Regioselective Synthesis of (*E*)-5-(Tributylstannylmethylidene)-5*H*-furan-2-ones and (*E*)-3-(Tributylstannylmethylidene)-3*H*-isobenzofuran-1-ones: Easy Access to γ-Alkylidenebutenolide and Phthalide Skeletons

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Abstract: Regio- and stereoselective synthesis of γ-alkylidenebutenolides and γ-alkylidenephthalides has been achieved through the palladium-catalysed tandem cross-coupling/cyclisation reactions of tributylstannyl-3-iodopropenoate or the 2-iodo benzoate derivatives with tributyltinacetylene. Iododestannylation occurred with inversion of the configuration of the exocyclic double bond in the case of butenolides, but with retention of configuration for the phthalide. The selectivity observed in the Stille reaction was found to be dependent on the nature of the vinyl or the aryl halide.

Key words: cross-coupling, cyclisation, alkylidenebutenolides, phthalides, retinoids

The heterocyclisation reaction is one of the most important in organic synthesis. The synthesis of five- and six-membered ring unsaturated lactones (butenolides, phthalides or α-pyrones) constitutes an important class of biologically active compounds and has been the focus of considerable attention in synthetic organic chemistry[1] and in medicinal chemistry.[2] An increasing amount of interest has developed over the past decade on the synthesis of stereodefined γ-alkylidene butenolide,[3] which has been isolated from natural sources. For example, freelingyne[4] displays antibiotic activity, and rubrolides,[5] which are marine tunicate metabolites, exhibit potent antibiotic activity in vitro. 3-Alkylidene (arylidene) phthalides possess a wide range of biological activities as antispasmodic, herbicidal and insecticidal agents,[6] pesticides[7] and cytotoxic agents.[8] 3-Arylidene- and alkylidene phthalides have also been used extensively as intermediates in the synthesis of various drugs[9] and naturally occurring compounds.[10] Numerous methods reported for the synthesis of these structures over the last decade have utilised transition metals (Ag, Hg, Rh, Pd) to promote intramolecular addition of carboxylic acids to alkynes.[11,12] In general, the lactonisation reaction of 4-alkynoic acids involves a stereoselective trans-addition reaction via a 5-*exo* process. In addition to the formation of γ-alkylidene butenolides or phthalides, in some cases, six-membered lactones have been obtained via the 6-*endo* mode. In each case the synthesis suffered from lack of selectivity. The construction of the γ-alkylidene moiety has typically been achieved by one of four major routes. Lewis acid catalysed coupling of aldehydes with oxofurans,[13] alkenylation of γ-lactones via their enolates[14] or phosphorus ylides,[15] and olefination of maleic anhydride with organometallic reagents[16] or phosphoranes[17] have all been described as effective but with a major drawback – the non-selective construction of the exocyclic double bond. The fourth route allowed complete control of the exocyclic double bond formation through a transition-metal (Pd, Ag)-catalysed lactonisation. However, although *Z*-selectivity of the exocyclic double bond is relatively easy to control, clean access to the *E*-stereoisomer still remains a challenge for organic chemists [with the exception of the stereoselective synthesis of γ-(*E*)-freelingyne].[18] Similarly, it has been found that (*Z*)-3-alkylidenephthalides can be obtained as major or minor products either by the reaction of *ortho*-iodobenzoic acid with terminal alkynes in the presence of palladium catalyst[19] or in the presence of zinc chloride.[20]

In order to prepare α-pyranone selectively, we recently reported two different approaches using palladium-catalysed sequences, with one involving a functional vinylstannane and acyl chlorides[21] and the second employing β-iodovinylic acids and allenylstannane.[22] In addition, we have previously described the synthesis of dienoic acids or enynes bearing a carboxylic acid function starting from β-iodovinylic acids and either vinyltin or alkynylzinc reagents.[23] In a continuation of our studies on the synthesis of unsaturated heterocycles,[24] we recently reported our preliminary results on the synthesis of γ-tributyltinmethylidene butenolides using alkynyltin reagents (Scheme 1).[25] We now present our full results in this field and their extension to regio- and stereoselective synthesis of γ-tributyltinmethylidene phthalides. The γ-tributyltinmethylidene butenolides and phthalides are useful intermediates in the selective synthesis of alkylidene- or arylidene butenolides and phthalides.

Our investigation began with the coupling of tributylstannylacetylene with (*Z*)-3-iodoprop-2-enoic acid (**1a**) under conditions defined by Lu [26] and Negishi.[5b] Unfortunately, only traces of stannylated butenolide **2a** were obtained together with a large amount of tin by-products and the starting iodovinylic acid.

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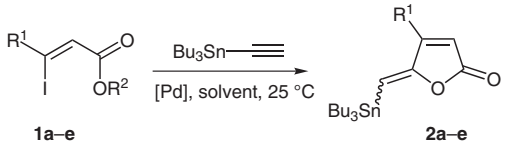


Scheme 1

In order to optimise the yields of **2a**, we examined the reaction under the range of conditions summarized in Table 1. Initially, the influence of the carboxylic acid function on conversion rates was examined.

Table 1 Experimental Conditions for the Synthesis of **2a**[a]

Entry	R^2	[Pd][b]	Additive	Solvent	Yield (%)
1	H	A	CuI (10%), Et_3N	DMF	5
2	Et	A		DMF	73[c]
3	Na	A		DMF	0
4	$SnBu_3$	A		DMF	67
5	$SnBu_3$	A		MeCN	0
6	$SnBu_3$	A		THF	0
7	$SnBu_3$	B		DMF	13
8	$SnBu_3$	C		DMF	54
9	$SnBu_3$	C	PPh_3	DMF	57
10	$SnBu_3$	A	CuI	DMF	60

[a] These experiments were performed with (*Z*)-3-iodoprop-2-enoic acid (**1a**; R^1 = H).
[b] A = $Pd(PPh_3)_4$; B = $PdCl_2(MeCN)_2$; C = $PdCl_2(PPh_3)_2$.
[c] 73% yield of ethyl (*Z*)-pent-2-en-4-ynoate was obtained.

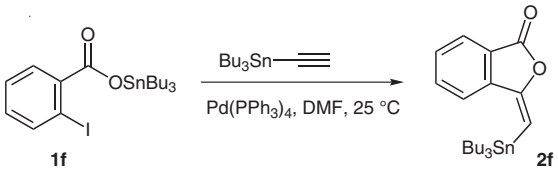
In the presence of 1% tetrakis(triphenylphosphine) palladium in DMF, free carboxylic acid (entry 1), ester (entry 2) and sodium salt derivatives (entry 3) did not yield the desired tin butenolide **2a**. Surprisingly, the use of tributyltin carboxylate[23d] (entry 4), under identical conditions, provided **2a** in 67% yield, with a clean configuration of the double bond. We then examined the influence of the solvent and the palladium complexes and found that while acetonitrile and tetrahydrofuran (entries 5 and 6) were ineffective, *N*,*N*-dimethylformamide (or dimethylacetamide) afforded fair yields of the cyclised product. We also observed that phosphine-ligated palladium appeared to be more efficient than other palladium chlorides (entry 7). Attempts to improve the yield through the addition of copper salt met with no success (entry 10).

