PREPARATION OF Boc-PROTECTED CINNAMYL-TYPE ALCOHOLS: A COMPARISON OF THE SUZUKI–MIYAURA COUPLING, CROSS-METATHESIS, AND HORNER–WADSWORTH–EMMONS APPROACHES AND THEIR MERIT IN PARALLEL SYNTHESIS

Jan ŠTAMBASKÝ, Andrei V. MALKOV[1,*] and Pavel KOČOVSKÝ[2,*]

Department of Chemistry, WestChem, University of Glasgow, Glasgow G12 8QQ, U.K.; e-mail: [1] amalkov@chem.gla.ac.uk, [2] pavelk@chem.gla.ac.uk

Received May 21, 2008
Accepted June 25, 2008
Published online July 31, 2008

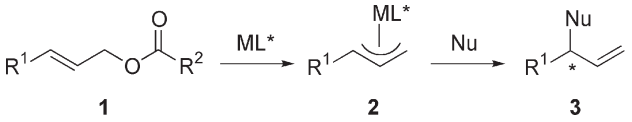
Three synthetic strategies for the construction of *tert*-butyl (*E*)-3-arylprop-2-en-1-ol carbonates are described. Complementary approaches employing Suzuki–Miyaura coupling and cross-metathesis reaction gave moderate yields of the title compounds in one-step, both methods are suitable for high-throughput and parallel chemistry. A detailed investigation into the Suzuki–Miyaura coupling reaction is provided along with the studies on the synthesis of pinacolyl 1-(*tert*-butyloxycarbonyl)propenol-3-ylboronate, the key building block. Conventional synthesis of the title compounds via the Horner–Wadsworth–Emmons reaction as a key step in a three-step-one-purification protocol was optimized and the results are compared with those of the latter reactions.

Keywords: C–C bond formation; Palladium; Ruthenium; Suzuki–Miyaura reaction; Metathesis.

Asymmetric allylic substitution is a versatile method for the construction of a new chiral center, starting with achiral allylic substrates, such as **1** (Scheme 1). This transformation is catalyzed by chiral complexes of transition metals, such as palladium[1,2], molybdenum[3], tungsten[3b,4], ruthenium[5], rhodium[6], iridium[7], nickel[8], platinum[9], and copper[10], and typically proceeds through the π-allyl intermediate **2**. To date, asymmetric allylic substitution has evolved into a powerful synthetic tool for the enantioselective formation of C–C, C–N, and C–O bonds[1–10]. Among the leaving groups, esters (**1**, R^2 = alkyl), carbonates (**1**, R^2 = OR′) and, in particular, *tert*-butyl carbonates (**1**, R^2 = *t*-BuO), hold a dominant position. Although the conversion of an alcohol into the corresponding Boc derivative is well established[11], expedient synthesis of even a small library of desirable carbonates may actually become considerably more cumbersome than expected. With

doi:10.1135/cccc20080705

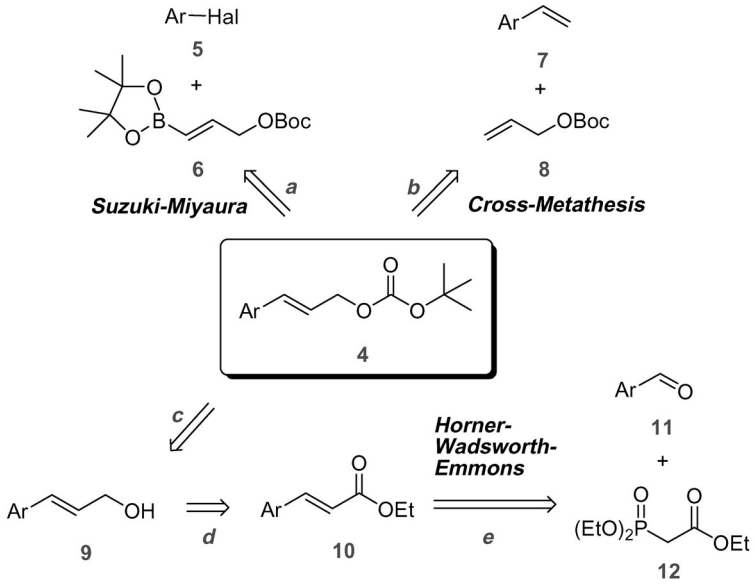
3-arylallyl alcohols, as precursors to **1**, there is little choice in diversity with a view of matching the portfolio of the commercially available aryl building blocks with a suitable methodology.



