Palladium-Catalyzed Cyclization of *o*-Alkynylphenols with Allyl Carbonates. A Regioselective Synthesis of 2-Substituted-3-allylbenzo[*b*]furans

Sandro Cacchi,* Giancarlo Fabrizi, Leonardo Moro

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy

Fax: + 39 (6) 4991.2780; e-mail: cacchi@axrma.uniroma1.it

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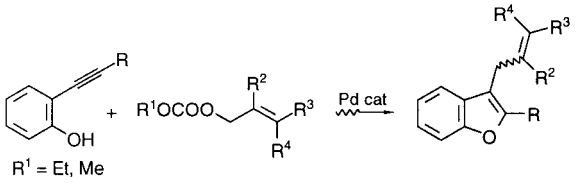
Abstract. 2-Substituted-3-allylbenzo[*b*]furans **3** can be prepared from *o*-alkynylphenols **1** and allyl carbonates **2** through a palladium-catalyzed O-allylation/cyclization sequence. Two basic procedures have been developed: a stepwise method based on the isolation of O-allyl derivatives **4** and their subsequent cyclization to **3** (procedure A) and a one-pot reaction omitting the isolation of **4** (procedure B). The cyclization of **4** in the presence of the electron-rich sterically-encumbered ligand tris(2,4,6-trimethoxyphenyl)phosphine (ttmpp) exhibits remarkable regioselectivity in that 3-allylbenzofurans in which the benzofuryl unit is bound to the less substituted allyl terminus are formed almost exclusively. Some loss of the stereochemistry of the carbon-carbon double bond is observed.

The cyclization of alkynes containing proximate nucleophilic centers promoted by organopalladium complexes is currently of great interest.[1] However, while numerous approaches to carbo- and heterocycles based on the activation of the carbon-carbon triple bond by σ-organopalladium complexes have been described, the utilization of η^3-allylpalladium complexes has received little attention.[2] Recently, we have found that 3-allylindoles can be prepared from *o*-alkynyltrifluoroacetanilides through a cyclization promoted by η^3-allylpalladium complexes.[3] We now report that this chemistry can be successfully applied to the synthesis of 2-substituted-3-allylbenzo[*b*]furans **3** from *o*-alkynylphenols **1**[4] (Scheme 1).

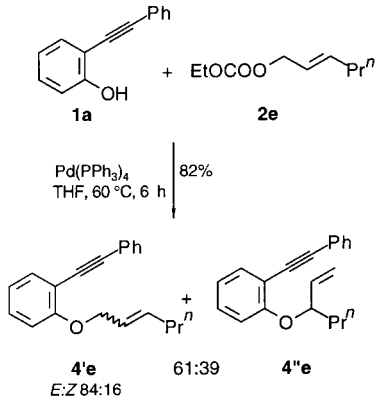


1 **2** **3**

Scheme 1

As found with *o*-alkynyltrifluoroacetanilides, the reaction of *o*-alkynylphenols **1** with allyl carbonates and $Pd(PPh_3)_4$ tends to afford preferentially O-allyl products instead of the desired benzo[*b*]furans, indicating that the nucleophilic attack of the oxygen on the η^3-allylpalladium intermediate is faster than the organopalladium-promoted cyclization. For example, treating **1a** and **2e** with $Pd(PPh_3)_4$ at 60 °C in THF for 6 h produced the O-allylation derivatives **4'e** and **4"e** as an approximately 61:39 mixture in 82% yield (Scheme 2).

Furthermore, whereas the reaction of *o*-alkynyltrifluoroacetanilides with allyl carbonates in the presence of $Pd_2(dba)_3$ and ttmpp [tris(2,4,6-trimethoxyphenyl)phosphine] affords regioselectively 3-allylindoles in high yield through a mechanism that does not involve the N-allylation step,[3] the extension of the same conditions to *o*-alkynylphenols appears to be flawed by competing side reactions. The trend is similar: 3-allylbenzo[*b*]furans were in fact isolated and none of the O-allyl products were formed. Yields, however, are low. For instance, subjection of **1a** and **2e** to the $Pd_2(dba)_3$/ttmpp combination (THF, 50 °C, 0.75 h) led to the isolation of the corresponding benzo[*b*]furans, **3'e** and **3"e**, in only 14% overall yield along with 2-phenylbenzo[*b*]furan (38% yield) and other unidentified products.