The reaction of tributylstannyl acetylene with a range of tributylstannyl (*Z*)-3-substituted 3-iodoprop-2-enoates **1a–e** proceeded with regio- and stereocontrol to provide fair yields of (*E*)-5-tributylstannylmethylidene-5*H*-furan-2-ones **2a–e** (Table 2).

Table 2 Synthesis of 3-Substituted (*E*)-5-(Tributylstannylmethylidene)-5*H*-furan-2-ones **2a–e**

Entry	R^1	**2**	Yield (%)
1	H	**2a**	67
2	Me	**2b**	62
3	$MeOCH_2$	**2c**	70
4	Ph	**2d**	67
5	Me_3Si	**2e**	65

Similarly, the reaction of tributylstannylacetylene with tributylstannyl-2-iodobenzoate regio- and stereoselectively yielded 75% (*E*)-3-(tributylstannylmethylidene)phthalide **2f** (Scheme 2).

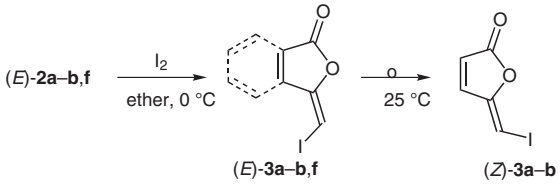


Scheme 2

The products **2a–f** could be easily purified by column chromatography, and the structures were confirmed by ^1H and ^{13}C NMR. According to the above authors,[11] the *Z*-isomer of **2a** was expected to be formed. However, analysis of the tin–carbon coupling constants, which has previously been shown to be a good tool with which to assign the stereochemistry of trisubstituted vinylstannanes,[27] revealed a very low $^3J_{Sn-C4}$ coupling constant (17 Hz), indicating a predominance of the *E*-isomer. Confirmation the *E* configuration of **2a** was obtained through a NOESY NMR experiment which showed that a strong cross-peak between H-4 and the α-CH_2 of the Bu_3Sn group existed, whilst no cross-peak between H-4 and H-6 was observed.

Though isomerisation of the double bond and cyclisation to the pyranones have previously been shown to occur under Sonogashira conditions,[18,26] nether of these processes were observed in this case. Furthermore, Stille cross-coupling products derived from **2a–f** and the starting iodopropenoic acid were not detected. The stereochemistry of all the products **2a–f** were assigned via the ^{13}C–^{119}Sn coupling constants and found to have been formed with full preference for the *E*-isomer.

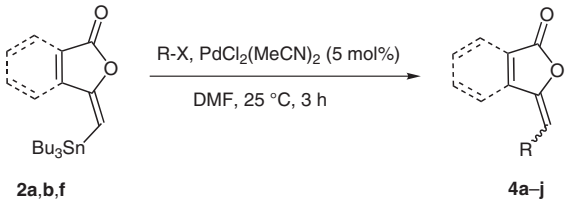
The reactivity of compounds **2a–f** was studied using iododestannylation and cross-coupling reactions. The iododestannylation of **2a**, **2b** and **2f** occurred stereoselectively, with good yields, in diethyl ether at 0 °C (Scheme 3).



Scheme 3

However, the iodobutenolides (*E*)-**3a** and (*E*)-**3b** formed were found to be unstable and quantitatively isomerised to the thermodynamically more stable *Z*-isomers (*Z*)-**3a** and (*Z*)-**3b**. Attempts at stabilising the *E*-isomers by lowering the temperature or changing the solvent (toluene, chloroform or dichloromethane) were unsuccessful and yielded mixtures of isomers which led to the thermodynamically more stable *Z*-isomers after a few hours. On the other hand, the iododestannylation of **2f** occurred with retention of configuration (confirmed by NOESY NMR experiments).

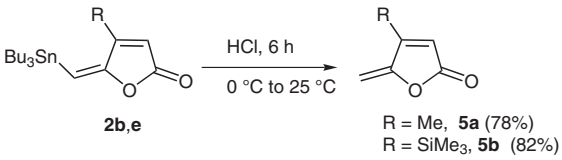
The reactivity of tin lactones (*E*)-**2a**, (*E*)-**2b** and **2f** were also studied using Stille coupling reactions[29] with various vinyl and aryl iodides in the presence of a catalytic amount of dichlorobis(acetonitrile) palladium(II) in *N*,*N*-dimethylformamide. The cross-coupling reactions provided good yields of the desired products **4a**–**j** (Scheme 4) and the results are reported in Table 3.



Scheme 4

It was found that the selectivity of butenolides was highly dependent on the nature of the substituent in position 4 and on the nature of the aryl iodide. Indeed, Stille cross-coupling of **2a**, **2b** or **2f** with 2-iodothiophene (entry 4), iodobenzene (entry 8) or (*E*)-1-iodo-2-trimethylsilylethylene (entry 10) gave the desired heteroaryl **4d**, aryl **4h** butenolide or allylidene phthalide **4j** (70%, 74% and 65% yields, respectively), with a clean *E*-configuration of the exocyclic double bond, demonstrating that Stille coupling occurred with retention of configuration (confirmed by NOESY NMR experiments). In contrast, in the case of **4b–c**,**e–g**,**i**, the Stille cross-coupling led to the desired 5-ylidenebutenolides but with inversion of the configuration of the exocyclic double bond whilst respecting the stereochemistry of the starting vinyl halide. This could be explained by the greater thermodynamic stability of the *Z*-isomer. A semiempirical AM1 calculation, when applied to both isomers of **4c** (entry 3), revealed a substantial interaction of the hydrogen borne by the C-4 carbon of the furanone cycle and the hydrogens in the ortho-position of the benzene ring of the *E*-isomer of **4c** (which would be expected to form during the cross-coupling).[30]

Good yields of the methyl and trimethylsilyl homologues of protoanemonin **5a** and **5b** (Scheme 5) were obtained, and no dimerisation product was detected,[31] when γ-tributylstannylmethylidene butenolides **2b** and **2e** were treated with 6 M hydrochloric acid in order to induce hydrodestannylation.