SCHEME 1
Metal-catalyzed asymmetric allylic substitution

Herein, we report on two new methods for the construction of *tert*-butyl (*E*)-3-arylprop-2-en-1-ol carbonates (**4**) from commercially available starting materials that are suitable for parallel synthesis techniques (Scheme 2). Also reported is an optimization of the conventional synthetic approach to these compounds, based on the Horner–Wadsworth–Emmons reaction (HWE).

Our approach to the target carbonates **4** was based upon the desire to develop a one-step synthetic protocol suitable for parallel synthesis (Scheme 2).



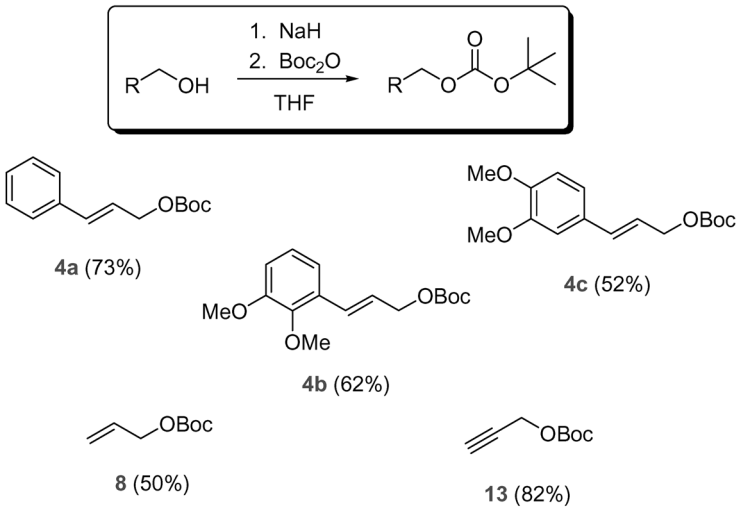
SCHEME 2
Retrosynthetic analysis of *tert*-butyl 3-arylprop-2-en-1-yl carbonates. For Ar, see the following Schemes

The main interest was laid upon the disconnection ***a*** employing the commercially available aryl halides **5** and the common building block **6**. Route ***b*** is based on the (*E*)-double bond construction via a cross-metathesis reaction of the commercially available styrenes **7** and the Boc-protected allyl alcohol **8** as common building blocks. The last part of our investigation was focused on the optimization of the Boc derivatization of the cinnamyl-type alcohols **9** (***c***). Some of these alcohols are commercially available or easy to make from the corresponding cinnamic acids, others can be synthesized using the Horner–Wadsworth–Emmons reaction. Optimization of the latter sequence, starting with the commercially available aldehydes **11** and the phosphonate reagent **12**, into a three-step-one-purification protocol (***c***–***e***) is also reported.

RESULTS AND DISCUSSION

Boc Derivatization

The Boc derivatization of cinnamyl alcohol (**9a**) was investigated under various conditions (Scheme 3)[11]. The procedure employing Boc_2O and NaOH with a phase-transfer catalyst failed[11a], while reactions[11b] with Boc_2O in CH_2Cl_2, catalyzed by $V(O)(OTf)_2$, gave only the symmetric carbonate

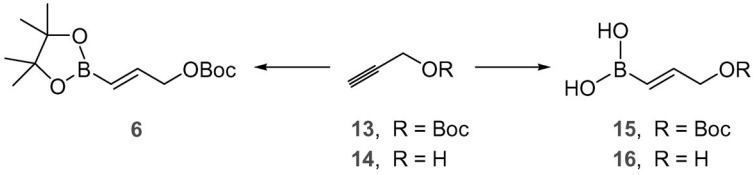


SCHEME 3
Formation of *tert*-butyl carbonates and isolated yields

$(PhCH{=}CHCH_2O)_2CO$ in high yield. On the other hand, by following the procedure[11c,11d], in which Boc_2O is added to a solution of the corresponding alkoxide in THF, we were able to isolate the desired product **4a** in about 40% yield along with the symmetric carbonate $(PhCH{=}CHCH_2O)_2CO$. A modified protocol, in which the alcoholate solution is transferred to an excess of the solution of Boc_2O, afforded **4a** in high yield and was then employed throughout this study (Scheme 3).