Scheme 2

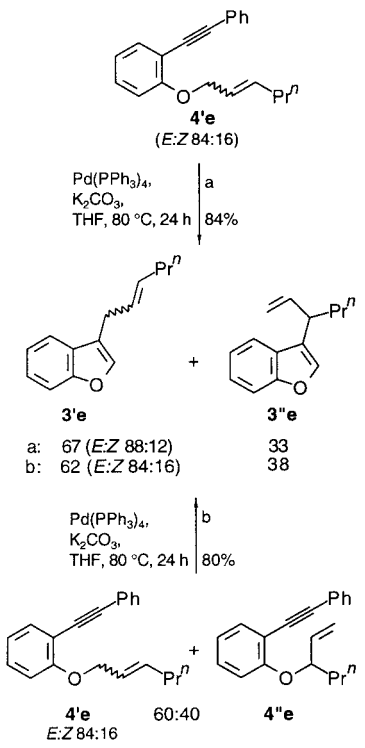
Therefore, in light of the observed tendency of O-allyl derivatives **4** to undergo a palladium-catalyzed cyclization to 3-allylbenzo[*b*]furans **3** (*vide infra*), we turned our attention to the development of a procedure based on the O-allylation/cyclization sequence.

Two different experimental protocols have been developed: a stepwise method, based on the preparation of stereo- and regioisomeric mixtures of the O-allyl derivatives **4'** and **4"** and their subsequent cyclization to benzo[*b*]furans (procedure A), and a one-pot protocol omitting the isolation of **4'** and **4"** (procedure B).

Stepwise Synthesis of 2-Substituted-3-allylbenzo[*b*]furans 3 (procedure A). Though the employment of $Pd(PPh_3)_4$ has been found to give good results, the O-allylation of *o*-alkynylphenols **1** has been best carried out as follows: **1**:**2**:$Pd_2(dba)_3$:dppb = 1:1.2:0.025:0.05 in THF at 60 °C.[5,6] The reaction gives rise to variable amounts of **4'** and **4"**. However, no attempts have been made to control the product selectivity. In fact, the regiochemistry of the C-C bond formed in the cyclization step and the stereochemistry of the olefin fragment of 3-allylbenzo[*b*]furans were found to be almost independent of the regio- and stereochemistry of the O-allyl derivatives, as shown by the reactions depicted in Scheme 3.

Attempting the cyclization reaction under the same conditions that give the highest yields in the O-allylation met with failure. For example, treatment of an approximately 60:40 regioisomeric mixture of **4'e** and **4"e**, our model system, with $Pd_2(dba)_3$ and dppb in THF at 80 °C produced *o*-phenylethynylphenol **1a** in 71% yield and none of the corresponding benzo[*b*]furan product was observed. The use of the following conditions, K_2CO_3:$Pd_2(dba)_3$:ttmpp = 5:0.025:0.1 in DME at 100 °C, produced regioselectively the corresponding 3-allyl benzo[*b*]furan derivative (**3'e**:**3"e**, 96:4) in 81% yield (2 h). These conditions have been generally employed for the cyclization step.[7] High yield (91%) but low regioselectivity (**3'e**:**3"e**, 70:30) were observed with $Pd(PPh_3)_4$ (2 h).

One-Pot Synthesis of 2-Substituted-3-allylbenzo[*b*]furans 3 (procedure B). The inability of $Pd_2(dba)_3$/ttmpp (that gives the best results in terms of regiochemistry of the new carbon-carbon bond in the



Scheme 3

cyclization step) and $Pd_2(dba)_3$/dppb (that gives the highest yields in the O-allylation step) to promote, respectively, the O-allylation of *o*-alkynylphenols and the cyclization of O-allyl derivatives led us to evolve a one-pot protocol based on the utilization of $Pd(PPh_3)_4$. The following conditions (procedure B) have been found to be satisfactory: **1**:**2**:$Pd(PPh_3)_4$ = 1:1.2:0.05 in THF at 60 °C till the disappearance of **1**, addition of K_2CO_3 (5 equiv) (lower yields were obtained when it was omitted), then raising the reaction temperature to 80 °C.[8]