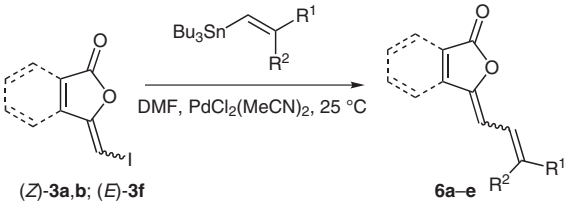


Scheme 5

Attention was then directed to the reactivity of iodobutenolides (*Z*)-**3a**, (*Z*)-**3b** and iodophthalide (*E*)-**3f**. Stille cross-coupling of these compounds with vinyltin, in the presence of a catalytic amount of dichlorobis(acetonitrile) palladium(II) in DMF, gave good yields of dienic butenolides and phthalides **6a–e** (Scheme 6, Table 4), with complete retention of the stereochemistry of the exocyclic double bond. The configuration of the starting vinyltin products was conserved.

Stille coupling of iodobutenolide (*Z*)-**3b** with an appropriate vinylstannane (entry 5), under the same conditions as described above, yielded 52% of the retinoid **6e** bearing a butenolide moiety. Good yields of the vinylstannane could be obtained using a previously described method.[32] Cross-coupling occurred with retention of configuration of the double bonds and no degradation products were observed.

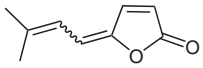
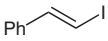
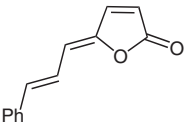
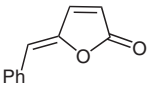
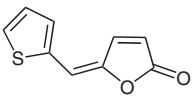
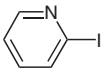
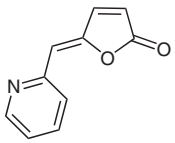
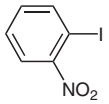
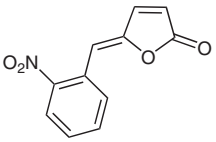
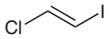
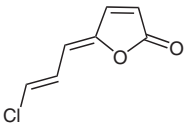
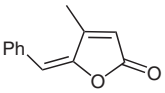
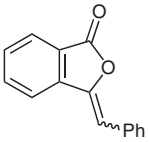
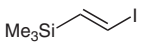
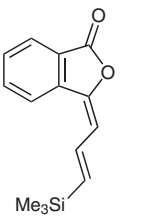
In all cases, the use of vinyltin or vinyliodide reagents permitted the transfer of a vinyl group to generate a range of alkylidenes butenolides or phthalides.

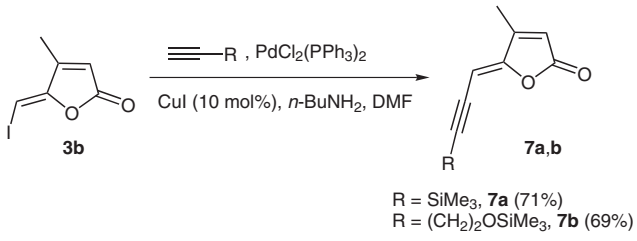


Scheme 6

We also investigated the synthesis of enyne butenolides **7** with alkynes and (*Z*)-**3b** under Sonogashira conditions[33] using dichlorobis(triphenylphosphine) palladium(II), copper iodide, butylamine and DMF as solvent at room temperature, and we obtained good yields of the corresponding enyne butenolides **7** (Scheme 7). The configuration of the double bond was unchanged.

Table 3 Cross-Coupling of **2** with Vinyl or Aryl Iodides

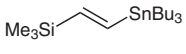
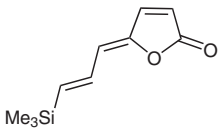
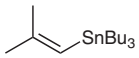
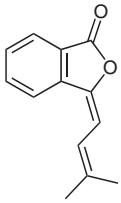
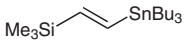
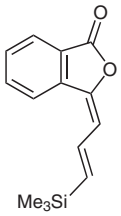
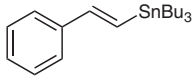
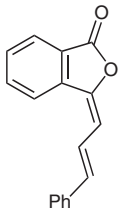
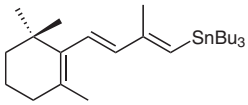
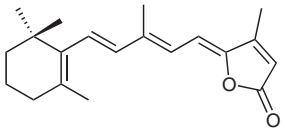
Entry	R–X	Product		5*E*:5*Z*	Yield (%)
1			**4a**	72:28	60
2			**4b**	0:100	77
3	PhI		**4c**	0:100	72
4			**4d**	100:0	70
5			**4e**	0:100	65
6			**4f**	0:100	58
7			**4g**	0:100	61
8	PhI		**4h**	100:0	74
9	PhI		**4i**	37:63	72
10			**4j**	100:0	65



Scheme 7

As a possible application of this chemistry, we investigated the synthesis of alkyne analogues of retinoic acid containing the alkylidene butenolide moeity.[34] The Sonogashira cross-coupling reaction of (*Z*)-**3b** with (7*E*)-1-(but-3-en-1-yn-4-yl)-2,6,6-trimethylcyclohex-1-ene (**8α**) or (7*E*)-1-(but-3-en-1-yn-4-yl)-2,6,6-trimethylcyclohex-2-ene (**8β**), under the same conditions as described above, yielded the desired retinoids **7c** or **7d** in 68% and 65% yields, respectively (Scheme 8). The cross-coupling occurred with retention of the configuration of the double

Table 4 Cross-Coupling of (*Z*)-**3a**, (*Z*)-**3b** and **3f** with Vinyltin Reagents

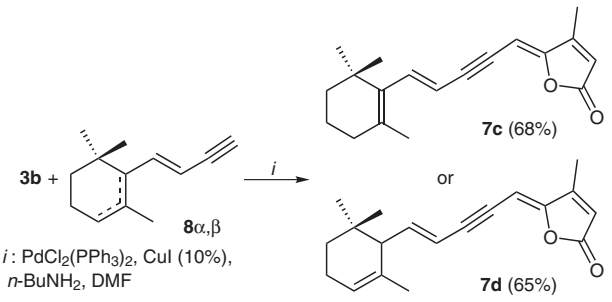
Entry	Vinyltin	Product	**6**	Yield (%)
1			**6a**	71
2			**6b**	70
3			**6c**[a]	78
4			**6d**	81
5			**6e**	52

[a] **6c** was found to be identical to **4j**.

bonds of **3b** and **8**. The dienyne **8** was obtained from α- or β-ionone according to the procedure described by Negishi.[32,35]