Suzuki–Miyaura Coupling

The synthesis of the building block **15** was based upon the procedure for the preparation of boronic acid **16** (Scheme 4)[12]. In our hands, the established protocol was successful only for propargyl alcohol **14**, which produced acid **16** (Table I, entry 1), and failed in the case of the Boc derivative **13** (entries 2 and 3). Alternative hydroboration conditions were also investigated[13]: thus, for instance, treatment of alkyne **13** with borane dibromide proved fruitless (entry 4) and an attempted reaction with dicyclohexyl-



6 **13**, R = Boc; **14**, R = H **15**, R = Boc; **16**, R = H

SCHEME 4
Hydroboration; for conditions, see Table I

TABLE I
Hydroboration of **12** and **13**

Entry	Conditions	Alkyne	Product	Yield, %[a]
1	Catecholborane (2 equiv.), neat, 70 °C, 1 h	**14**	**16**	40
2	Catecholborane, THF, 70 °C, 12 h	**13**	**15**	0
3	Catecholborane, neat, 70 °C, 12 h	**13**	**15**	0
4	$Br_2BH{\cdot}Me_2S$, DCM, 0 °C to 20 °C, 6 h	**13**	**15**	0
5	*c*-Hex_2BH, Me_3NO, THF, 0 °C to 20 °C, 1.5 h	**13**	**15**	40
6	Catecholborane, *c*-Hex_2BH (10%), neat, 20 °C, 12 h	**13**	**15**	62
7	Pinacolborane, *c*-Hex_2BH (10%), neat, 20 °C, 12 h	**13**	**6**	95

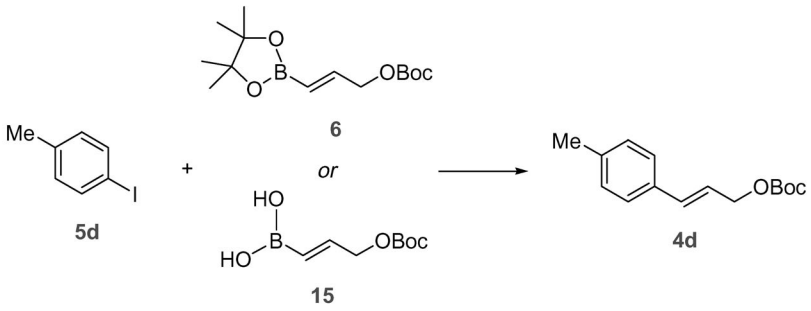
[a] Isolated yields.

borane, followed by addition of trimethylammonium *N*-oxide, gave only moderate yield (entry 5). On the other hand, employing dicyclohexylborane as catalyst[14], with a stoichiometric amount of catecholborane, afforded the desired product **15** in good yield (entry 6)[15]. Finally, a reaction of **13** with pinacolborane, catalyzed by dicyclohexylborane, produced vinyl boronate **6** in an excellent isolated yield (entry 7). In the latter protocol, the high purity of the hydroborating reagents proved to be crucial for attaining high yields.

The published procedure[16] for the Suzuki-type coupling reactions of the hydroxy acid **16** required the presence of thallium ethoxide in aqueous medium. Application of the latter protocol to the coupling of the Boc-protected acid **15** with *p*-iodotoluene resulted in the formation of only traces of the desired product **4d** (Scheme 5, Table II, entry 1). By contrast, simple standard conditions for the aqueous Suzuki–Miyaura coupling reactions, employing K_2CO_3 as a base, gave rise to the formation of **4d** in good yield (entry 2).