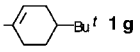
Using procedures A and B a variety of *o*-alkynylphenols and allyl carbonates with a range of substitution patterns can be converted into 2-substituted-3-allylbenzo[*b*]furans in good yields as summarized in the Table. Procedure A has been found to be the method of choice when steric differences between the two allylic termini are small, as it is in the case of 2-hexen-1-yl and 1-octen-3-yl carbonates (Table, entries 1, 7, 13, 17, 21, 25, 28). Procedure B has been successfully employed when the reaction proceeds through symmetric η^3-allylpalladium complexes (Table, entries 4, 9, 14, 19, 23, 29) and even when the two allylic termini are markedly different from a steric point of view (Table, entries 10-12, 15, 16, 18, 20, 22, 24, 26). The process is accompanied by some loss of the stereochemistry of the carbon-carbon double bond.

Mechanism of Cyclization and Regiochemistry of the New C-C Bond. Very likely, as suggested for the related cyclization of the *o*-alkynyl-*N*-allyltrifluoroacetanilides,[3] the cyclization of the O-allyl derivatives proceeds through the basic steps outlined in Scheme 4 for one of the O-allyl isomers: (1) formation of **6'** and **6"**, resulting from the palladium-promoted ionization of the O–C_{allyl} bond and the displacement of one ligand to the palladium by the carbon-carbon triple

Table. Palladium-Catalyzed Synthesis of 2-Substituted-3-allylbenzo[*b*]furans **3** from *o*-Alkynylphenols **1** and Allyl Carbonates **2**

entry	*o*-alkynylphenol **1**	allyl carbonate **2**	procedure[a]	O-allyl derivative **4**	overall yield %[b] (time)	benzo[*b*]furan **3**	overall yield %[b] (time)
1	Ph **1a**	**2a**	A	**4'a** (64) [*E*/*Z* 89:11] + **4"a** (36)	96 (0.5 h)	**3'a** (96) [*E*:*Z* 89:11] + **3"a** (4)	86 (2 h)
2	**1a**	**2a**	B			**3'a** (67) [*E*:*Z* 87:13] + **3"a** (33)	84 (2 h; 15 h)
3	**1a**	**2b**	A	**4b**	79 (3 h)	**3b**	89 (3 h)[c]
4	**1a**	**2b**	B			**3b**	86 (2 h; 21 h)
5	**1a**	**2c**	A	**4c**	53 (24 h)[d]	**3c**	80 (9 h)[c]
6	**1a**	**2d**	A	**4d**	43 (24h)[d]		- (5 h)[e]
7	**1a**	**2e**	A	**4'e** (60) [*E*:*Z* 84:16] + **4"e** (40)	91 (1 h)	**3'e** (96) [*E*:*Z* 87:13] + **3"e** (4)	81 (2 h)
8	**1a**	**2e**	B			**3'e** (62) [*E*:*Z* 88:12] + **3"e** (38)	87 (6 h; 15 h)
9	**1a**	**2f**	B			**3f**	91 (1 h; 3.5 h)
10	**1a**	**2g**	B			**3g**	90 (1.5 h; 8 h)
11	**1a**	**2h**	B			**3h** [*E*:*Z* 8:92]	84 (8 h; 15 h)
12	**1a**	**2i**	B			**3i**	73 (9 h; 15 h)

Table. (continued)