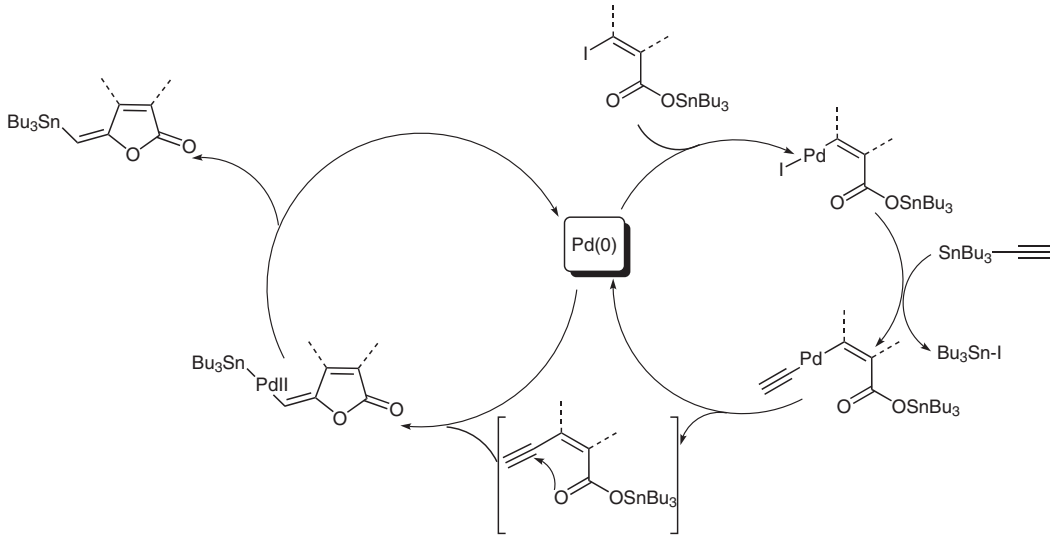
A plausible mechanism for the heteroannulation reaction is shown in Scheme 9. Initially, a Stille mechanism[29] would yield the tributylstannyl 3-enynoate by oxidative addition, transmetallation and reductive elimination. Cyclisation would then occur via an attack on the carboxylate function at the α-position (5-*exo* mode cyclisation) of the alkynyl moiety, which would lead to the palladium(II) intermediate. This intermediate would subsequently provide the stannylalkylidenebutenolide and regenerate the palladium(0) catalyst.[36]

In conclusion, we have demonstrated that the palladium-catalysed tandem cross-coupling/cyclisation reactions of tributylstannyl-3-iodopropenoate or tributylstannyl-2-iodo benzoate with tributyltinacetylene afford (*E*)-γ-tributylstannylmethylidene butenolides or phthalides, which are potential precursors for numerous alkylidene butenolides or phthalides. This methodology has been applied to the stereoselective synthesis of a retinoid containing an alkylidene butenolide core with fixed configuration of the double bonds.



Scheme 8

All reactions were carried out under inert atmosphere (Ar or N_2). THF and Et_2O were dried and freshly distilled from sodium/benzophenone. Acetonitrile was distilled from calcium chloride. DMF was dried by distillation over calcium hydride prior to use. Flash chromatography was performed with Merck silica gel (silica gel, 230–400 mesh). ^1H NMR spectra were recorded at 200 MHz in $CDCl_3$ using the residual solvent proton resonance (δ_H = 7.25 ppm)



Scheme 9 Proposed mechanism for the formation of tributylstannylmethylidene butenolides and phthalides.

as internal reference. Coupling constants (*J*) are in Hz. ^{13}C NMR were recorded at 50.32 MHz using the $CDCl_3$ solvent peak (δ_C = 77.0 ppm) as reference. Mass spectra were obtained in the GC/MS (70 eV) mode. The isotopic patterns are given for ^{120}Sn (isotopic values 33%) in organotin fragments; this means that the reported values for organotin fragments are roughly one third of the correct value, taking into account the 10 isotopes of tin compared with those of organic fragment. IR spectra were recorded on a Perkin-Elmer 781 FT-IR spectrophotometer and are reported in cm^{-1}. Melting points are uncorrected. 2-Iodobenzoic acid was commercially available. Tributyl(isobutenyl)stannane was prepared from isobutenylmagnesium bromide and bis(tributyltin)oxide.[43] (*E*)-1-(Tributylstannyl)-2-(trimethylsilyl)ethene was prepared by hydrostannation of (trimethylsilyl)acetylene.[44] (*E*)-Tributyl(β-styryl)stannane was prepared by hydrostannation of phenylacetylene.[45] (Tributylstannyl)acetylene was prepared from ethynyllithium-ethylenediamine complex and Bu_3SnCl.[46] Vinyliodides were prepared by iododestannylation of tributyl(vinyl)stannanes.[47] (*E*)-1-Chloro-2-iodoethylene was prepared by the method described by Negishi [acetylene gas was bubbled through a cooled solution (–10 °C) of ICl (10 g, 60.6 mmol) in HCl (6 N, 70 mL)].[48] Alcynes **8α** and **8β** were prepared according to the method described by Negishi.[35] Tributylstannyl-(*Z*)-3-iodopropenoate **1a–e** and 2-iodobenzoate **1f** were synthesized according to a literature method.[23d]

Preparation of 2: Typical Procedure

To a solution of tributylstannyl-2-iodo benzoate (**1f;** 5.37 g, 10 mmol) and palladium(0) tetrakis(triphenylphosphine) (0.115 g, 0.1 mmol) in DMF (35 mL) was added, dropwise, tributyl(ethynyl)stannane (5.67 g, 18 mmol) dissolved in DMF (5 mL). The mixture was stirred at 25 °C for 16 h, and then extracted with Et_2O (4 × 25 mL). The combined organic layer was washed with sat. NH_4Cl (3 × 25 mL), dried ($MgSO_4$) and concentrated in vacuo to give (*E*)-3-tributylstannylmethylidene phthalide **2f** (3.26 g), which was purified by column chromatography on silica gel (hexane–Et_2O–Et_3N, 90:8:2).

Products **2a–e** have been described previously.[25]

(*E*)-3-Tributylstannylmethylidenephthalide (2f)

Yield: 75%; colourless oil.

IR (neat): 3090, 2980, 2952, 2891, 2885, 1798, 1632, 1618, 1481, 1469 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.3 Hz, 9 H), 1.04–1.59 (m, 18 H), 6.93 (s J_{Sn-H} = 16.4 Hz, 1 H), 7.47–7.69 (m, 3 H), 7.84 (d, *J* = 7.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.2 (3 × C), 14.1 (3 × C, J_{Sn-C} = 387 Hz), 27.6 (3 × C, J_{Sn-C} = 57–60 Hz), 29.4 (3 × C, J_{Sn-C} = 22 Hz), 107 (J_{Sn-C} = 292 Hz), 121.4, 125.8, 127.5, 130.4, 134.4, 140.0 (J_{Sn-C} = 10 Hz), 154 (J_{Sn-C} = 33 Hz), 167.4.