A considerable drawback to the latter protocol is the behavior of the acid **15**: when freshly prepared, it is a white solid, which in the air (moisture) melts to a very viscous oil containing variable amount of the corresponding oligomers; upon prolonged standing, both forms (oil or solid) become a sticky brown-grey solid, containing products of decomposition. These features, in conjunction with the lower yield of the hydroboration, drew our attention to boronate **6**, a colorless, bench stable[17], well-defined liquid that can be distilled.

Initially, we chose alkali carbonates in aqueous 1,2-dimethoxyethane (DME) as the reaction medium for the **5d** + **6** coupling. An overnight heating with alkali carbonates gave the desired product **4d** in about 10% yield (Table II, entries 3 and 4). Higher loading of the iodide **5d** and the base led to an improvement (entries 5 and 6), whereas a significant decrease of the yield was observed when potassium *tert*-butoxide was employed (entry 7), although the use of a toluene–water two-phase system resulted in some improvement (entry 8). The reaction failed when a larger amount of water (>80%) was used in the solvent mixture, when thallium ethoxide was used as a base, or when DMF was chosen as a solvent. The best results were attained when the reaction time was kept short (entry 9). Other published conditions did not lead to any further improvement[18]. Furthermore, the recyclable microencapsulated palladium[19] gave lower yields along with a relatively high amount of unidentified side-products (entries 10 and 11), whereas the use of an advanced ligand[20], such as S-Phos (2-dicyclohexyl-



SCHEME 5
Suzuki–Miyaura coupling

TABLE II
Optimization of the Suzuki–Miyaura coupling[a]

Entry	**5d** equiv	allyl carbonate	catalyst mole %	base equiv	solvent	conditions	yield[b] %
1	2.0	**15**	$(Ph_3P_4)Pd$ (5)	EtOTl (2.1)	DME–H_2O (7:3)	20 °C, 1 h	traces
2	0.7	**15**	$(Ph_3P_4)Pd$ (5)	K_2CO_3 (1.8)	DME–H_2O (20:3)	85 °C, 20 h	61
3	1.0	**6**	$(Ph_3P_4)Pd$ (5)	Na_2CO_3 (5.3)	DME–H_2O (7:5)	100 °C, 15 h	8
4	1.0	**6**	$(Ph_3P_4)Pd$ (5)	K_2CO_3 (2.5)	DME–H_2O (20:3)	80 °C, 18 h	12
5	1.8	**6**	$(Ph_3P_4)Pd$ (5)	K_2CO_3 (7.8)	DME–H_2O (20:3)	85 °C, 18 h	33
6	3.3	**6**	$(Ph_3P_4)Pd$ (5)	K_2CO_3 (5.5)	DME–H_2O (4:1)	100 °C, 20 h	40
7	1.9	**6**	$(Ph_3P_4)Pd$ (5)	*t*-BuOK (4.8)	DME–H_2O (4:1)	100 °C, 20 h	6
8	2.2	**6**	$(Ph_3P_4)Pd$ (5)	*t*-BuOK (5.2)	Toluene–H_2O (4:1)	100 °C, 20 h	26
9	5.0	**6**	$(Ph_3P_4)Pd$ (5)	K_2CO_3 (4.0)	DME–H_2O (1:1)	80 °C, 2 h	42
10	1.4	**6**	Pd(0) EnCat™	K_2CO_3 (3.3)	DME–H_2O (1:1)	80 °C, 14.5 h	25
11	0.9	**6**	Pd(0) EnCat™	K_2CO_3 (2.7)	DME–H_2O (1:1)	80 °C, 2 h	16

[a] Reactions were performed on 1 mmol scale, using 10 ml of the solvent mixture, all the equivalents are based on the boronate (boronic acid). [b] Isolated yields.

phosphino-2′,6′-dimethoxybiphenyl), resulted in no reaction or gave only traces of **4d**.