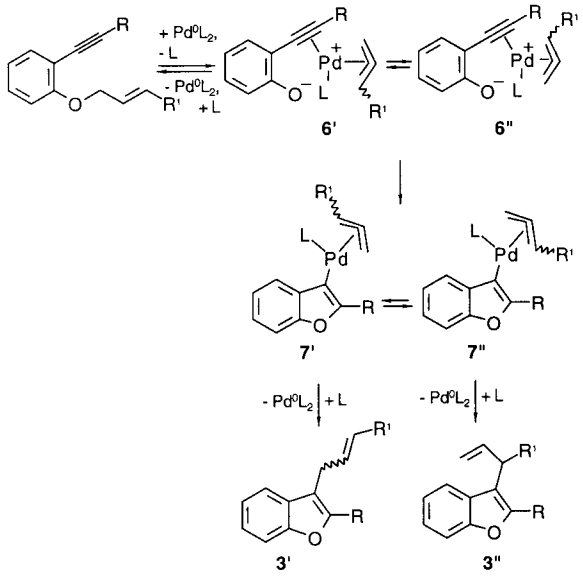
entry	*o*-alkynylphenol **1**	allyl carbonate **2**	procedure[a]	O-allyl derivative **4**	overall yield %[b] (time)	benzo[*b*]furan **3**	overall yield %[b] (time)
13	C_6H_4-*p*-COMe **1b**	**2e**	A	**4'j** (66) [*E*:*Z* 84:16] **4"j** (34)	95 (1 h)	**3'j** (97) [*E*:*Z* 84:16] + **3"j** (3)	66 (2.5 h)
14	**1b**	**2b**	B			**3k**	69 (6 h; 24 h)
15	**1b**	**2g**	B			**3l**	89 (6 h; 21 h)
16	**1b**	**2i**	B			**3m**	85 (22h; 5 h)
17	C_6H_4-*p*-OMe **1c**	**2e**	A	**4'n** (71) [*E*:*Z* 89:11] **4"n** (29)	93 (2 h)	**3'n** (98) [*E*:*Z* 89:11] + **3"n** (2)	72 (8 h)
18	**1c**	**2i**	B			**3o**	72 (9 h; 16 h)
19	**1c**	**2b**	B			**3p**	63 (24 h; 8 h)
20	**1c**	**2g**	B			**3q**	84 (6 h; 22 h)
21	C_5H_{11}-*n* **1d**	**2e**	A	**4'z** (50) [*E*:*Z* 86:14] **4"r** (50)	91 (1.5 h)	**3'r** (98) [*E*:*Z* 90:10] + **3"r** (2)	75 (4 h)
22	**1d**	**2g**	B			**3s**	96 (2 h; 6 h)
23	**1d**	**2f**	B			**3t**	91 (2 h; 5 h)
24	**1d**	**2i**	B			**3u**	77 (6 h; 15 h)
25	$CH_2NHCOEt$ **1e**	**2e**	A	**4'v** (55) [*E*:*Z* 86:14] **4"v** (45)	89 (1 h)	**3'v** (96) [*E*:*Z* 87:13] + **3"v** (4)	51 (1.5 h)
26	**1e**	**2g**	B			**3w**	80 (5 h; 18 h)
27	H **1f**	**2e**	A	**4'y** (59) [*E*:*Z* 88:12] **4"y** (41)	96 (2 h)		- (3 h)
28	 **1g**	**2e**	A	**4'z** (36) [*E*:*Z* 78:22] **4"z** (64)	86 (1 h)	**3'z** (95) [*E*:*Z* 89:11] + **3"z** (5)	72 (3 h)
29	**1g**	**2f**	B			**3za**	91 (1.5 h; 4 h)

[a] Procedure A: see Ref 6 and 7; Procedure B: see Ref 8. [b] Yields refer to isolated products. [c] In the presence of 5 mol % of $Pd(PPh_3)_4$. [d] At 40 °C. [e] In THF at 80 °C, in the presence of 5 mol % of $Pd(PPh_3)_4$. 2-Phenylbenzo[*b*]furans was isolated in 57% yield

bond; (2) intramolecular nucleophilic attack of the oxygen across the activated carbon-carbon triple bond to afford **7'** and **7"**; (3) reductive elimination of Pd(0) through the transfer of the benzofuryl fragment to the allyl group in a *cis* fashion,[9] which gives the benzo[*b*]furan product and regenerates the active catalyst.

The regioselectivity of the *cis*-migration step, favoring the isomeric product **3'** over **3"** (with all the ligands we examined), may reflect the preferential formation of the geometrical isomer **7'** over **7"**. Such a preference may be influenced by steric and electronic factors.

Steric factors are expected to act so as to minimize steric strain and appear to favor the location of the less sterically congested allylic terminus *cis* to the 2-substituted-benzofuryl unit rather than to the phosphine ligand. Previous work on η^3-allylpalladium intermediates which react by transfer of a carbon fragment from the palladium to an allylic carbon showed that the new C-C bond is formed preferentially at the more crowded allyl terminus.[10] This was assumed to indicate a strong preference for the large triphenylphosphine to reside *trans* to the more hindered allyl terminus. However, the less sterically demanding phenyl and linear vinyl groups were investigated. In our case, it seems that the steric requirements of the phosphine ligand are smaller than those of the substituted benzofuryl unit.



