz, 2H), 4.88 (d, J = 1.7 Hz, 2H), 5.36 (tt, J = 1.7, 1.7, 7.0, 7.0 Hz, 1H), 7.40 (q, J = 1.7, 1.7, 1.7 Hz, 1H), 8.00 (d, J = 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -5.48, 18.04, 18.31, 25.60, 25.89, 29.68, 40.33, 58.56, 116.31, 125.02, 127.18, 135.49, 141.58, 148.37, 194.16. Anal. Calcd. for $C_{17}H_{28}O_3Si$: C, 66.18; H, 9.15. Found: C, 66.33; H, 9.09.

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