^{119}Sn NMR ($CDCl_3$): δ = –44.2.

MS (EI, 70 eV): *m*/*z* (%) = 379 (100) [M$^{+\cdot}$ – 57], 44 (52), 41 (33), 39 (40).

Preparation of 3a, 3b and 3f; Typical Procedure

Iodine (1.78 g, 7 mmol) in Et_2O (50 mL) was added dropwise at 0 °C to a solution of **2a** (2.31 g, 6 mmol) in Et_2O (30 mL). The mixture was stirred at 0 °C for 1 h, then washed with sodium thiosulfate (5%, 3 × 15 mL), dried ($MgSO_4$) and concentrated in vacuo. The mixture of (*E*/*Z*)-5-iodomethylidene-5*H*-furan-2-one (**2**; 1.99 g, 90% yield) was obtained and isomerised quantitatively to (*Z*)-5-iodomethylidene-5*H*-furan-2-one **3a** after 6 h.

5-Iodomethylidene-5*H*-furan-2-one (3a)

Z-Isomer

Yield: 75%; yellow solid; mp 83–85 °C.

IR (KBr): 3056, 1775, 1753, 1627, 1290, 1151 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.29 (s, 1 H), 6.33 (d, *J* = 5.4 Hz, 1 H), 7.36 (d, *J* = 5.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 63.7, 121.7, 141.2, 156.8, 168.5.

MS (EI, 70 eV): *m*/*z* (%) = 222 (5) [M$^{+\cdot}$], 127 (15), 95 (16), 54 (15), 39 (100).

Anal. Calcd for $C_5H_3IO_2$: C, 27.05; H, 1.36. Found: C, 27.16; H, 1.39.

E-Isomer

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.42 (dd, *J* = 5.6 Hz, *J* = 1.8 Hz, 1 H), 6.61 (d, *J* = 1.8 Hz, 1 H), 7.71 (d, *J* = 5.6 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 66.0, 124.5, 143.1, 156.4, 170.3.

4-Methyl-5-iodomethylidene-5*H*-furan-2-one (3b)[24a]

Z-Isomer

Yield: 71%; yellow solid; mp 86–88 °C.

IR (KBr): 1775, 1753, 1627, 1290, 1151 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.14 (s, 3 H), 6.13 (s, 1 H), 6.20 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.6, 60.6, 118.6, 153.2, 158.6, 168.3.

MS (EI, 70 eV): *m*/*z* (%) = 236 (91) [M^+], 168 (26), 53 (100), 40 (67), 38 (28).

***E*-Isomer**

^1H NMR (200 MHz, $CDCl_3$): δ = 2.50 (s, 3 H), 6.19 (d, *J* = 1.5 Hz, 1 H), 6.57 (d, *J* = 1.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.3, 61.6, 121.8, 153.7, 155.2, 170.8.

(*E*)-3-Iodomethylidenephthalide (3f)[37]

Yield: 70%; colourless solid; mp 79–81 °C (Lit.[37] 80–82 °C).

IR (KBr): 1775, 1761, 1624, 1605, 1588, 1470, 1270 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.39 (s, 1 H), 7.63 (dd, *J* = 7.1 Hz, *J* = 6.8 Hz, 1 H), 7.75 (dd, *J* = 7.5 Hz, *J* = 6.8 Hz, 1 H), 7.90 (m, 1 H), 8.66 (d, *J* = 7.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 58.2, 124.6, 126.3, 126.9, 131.6, 135.0, 138.3, 149.3, 166.2.

MS (EI, 70 eV): *m*/*z* (%) = 272 (100) [M^+], 231 (8), 89 (18).

Anal. Calcd for $C_9H_5IO_2$: C, 39.74; H, 1.85. Found: C, 39.75; H, 1.87.

Preparation of 4a–j; Typical Procedure

To a solution of the vinyl (or aryl) iodide (8.4 mmol) in DMF (50 mL), either (*E*)-5-tributylstannylmethylidene-5*H*-furan-2-one (**2a**; 3.9 g, 10.1 mmol) or (*E*)-3-tributylstannylmethylidene phthalide (**2f**; 4.4 g, 10.1 mmol) diluted in DMF (10 mL) was added dropwise. At the end of the addition, dichlorobis(acetonitrile) palladium(II) (129 mg, 0.5 mmol) was added and the mixture was stirred for 3 h at 25 °C. Sat. NH_4Cl (3 × 25 mL) was added and the aqueous layer was extracted with Et_2O (3 × 20 mL), dried ($MgSO_4$) and the solvent was evaporated to give the crude product **4a–j** which was purified by column chromatography on silica gel (PE–Et_2O–Et_3N, 88:10:2).

5-(3-Methylbut-2-enylidene)furan-2-(5*H*)-one (4a)

Yield: 60%; colourless oil; ratio *E*/*Z* = 72:28.

IR (neat): 2976, 1777, 1747, 1630, 1116 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 223 (68) [M^+], 135 (100), 79 (67), 41 (47), 39 (55).

***Z*-Isomer**

^1H NMR (200 MHz, $CDCl_3$): δ = 1.9 (s, 3 H), 1.96 (s, 3 H), 6.17 (d, *J* = 12 Hz, 1 H), 6.22 (d, *J* = 5.5 Hz, 1 H), 6.57 (d, *J* = 12 Hz, 1 H), 7.77 (d, *J* = 5.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.4 (2 × C), 113.3, 118.3, 119.4, 139.0, 144.8, 150.0, 170.5.

***E*-Isomer**

^1H NMR (200 MHz, $CDCl_3$): δ = 1.9 (s, 3 H), 1.96 (s, 3 H), 6.05 (d, *J* = 12 Hz, 1 H), 6.17 (d, *J* = 5.2 Hz, 1 H), 6.45 (d, *J* = 12 Hz, 1 H), 7.42 (d, *J* = 5.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.4 (2 × C), 112.2, 118.2, 119.6, 144.0, 145.6, 148.0, 170.4.

(5*Z*)-5-[(*E*)-3-Phenylallylidene]-5*H*-furan-2-one (4b)[38]

Yield: 77%; colourless oil.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.04 (d, *J* = 11 Hz, 1 H), 6.22 (d, *J* = 5.2 Hz, 1 H), 6.86 (d, *J* = 16.2 Hz, 1 H), 7.09 (dd, *J* = 16.2 Hz, *J* = 11 Hz, 1 H), 7.90 (d, *J* = 5.2 Hz, 1 H), 7.30–7.51 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 115.1, 118.5, 121.4, 127.1, 128.7, 129.0, 138.3, 138.4, 142.9, 149.0, 169.0.