Scheme 4

Electronic factors associated with the donor-acceptor properties of the ligands may create an asymmetric electronic distribution at the allylic system.[11] Specifically, stronger π-acceptor ligands may enhance electron donation from the allylic system to the metal and locate some positive charge character on it. This positive charge character is preferentially accommodated on the more substituted carbon atom. Furthermore, it has been observed that π-acceptors prefer to relay their properties in a *trans* manner across the square planar complexes.[12] By these arguments, electron-withdrawing ligands are expected to favor the formation of the η^3-allylpalladium complex **7"** and, ultimately, the benzo[*b*]furan derivative **3"**; the amount of **7'**, and then **3'**, should increase on going from electron-withdrawing to electron-donating ligands. Accordingly, we observed that **3'e**:**3"e** obtained by subjecting an approximately 60:40 mixture of **4'e** and **4"e** to phosphine ligands with different donor-acceptor properties increased in the order: (p-Cl-$C_6H_4)_3P$ (53:47) < Ph_3P (70:30) < (p-MeO-$C_6H_4)_3P$ (87:13). This result is in agreement with previous observations on the thermolysis of a series of Pd(η^3-$CH_2CHCHMe$)($C_6H_3Cl_2$)(PR_3) complexes which showed that the bond formation at the less substituted allyl end increases with decrease in the electron-withdrawing ability of the ligand.[9] Presumably, the strong electron-donating power of ttmpp[13] can account for most of its remarkable effect on the regiochemistry of the new carbon-carbon bond. The steric encumbrance of the ligand, however, by virtue of the likely influence on the electronic properties and geometrical features of the square planar complexes,[14] might also play a role.

In conclusion, the present palladium-catalyzed allylation/cyclization of *o*-alkynylphenols provides a valuable approach to the synthesis of 2-substituted-3-allylbenzo[*b*]furans.[15] The overall high yields generally observed and the almost complete regioselectivity toward the formation of 3-allylbenzofuran in which the benzofuryl unit is bound to the less substituted allyl terminus suggest a vast synthetic potential for the preparation of this class of compounds.

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References and Notes

1. For a recent leading reference, see: (a) Cacchi, S.; Fabrizi, G.; Marinelli, F.; Moro, L.; Pace, P. *Synlett* **1997**, 1363. (b) Cacchi, S.; Fabrizi, G.; Moro, L. *J. Org. Chem.* **1997**, *62*, 5327. (c) Bouyssi, D.; Cavicchioli, M.; Balme, G. *Synlett* **1997**, 944. (d) Arcadi, A. *Synlett* **1997**, 941. (e) Arcadi, A.; Anacardio, R.; D'Anniballe, G.; Gentile, M. *Synlett* **1997**, 1315. (f) Arcadi, A.; Cacchi, S.; Del Rosario, M.; Fabrizi, G.; Marinelli, F. *J. Org. Chem.* **1996**, *61*, 9280. (g) Cavicchioli, M.; Decortiat, S.; Bouyssi, D.; Gore, J.; Balme, G. *Tetrahedron* **1996**, *52*, 11463. (h) Arcadi, A.; Rossi, E. *Tetrahedron Lett.* **1996**, *37*, 6811. (i) Saulnier, M.G.; Frennesson, D.B.; Deshpande, M.S.; Vyas, D.M. *Tetrahedron Lett.* **1995**, *36*, 7841. (j) Arcadi, A.; Cacchi, S.; Carnicelli, V.; Marinelli, F. *Tetrahedron* **1994**, *50*, 437. (k) Balme, G.; Bouyssi, D. *Tetrahedron* **1994**, *50*, 403. (l) Arcadi, A.; Cacchi, S.; Larock, R.C.; Marinelli, F. *Tetrahedron Lett.* **1993**, *34*, 2813. (m) Bouyssi, D.; Gore, J.; Balme, G.; Louis, D.; Wallach, J. *Tetrahedron Lett.* **1993**, *34*, 3129.

2 Mandai, T.; Ohta, K.; Baba, N.; Kawada, M.; Tsuji, J. *Synlett* **1992**, 671. Tsuda, T.; Ohashi, Y.; Nagahama, N.; Sumiya, R.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 2650.