Having thus identified potassium carbonate as the optimal base, a DME–water mixture (1:1) as the optimal solvent system, and $(Ph_3P)_4Pd$ as the most suitable pre-catalyst, we then investigated the role of the reaction time in the range of 1–32 h at 40 °C (Chart 1). The data clearly show an increase in the yield of **4d** with a maximum reached in 8 h and suggest that both the product **4d** and the starting boronate **6** are unstable under the reaction conditions and gradually decompose.

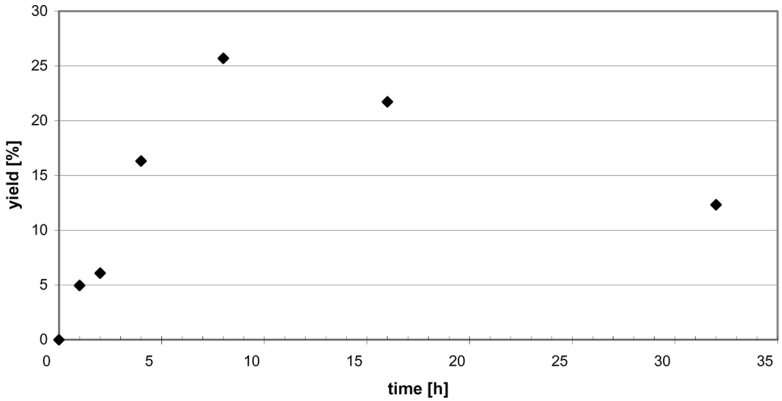


CHART 1

Suzuki–Miyaura coupling of **5d** with **6**: isolated yields versus reaction time. Reactions were performed on 1 mmol scale; conditions: aryl iodide (0.9 equiv.), K_2CO_3 (3 equiv.), DME–H_2O (1:1, 10 ml), 40 °C, $(Ph_3P)_4Pd$, isolated yields.

A deeper insight was obtained via monitoring the reaction by ^1H NMR spectroscopy. The coupling was performed at a higher temperature (80 °C), with sampling every 20 min (Chart 2). The spectra plot showed an increasing amount of the product **4d**, reaching the maximum in about 2 h. After this point, both signals begun to disappear slowly into the baseline noise. Hence, at the temperatures ranging from 40 to 80 °C, boronate **6** is sufficiently reactive to form a significant amount of the product **4d**, whose rate of formation is estimated to be one order of magnitude faster than the rate of its decomposition. These results also show that 80 °C for 2 h are optimal reaction parameters for this process.

The last sets of parameters to be optimized were the ratios of the starting iodide and the base employed (Table III). These experiments also demonstrated the need for higher amounts of water (50%), combined with higher