MS (EI, 70 eV): *m*/*z* (%) = 198 (46) [M^+], 170 (25), 115 (100), 51 (15), 39 (16).

(5*Z*)-5-Benzylidene-5*H*-furan-2-one (4c)[38,39]

Yield: 72%; colourless solid; mp 85–86 °C (Lit.[38,39] 86–87 °C).

IR (KBr): 1784, 1747, 1550, 1447, 1229 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.02 (s, 1 H), 6.20 (d, *J* = 5.3 Hz, 1 H), 7.31–7.42 (m, 3 H), 7.49 (d, *J* = 5.3 Hz, 1 H), 7.74–7.81 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 114.8, 118.7, 129.4 (2 × C), 130.0, 131.3 (2 × C), 133.4, 145.8, 149.0, 170.8.

MS (EI, 70 eV): *m*/*z* (%) = 172 (100) [M^+], 144 (33), 115 (68), 89 (46), 51 (17).

(5*E*)-5-[(Thiophen-2-yl)methylidene]-5*H*-furan-2-one (4d)[25]

Yield: 70%; colourless solid; mp 104–106 °C.

IR (KBr): 1792, 1762, 1545, 1435 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.31 (d, *J* = 5.5 Hz, 1 H), 6.83 (br s, 1 H), 7.04 (dd, *J* = 4.8 Hz, *J* = 2.9 Hz, 1 H), 7.14 (d, *J* = 2.9 Hz, 1 H), 7.38 (d, *J* = 4.8 Hz, 1 H), 8.01 (d, *J* = 5.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 110.0, 121.7, 128.6, 129.0, 132.0, 135.0, 140.4, 149.4, 169.7.

MS (70 eV, EI): *m*/*z* (%) = 178 (100) [M^+], 150 (19), 96 (57).

Anal. Calcd for $C_9H_6O_2S$: C, 60.67; H, 3.39. Found: C, 60.87; H, 3.38.

(5*Z*)-5-[(Pyridin-2-yl)methylene]-5*H*-furan-2-one (4e)

Yield: 65%; colourless solid; mp 82–84 °C.

IR (KBr): 1780, 1753, 1556, 1443 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.33 (d, *J* = 5.5 Hz, 1 H), 6.55 (br s, 1 H), 7.14–7.27 (m, 2 H), 7.66 (dd, *J* = 7.6 Hz, *J* = 7.4 Hz, 1 H), 8.6 (d, *J* = 3.9 Hz, 1 H), 8.78 (d, *J* = 5.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 113.3, 121.5, 122.2, 126.3, 137.2, 143.2, 144.1, 150.5, 153.4, 169.2.

MS (EI, 70 eV): *m*/*z* (%) = 173 (100) [M^+], 145 (44).

Anal. Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.07. Found: C, 69.43; H, 3.98.

(5*Z*)-5-(2-Nitrobenzylidene)-5*H*-furan-2-one (4f)

Yield: 58%; colourless solid; mp 88–90 °C.

IR (KBr): 1786, 1763, 1523, 1342 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.42 (d, *J* = 5.5 Hz, 1 H), 7.28 (s, 1 H), 7.46 (d, *J* = 7.5 Hz, 1 H, H_{ar}), 7.53–7.79 (m, 2 H, H_{ar}), 7.58 (d, *J* = 5.5 Hz, 1 H), 8.25 (d, *J* = 8.0 Hz, 1 H, H_{ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 112.6, 123.4, 126.3, 129.0, 133.0, 141.0, 146.1, 148.8, 151.8, 169.4.

MS (EI, 70 eV): *m*/*z* (%) = 217 (3) [M^+], 119 (38), 82 (100), 54 (71).

Anal. Calcd for $C_{11}H_7NO_4$: C, 60.83; H, 3.25. Found: C, 59.98; H, 3.34.

(5*Z*)-5-[(*E*)-3-Chloroallylidene]-5*H*-furan-2-one (4g)

Yield: 61%; colourless solid; mp 98–100 °C.

IR (KBr): 1785, 1755, 1592, 1120 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.27–6.57 (m, 3 H), 6.74 (dd, *J* = 18.1 Hz, *J* = 12.4 Hz, 1 H), 7.74 (d, *J* = 5.3 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 111.6, 121.1, 126.7, 138.8, 140.5, 151.0, 169.5.

MS (EI, 70 eV): *m*/*z* (%) = 156 (56) [$M^{+\cdot}$], 85 (78), 83 (100).

Anal. Calcd for $C_7H_5ClO_2$: C, 53.70; H, 3.22. Found: C, 52.55, H, 3.28.

(5*E*)-5-Benzylidene-4-methyl-5*H*-furan-2-one (4h)[24a,e]
Yield: 74%; colourless solid; mp 62 °C.

IR (KBr): 1773, 1754, 1645, 1596, 1386 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83 (s, 3 H), 6.0 (s, 1 H), 6.87 (s, 1 H), 7.25–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.8, 116.1, 120.8, 128.8, 129.0, 130.0, 133.0, 151.0, 154.4, 169.2.

MS (70 eV, EI): *m*/*z* (%) = 186 (100) [$M^{+\cdot}$], 158 (25), 90 (46), 39 (42).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 78.49; H, 5.52.

3-Benzylidene-3*H*-isobenzofuran-1-one (4i)[40]
Yield: 72%; colourless oil; ratio *E*/*Z* = 37:63.

IR (neat): 1771, 1763, 1663, 1608 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 223 (100) [$M^{+\cdot}$], 201 (12), 146 (62), 77 (15), 51 (35).

***Z*-Isomer**
^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.39 (s, 1 H), 7.23–7.90 (m, 9 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 107.5, 120.3, 123.7, 125.9, 128.9, 129.2, 129.6, 130.2, 133.5, 138.0, 138.1, 145.0, 167.2.

***E*-Isomer**
^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.88 (s, 1 H), 7.23–7.90 (m, 9 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 113.4, 123.3, 125.8, 126.5, 129.3, 129.6, 130.6, 130.8, 133.4, 134.5, 141.0, 147.0, 167.4.

(3*E*)-3-[(*E*)-3-(Trimethylsilyl)allylidene]-3*H*-isobenzofuran-1-one (4j = 6c)
Yield: 65%; colourless solid; mp 166–168 °C.