3. Cacchi, S.; Fabrizi, G.; Pace, P. *J. Org. Chem.* **1998**, *62*, 1001.

4. Typical procedure for the preparation of *o*-alkynylphenols **1** from *o*-iodophenyl tetrahydropyranyl ether and 1-alkynes. To a solution of *o*-iodophenyl tetrahydropyranyl ether (5.00 g, 16.45 mmol) and phenylacetylene (2.16 mL, 19.74 mmol) in Et_3N (8 mL) and DMF (2 mL) were added, under argon, $PdCl_2(PPh_3)_2$ (0.230 g, 0.33 mmol) and CuI (0.13 g, 0.66 mmol). The reaction mixture was stirred at 45 °C for 2 h. Then, diethyl ether and water were added, the organic layer was separated, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was dissolved in Me_2CO/H_2O 80/20 (10 mL), TsOH (0.31g, 1.64 mmol) was added and the solution was stirred overnight at room temperature. After usual workup, the residue was purified by chromatography eluting with a *n*-hexane/EtOAc (85/15 v/v) mixture to give 2.74 g (86% overall yield) of *o*-phenylethynylphenol **1a**: mp 47-48 °C (lit.[1f] 47-48 °C). Typical procedure for the preparation of *o*-alkynylphenols **1** from *o*-iodophenyl tetrahydropyranyl ether, trimethylsilylacetylene and aryl halides or vinyl triflates. To a solution of *o*-iodophenyl tetrahydropyranyl ether (2.00 g, 6.56 mmol) and trimethylsilylacetylene (1.12 mL, 7.89 mmol) in Et_3N (4 mL) and DMF (1 mL) were added, under argon, $PdCl_2(PPh_3)_2$ (0.092 g, 0.13 mmol) and CuI (0.050 g, 0.26 mmol). The reaction mixture was stirred at 45 °C for 2 h. After the usual workup the residue was dissolved in MeOH (5 mL), K_2CO_3 (0.091 g, 0.66 mmol) was added and the reaction mixture was stirred overnight at room temperature. Then, diethyl ether and water were added, the organic layer was separated, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was dissolved in Et_3N (4 mL) and DMF (1 mL). Then, *p*-iodoanisole (1.85 g, 7.89 mmol), $PdCl_2(PPh_3)_2$ (0.092 g, 0.13 mmol) and CuI (0.050 g, 0.26 mmol) were added under an argon atmosphere. The reaction mixture was stirred for 2 h at 45°C. After usual work-up, the residue was dissolved in Me_2CO/H_2O 80/20 (10 mL), TsOH (0.130 g, 0.66 mmol) was added and the solution was stirred overnight at room temperature. After this time, ethylacetate was added and the organic mixture was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by chromatography eluting with a *n*-hexane/EtOAc (87/13 v/v) mixture to give 0.94 g (61% overall yield) of *o*-(*p*-methoxyphenyl)ethynylphenol **1c**: mp 53-55 °C; IR (KBr) 3427, 2213, 835, 761 cm^{-1}; ^1H NMR δ 7.50-7.40 (m, 3 H), 7.25 (t, J = 7.0 Hz, 1 H), 7.01-6.86 (m, 4 H), 5.98 (s, 1 H), 3.81 (s, 3 H); ^{13}C NMR δ 160.1, 156.5, 133.2, 131.6, 130.2, 120.4, 114.7, 114.5, 114.2, 110.1, 96.4, 81.8, 55.4; MS *m/e* (relative intensity) 324 (M^+, 100), 209 (97), 181 (71); Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.40. Found: C, 80.39; H, 5.45.

5. Goux, C.; Lhoste, P.; Sinou, D. *Synlett* **1992**, 725.

6. Typical procedure for the O-allylation of *o*-alkynylphenols **1** (First step of procedure A). To a solution of *o*-phenylethynylphenol **1a** (0.20 g, 1.03 mmol) and 2-hexen-1-yl ethyl carbonate **2e** (0.21 g, 1.24 mmol) in anhydrous THF (4 mL) were added, under argon, Pd_2dba_3 (0.024 g, 0.02 mmol) and dppb (0.022 g, 0.05 mmol). The reaction mixture was stirred at 60 °C for 1 h. After this time, ethylacetate was added and the organic mixture was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by chromatography eluting with a *n*-hexane/EtOAc (99/1 v/v) mixture to give 0.155g (55 % yield) of **4e**, as an about 84:16 *E*:*Z* mixture, and 0.104 g (36 % yield) of **4e**; **4e**: oil; IR (liquid film) 2221, 752, 690 cm^{-1}; ^1H NMR δ 7.65-7.50 (m, 3 H), 7.45-7.22 (m, 4 H), 7.00-6.87 (m, 2 H), 5.95 (dt, J = 15.3 Hz, J = 6.4 Hz, 1 H, -H_2C-CH=C<u>H</u>-), 5.77 (dt, J = 15.3 Hz, J = 5.2 Hz, 1 H, -H_2C-C<u>H</u>=CH-), 4.70 (d, J = 5.4 Hz, 0.32 H, isom. *Z*), 4.58 (dd, J = 9.9 Hz, J = 5.2 Hz, 1.68 H, -<u>H_2</u>C-CH=CH-), 2.07