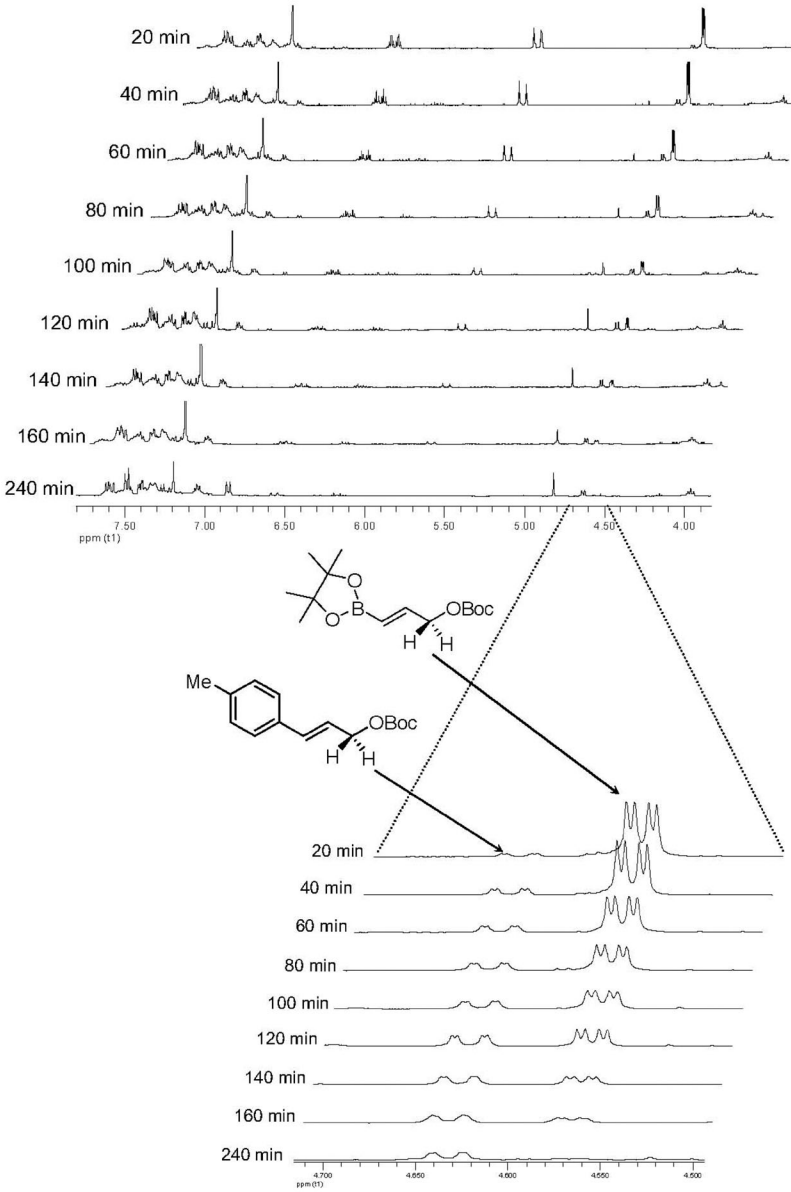


CHART 2

^{1}H NMR spectra plot based on Scheme 5, reaction was performed on 1 mmol scale; conditions: aryl iodide (0.9 equiv.), K_2CO_3 (2.5 equiv.), DME–H_2O (1:1, 10 ml), 80 °C, $(Ph_3P)_4Pd$ (5.4 mol %)

dilution. Under these conditions, the reactions were homogeneous (compare entries 2 versus 3). The other results show the highest yields when either excess of boronate **6** (entry 4) or iodide **5d** (entry 6) were used along with an excess of base. A further increase in loading of the base (entries 6 and 7) had a more negative effect than the increase in the loading of the iodide (entries 5 and 6).

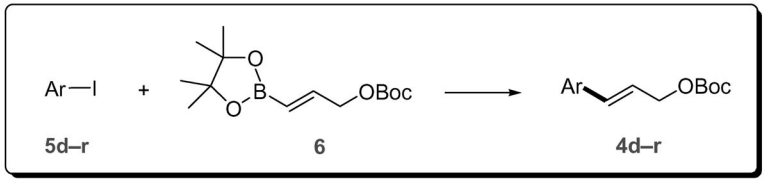
TABLE III
The influence of the molar ratios on the Suzuki–Miyaura coupling of **5d** with **6**[a]

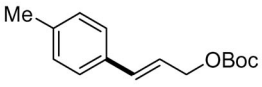
Entry	Iodide equiv	Base equiv	Solvent	Pd(0) mole %	Yield[b] %
1	1.4	2.9	2 ml, DME–H_2O (9:1)	5.2	11[c]
2	0.8	1.7	2 ml, DME–H_2O (9:1)	5.2	9[c]
3	0.8	2.3	10 ml, DME–H_2O (1:1)	4.0	20
4	0.6	1.7	10 ml, DME–H_2O (1:1)	3.1	36
5	4.7	2.9	10 ml, DME–H_2O (1:1)	5.6	33
6	3.1	3.0	10 ml, DME–H_2O (1:1)	6.0	36
7	4.6	4.6	10 ml, DME–H_2O (1:1)	4.8	24

[a] Reactions were performed on 1 mmol scale; conditions: 80 °C, 2 h, $(Ph_3P)_4Pd$, all equivalents are based on the boronate. [b] Isolated yields. [c] The yield was determined by ^1H NMR spectroscopy in the reaction mixture after the work up.