IR (neat): 1775, 1758, 1649, 1603, 1258 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.23 (d, *J* = 18 Hz, 1 H), 6.37 (d, *J* = 11.5 Hz, 1 H), 7.15 (dd, *J* = 18 Hz, *J* = 11.5 Hz, 1 H), 7.51 (dd, *J* = 8.3 Hz, *J* = 7.5 Hz, 1 H), 7.71 (dd, *J* = 7.9 Hz, *J* = 7.5 Hz, 1 H), 7.80 (d, *J* = 8.3 Hz, 1 H), 7.87 (d, *J* = 7.9 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.0 (3 × C), 116.3, 123.7, 126.1, 126.3, 130.4, 134.9, 135.8, 138.1, 142.3, 146.4, 167.1.

MS (EI, 70 eV): *m*/*z* (%) = 244 (15) [$M^{+\cdot}$], 230 (18), 229 (100), 201 (15), 155 (13).

Anal. Calcd for $C_{14}H_{16}O_2Si$: C, 68.81; H, 6.60. Found: C, 68.84; H, 6.62.

Preparation of 6a–e; Typical Procedure
To a solution of the iodovinylic phthalide (**3f**; 2.24 g, 10.1 mmol) in DMF (20 mL), vinyltributyltin (11.2 mmol) diluted in DMF (10 mL) was added dropwise. At the end of the addition, dichlorobis(acetonitrile) palladium(II) (13 mg, 0.05 mmol) was added. The mixture was stirred for 3 h at r.t. then hydrolysed with sat. NH_4Cl (3 × 25 mL). The aqueous layer was extracted with Et_2O (3 × 25 mL), dried ($MgSO_4$) and the solvent removed under vacuum to give the crude products **6a–c**, which were purified by crystallisation or by column chromatography on silica gel (PE–Et_2O–Et_3N, 88:10:2).

(5*Z*)-5-[(*E*)-3-(Trimethylsilyl)allylidene]-(5*H*)-furan-2-one (6a)[41]
Yield: 71%; colourless oil.

IR (neat): 3090, 1785, 1620, 1200 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20 (s, 9 H), 5.80 (d, *J* = 11 Hz, 1 H), 6.22 (d, *J* = 5 Hz, 1 H), 6.33 (d, *J* = 18.5 Hz, 1 H), 7.0 (dd, *J* = 18.5 Hz, *J* = 11 Hz, 1 H), 7.43 (d, *J* = 5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.9 (3 × C), 117.7, 120.0, 137.0, 145.0, 145.3, 150.0, 171.0.

MS (EI, 70 eV): *m*/*z* (%) = 194 (18) [$M^{+\cdot}$], 179 (23), 151 (68), 75 (100), 73 (51), 43 (79).

Anal. Calcd for $C_{10}H_{14}O_2Si$: C, 61.81; H, 7.26. Found: C, 61.69; H, 7.31.

(*E*)-3-(3-Methylbut-2-enylidene)-(3*H*)-isobenzofuran-1-one (6b)
Yield: 70%; colourless solid; mp 118–120 °C.

IR (KBr): 1772, 1762, 1653, 1607, 1473 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.88 (s, 6 H), 6.32 (d, *J* = 11.7 Hz, 1 H), 6.45 (d, *J* = 11.7 Hz, 1 H), 7.40–7.70 (m, 3 H), 7.84 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.2, 27.1, 105.2, 118.6, 120.0, 124.4, 126.0, 129.5, 134.6, 140.2, 141.8, 143.7, 167.3.

MS (EI, 70 eV): *m*/*z* (%) = 200 (100) [$M^{+\cdot}$], 172 (14), 157 (20).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.57; H, 5.97.

(3*E*)-3-[(*E*)-3-Phenylallylidene]-(3*H*)-isobenzofuran-1-one (6d)
Yield: 81%; colourless solid; mp 154–156 °C.

IR (KBr): 1769, 1758, 1606, 1471, 1384, 1013 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.57 (d, *J* = 12.2 Hz, 1 H), 6.82 (d, *J* = 15.3 Hz, 1 H), 7.27–7.57 (m, 6 H), 7.75 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1 H), 7.92 (d, *J* = 8.6 Hz, 1 H), 7.97 (d, *J* = 8.4 Hz; 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 114.5, 121.4, 123.6, 126.1, 126.2, 127.2, 129.0, 129.3, 130.2, 135.0, 137.0, 138.0, 138.1, 146.5, 167.1.

MS (EI, 70 eV): *m*/*z* (%) = 248 (100) [$M^{+\cdot}$], 230 (18), 171 (32), 103 (18), 77 (18).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.32; H, 4.79.

(5*Z*,2′*E*,4′*E*)-4-Methyl-5-[3-methyl-5-(2,6,6-trimethylcyclohex-1-enyl)penta-2,4-dienylidene]-(5*H*)-furan-2-one (6e)[42]
Yield: 52%; colourless oil.

IR (neat): 2961, 2944, 1770, 1751 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.0 (s, 6 H), 1.42–1.46 (m, 2 H), 1.55–1.60 (m, 2 H), 1.69 (s, 3 H), 2.0 (s, 3 H), 2.15–2.17 (m, 5 H), 5.86 (s, 1 H), 6.16 (d, *J* = 12.2 Hz, 1 H), 6.20 (d, *J* = 16.3 Hz, 1 H), 6.27 (d, *J* = 12.2 Hz, 1 H), 6.58 (d, *J* = 16.3 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.2, 19.5, 22.2, 22.3, 29.4, 33.6, 34.6, 40.0, 115.8, 122.9, 128.8, 130.7, 132.5, 137.4, 137.9, 142.6, 150.0, 154.3, 169.6.

MS (EI, 70 eV): *m*/*z* (%) = 298 (64) [$M^{+\cdot}$], 283 (44), 105 (65), 91 (98), 41 (100).

Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.64; H, 8.67.

Preparation of 7a–d; General Procedure
A solution of butyl amine (0.2 mL, 2.06 mmol) and alkyne (4.06 mmol) in DMF (6 mL) was stirred under an argon atmosphere at r.t. for 15 min. Butenolide **3b** (479 mg, 2.03 mmol), [$PdCl_2(PPh_3)_2$] (50

mg, 0.1 mmol) and CuI (20 mg, 0.1 mmol) were added and the mixture was stirred at r.t. for 4 h. After this time, the mixture was poured into H_2O (10 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with sat. NH_4Cl (3 × 25 mL), dried ($MgSO_4$) and the solvents were evaporated under reduced pressure to give the crude products **7a–d** which were purified by column chromatography on silica gel (PE–Et_2O–Et_3N, 97:2:1).

(5*Z*)-4-Methyl-5-[3-(trimethylsilyl)prop-2-ynylidene]-(5*H*)-furan-2-one (7a)
Yield: 71%; colourless oil.