(bq, J = 6.4 Hz, 2 H), 1.42 (q, J = 7.3 Hz, 2 H), 0.90 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 159.4, 134.9, 134.1, 133.5, 131.7, 129.7, 128.3, 128.1, 124.9, 123.8, 120.7, 112.8, 98.6, 86.1, 69.5 (O-CH$_2$, **4'e** *E* isomer), 65.1 (O-CH$_2$, **4'e** *Z* isomer); MS *m/e* (relative intensity) 276 (M$^+$, 6), 247 (6), 194 (100); Anal. Calcd for $C_{20}H_{20}O$: C, 86.91; H, 7.30. Found: C, 86.95; H, 7.35; **4''e**: oil; IR (liquid film) 2221, 750, 695 cm^{-1}; ^{1}H NMR 7.61-7.15 (m, 7 H), 7.00-6.88 (m, 2 H), 5.95 (ddd, J = 17.2 Hz, J = 10.7, J = 6.4 Hz, 1 H, H$_2$C=CH-CH-), 5.32 (d, J = 17.2 Hz, 1 H, H$_2$C=CH-CH-), 5.06 (d, J = 10.7 Hz, 1 H, H$_2$C=CH-CH-), 4.72 (q, J = 6.4 Hz, 1 H, H$_2$C=CH-CH-), 2.00-1.50 (m, 4 H), 1.00 (t, J = 7.2 Hz, 3 H); ^{13}C NMR 159.3, 138.2, 133.3, 131.6, 129.4, 128.4, 128.0, 124.0, 120.8, 116.5, 115.0, 114.0, 86.3, 80.3, 37.9, 18.5, 14.1; MS *m/e* (relative intensity) 276 (M$^+$, 10), 194 (100); Anal. Calcd for $C_{20}H_{20}O$: C, 86.91; H, 7.30. Found: C, 86.87; H, 7.31.

7. Typical procedure for the cyclization of allylic *o*-alkynylphenyl ethers **4** (Second step of procedure B). To a solution of an approximately 60:40 **4'e** (84:16, *E*:*Z*):**4"e** mixture (0.100 g, 0.36 mmol) in anhydrous DME (2 mL) were added, under argon, K_2CO_3 (0.250 g, 1.81 mmol), Pd_2dba_3 (0.008 g, 0.009 mmol) and ttmpp (0.019 g, 0.036 mmol). The reaction mixture was stirred at 100 °C for 2 h and worked-up as before to afford a residue which was purified by chromatography eluting with a *n*-hexane/EtOAc (98/2 v/v) mixture to provide 0.081g (81 % yield) of **3'e** and **3''e** as a 96:4 mixture. The presence of **3''e** was indicated by a multiplet (ddd) at 6.45-6.30 (H$_2$C=CH-CH-) and a multiplet at 5.20-5.15 ppm (H$_2$C=CH-CH-); **3'e** was obtained as an about 87:13 *E:Z* mixture: IR (liquid film) 1453, 786, 697 cm^{-1}; ^{1}H NMR δ 7.95-7.30 (m, 9 H), 5.85-5.50 (m, 1.92 H), 3.75 (d, J = 6.5 Hz, 0.26 H), 3.68 (d, J = 7.0 Hz, 1.66 H), 2.35 (m, 0.26 H), 2.10 (dd, J = 12.0 Hz, J = 6.0 Hz, 1.74 H), 1.68-1.24 (m, 2 H), 1.08 (t, J = 7.1 Hz, 0.39 H, **3'e** *Z* isomer), 0.95 (t, J = 7.1 Hz, 2.61 H, **3'e** *E* isomer); ^{13}C NMR δ 154.1, 151.4, 132.2, 131.2, 130.6, 128.7, 128.5, 128.0, 126.8, 124.7, 122.5, 119.9, 114.2, 111.1, 34.7, 27.5, 22.6, 13.7; MS *m/e* (relative intensity) 276 (M$^+$, 96), 233 (80), 194 (100).