IR (neat): 2975, 1791, 1675, 1202 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.20 (s, 9 H), 2.40 (d, *J* = 1.5 Hz, 3 H), 5.75 (d, *J* = 1.6 Hz, 1 H), 6.00 (dq, *J* = 1.6, 1.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.1 (3 × C, J_{Si-C} = 29 Hz), 9.0, 90.8, 98.0, 108.5, 118.0, 154.3, 158.6, 168.5.

MS (EI, 70 eV): *m*/*z* (%) = 206 (10) [M^+], 192 (16), 191 (100), 178 (15).

HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}O_2Si$: 206.0763; found: 206.0776.

(5*Z*)-4-Methyl-5-[5-(trimethylsiloxy)pent-2-ynylidene]-(5*H*)-furan-2-one (7b)
Yield: 69%; colourless oil.

IR (neat): 2980, 2958, 1793, 1610, 1205, 1115 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.02 (s, 9 H), 2.38 (s, 3 H), 2.61 (td, *J* = 6.8, 2.4 Hz, 2 H), 3.82 (t, *J* = 6.8 Hz, 2 H), 5.73 (br s, 1 H), 5.96 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.3 (3 × C), 18.4, 25.0, 62.1, 95.2, 100.0, 111.0, 119.2, 154.8, 157.8, 168.5.

MS (EI, 70 eV): *m*/*z* (%) = 174 (22), 131 (100), 103 (58), 75 (56), 61 (27).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{18}O_3Si$: 250.1025; found: 250.1041.

(5*Z*)-4-Methyl-5-[(4*E*)-5-(2,6,6-trimethylcyclohex-1-enyl)pent-4-en-2-ynylidene]-(5*H*)-furan-2-one (7c)[24a]
Yield: 68%; colourless oil.

IR (neat): 2958, 2915, 2181, 1778, 1601 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.0 (s, 6 H), 1.39–1.45 (m, 2 H), 1.53–1.60 (m, 2 H), 1.72 (s, 3 H), 2.0 (t, *J* = 6.1 Hz, 2 H), 2.43 (d, *J* = 1.4 Hz, 3 H), 5.65 (dd, *J* = 16.3, 2.9 Hz, 1 H), 5.90 (dd, *J* = 2.9, 1.6 Hz, 1 H), 5.95 (dq, *J* = 1.6, 1.4 Hz, 1 H), 6.65 (d, *J* = 16.3 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.2, 19.6, 22.2, 29.4 (2 × C), 34.0, 34.7, 40.3, 85.5, 95.4, 101.5, 111.7, 119.3, 134.0, 137.5, 143.2, 154.6, 157.5, 168.4.

MS (EI, 70 eV): *m*/*z* (%) = 282 (35) [M^+], 267 (29), 34 (34), 41 (100), 39 (68).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{22}O_2$: 282.1620; found: 282.1605.

(5*Z*)-4-Methyl-5-[(4*E*)-5-(2,6,6-trimethylcyclohex-2-enyl)pent-4-en-2-ynylidene]-(5*H*)-furan-2-one (7d)
Yield: 65%; colourless oil.

IR (neat): 3026, 2960, 2183, 1776, 1603 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (s, 3 H), 0.92 (s, 3 H), 1.20 (dt, *J* = 13.5 Hz, *J* = 5.2 Hz, 1 H), 1.43 (dt, *J* = 13.5 Hz, *J* = 8.2 Hz, 1 H), 1.60 (s, 3 H), 1.98–2.04 (m, 2 H), 2.23 (d, *J* = 10 Hz, 1 H), 2.45 (d, *J* = 1.5 Hz, 3 H), 5.48 (br s, 1 H), 5.65 (dd, *J* = 15.8 Hz, *J* = 2.8 Hz, 1 H), 6.0 (dd, *J* = 2.8 Hz, *J* = 1.6 Hz, 1 H), 6.02 (dd, *J* = 1.6 Hz, *J* = 1.5 Hz, 1 H), 6.09 (dd, *J* = 15.8 Hz, *J* = 10 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.1, 23.4, 23.6, 27.4, 28.2, 32.0, 33.2, 55.7, 84.0, 95.2, 100.4, 111.0, 119.4, 122.8, 133.0, 148.2, 154.7, 157.6, 168.4.

MS (EI, 70 eV): *m*/*z* (%) = 282 (32) [M^+], 226 (87), 122 (100), 107 (55), 41 (63).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{22}O_2$: 282.1620; found: 282.1615.

Preparation of 5a,b; Typical Procedure
A solution of (*E*)-5-(tributylstannylmethylidene)-5*H*-furan-2-one **2a** or **2b** (10 mmol) in Et_2O (10 mL) was added dropwise to a solution of HCl (2 M, 20 mL). The mixture was stirred for 6 h at r.t. then hydrolysed with a solution of KF (1 M, 25 mL) in acetone (25 mL) to precipitate the Bu_3SnCl formed. After stirring vigorously for 1 h, the reaction mixture was filtered, washed with HCl (0.1 M, 2 × 10 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and the solvents were removed under vacuum to give the crude products **5a**,**b** which were purified by chromatography on silica gel (PE–Et_2O, 95:5).

4-Methyl-5-methylidene-5*H*-furan-2-one (5a)
Yield: 78%; colourless oil.

IR (neat): 1788, 1649, 1603, 1253, 908 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.16 (d, *J* = 1.4 Hz, 3 H), 4.90 (dd, *J* = 2.8, 0.8 Hz, 1 H), 5.11 (dd, *J* = 2.8, 1.8 Hz, 1 H), 5.96–5.98 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.2, 94.7, 118.4, 155.4, 157.1, 169.5.

MS (EI, 70 eV): *m*/*z* (%) = 110 (100) [M^+], 82 (22), 40 (93), 39 (96).

Anal. Calcd for $C_6H_6O_2$: C, 65.45; H, 5.49. Found: C, 64.83; H, 5.51.

4-Trimethysilyl-5-methylidene-5*H*-furan-2-one (5b)
Yield: 82%; colourless oil.

IR (neat): 2964, 1763, 1650, 1267, 905 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 9 H), 4.90 (dd, *J* = 2.5, 0.7 Hz, 1 H), 5.28 (dd, *J* = 2.5, 2 Hz, 1 H), 6.37 (dd, *J* = 2, 0.7 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.6 (3 × C), 98.7, 130.2, 160.0, 161.0, 170.0.

MS (EI, 70 eV): *m*/*z* (%) = 168 (13) [M^+], 153 (63), 83 (100), 75 (22), 73 (30).

Anal. Calcd for $C_8H_{12}O_2Si$: C, 57.10; H, 7.19. Found: C, 57.39; H, 6.98.

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