8. Typical procedure for the one-pot synthesis of 3-allylbenzo[*b*]furans **3** **(**Procedure B**).** To a solution of *o*-phenylethynylphenol **1a** (0.200 g, 1.03 mmol) and allyl ethyl carbonate **2f** (0.140 g, 1.24 mmol) in anhydrous THF (3 mL) was added, under argon, Pd(PPh$_3$)$_4$ (0.061 g, 0.05 mmol). The mixture was stirred at 60°C for 1 h till the disappearance of **1a**. Then, K_2CO_3 (0.710 g, 5.15 mmol) was added and the mixture was stirred at 80°C for 3.5 h. Usual workup gave a residue which was purified by chromatography eluting with a (99/1 v/v) *n*-hexane/EtOAc mixture to provide 0.220 g (91 % yield) of **3f**: oil; IR (liquid film) 1458, 745, 695 cm^{-1}; ^{1}H NMR δ 7.78 (d, J = 8.4 Hz, 2 H), 7.55-7.18 (m, 7 H), 6.10 (ddd, J = 17.8 Hz, J = 10.9 Hz, 5.4 Hz, 1 H), 5.18 (d, J = 10.9 Hz, 1 H), 5.04 (d, J = 17.8 Hz, 1 H), 3.64 (d, J = 5.4 Hz, 2 H); ^{13}C NMR δ 154.1, 151.7, 135.2, 131.0, 130.4, 128.7, 128.3, 127.0, 124.4, 122.5, 119.8, 116.2, 113.1, 111.1, 28.5; MS *m/e* (relative intensity) 234 (M$^+$, 100), 194 (45); Anal. Calcd for $C_{17}H_{14}O$: C, 87.14; H, 6.03. Found: C, 87.20; H, 6.09.

9. Kurosawa, H.; Shiba, K.; Hirako, K.; Kakiuchi, K.; Ikeda, I. *J. Chem. Soc., Chem. Commun.* **1994**, 1099. Trost, B.M.; Weber, L.; Strege, P.E.; Fullerton, T.J.; Dietsche, T.J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.

10. Keinan, E.; Sahai, M. *J. Chem. Soc., Chem. Commun.* **1984**, 648. Temple, J.S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310. Hayasi, Y.; Riediker, M.; Temple, J.S.; Schwartz, J. *Tetrahedron Lett.* **1981**, *22*, 2629.

11. Aranyos, A.; Szabó, K.J., Castaño, A.M.; Bäckvall, J.-E. *Organometallics* **1997**, *16*, 1058. Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P.S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. Szabó, K.J. *Organometallics* **1996**, *15*, 1128. Szabó, K.J. *J. Am. Chem. Soc.* **1996**, *118*, 7818. Ward, T.R. *Organometallics* **1996**, *15*, 2836. Castaño, A.M.; Aranyos, A.; Szabó, K.J.; Bäckvall, J.-E. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2551. Hoffmann, H.M.R.; Otte, A.R.; Wilde, A.; Menzer, S.; Wiliams, D.J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 100. Åkermark, B.; Krakenberger, B.; Hansson, S.; Krakenberg, B.; Vitagliano, A. *J. Organomet. Chem.* **1987**, *335*, 133. Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620. Åkermark, B.; Vitagliano, A. *Organometallics* **1985**, *4*, 1275. Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zettreberg, K. *Organometallics* **1984**, *3*, 679.

12. Appleton, T.G.; Clark, H.C.; Manzer, L.E. *Coord. Chem. Rev.* **1973**, *10* , 335. Faller, J.W.; Mattina, M.J. *Inorg. Chem.* **1972**, *11*, 1296. Faller, J.W.; Incoura, M.J. *J. Organomet. Chem.* **1969**, *19*, P13.

13. Wada, M.; Higashizaki, S. *J. Chem. Soc., Chem. Commun.* **1984**, 482.

14. Tolman, C.A. *Chem. Rev.* **1977**, *77*, 313.

15. A similar approach to the synthesis of 2-substituted-3-allyl-benzo[*b*]furans has been developed independently by Balme and coworkers: *Synlett* **1998**, 746.