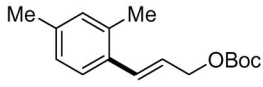
The optimized reaction protocol was employed in the synthesis of a series of various carbonates **4d**–**4r** (Scheme 6). The results fully correspond to the previous observations as well as to the common reactivity of aryl halides in the Suzuki–Miyaura coupling reaction. The highest yields were attained with electron-poor aryl iodides lacking *ortho* substituents. Aryl bromides did not reacted under any variation of the reaction conditions, suggesting that this effect can be utilized for discriminating between the reaction sites of polyhalogenated substrates. Indeed, 4-bromoiodobenzene (**5f**) selectively reacted at the C–I bond to produce **4f**, leaving the bromide moiety intact. In some cases, the excess of aryl iodide was successfully recovered (**4e**, **4j**, **4l**, and **4n**). Higher loading of both the iodide **5** and base further improved the yields, even in the case of *ortho*-substituted iodides (**5e** and **5j**). 3-Iodopyridine (**5q**) did also react to afford **4q**. Despite the low to moderate yields, the main synthetic utility of this method lies in the fast reaction and mild reaction conditions. An aqueous workup generally gave mixtures containing mainly the unreacted starting iodide (in excess) and the desired

product. With the subsequent simple chromatography, the whole reaction-purification procedure did not exceed 3 h, which is very convenient for automation. These advantages were demonstrated in the reaction of salicylate **5r** [21] that afforded the highly substituted carbonate **4r**.

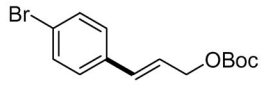




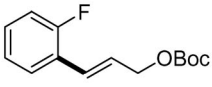
4d (42%)



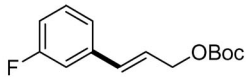
4e (12%)



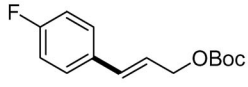
4f (41%)



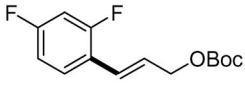
4g (10%)



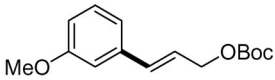
4h (40%)



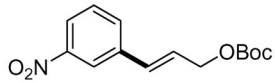
4i (29%)



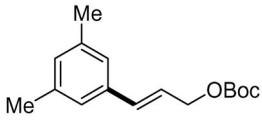
4j (15%)



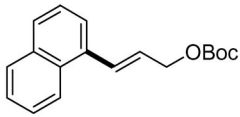
4k (25%)



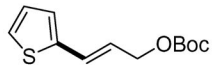
4l (57%)



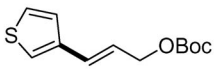
4m (33%)



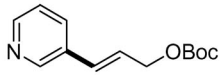
4n (56%)



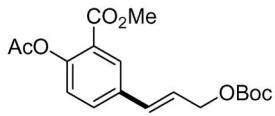
4o (31%)



4p (44%)



4q (18%)



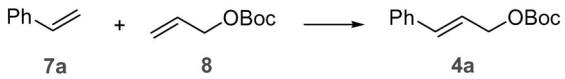
4r (22%)

SCHEME 6
Suzuki–Miyaura coupling of aryl and heteroaryl halides **5** with vinyl boronate **6**

Cross-Metathesis

The cross-metathesis reaction[22] was investigated as an alternative synthetic approach to carbonates **4** (Scheme 7). Many of the starting vinyl aromatics **7** are commercially available or are readily accessible in one step by the well-developed vinylation of aryl halides **5** [23], which renders this approach attractive.

Employing styrene (**7a**) and allyl *tert*-butyl carbonate (**8**) as model substrates, a brief screening of the reaction conditions was conducted to find an optimal protocol. The second-generation Grubbs catalyst gave generally twice as high yields as the Grubbs first-generation catalyst, along with the full conversion of allyl carbonate **8** (Table IV, entries 1 and 2). In both cases, *trans*-stilbene was isolated as the major product as a result of self-metathesis of **7a**. On the other hand, self-metathesis of allyl carbonate **8** was observed only as a very minor side reaction. The higher yields of the desired product **4a** were attained by increasing the excess of styrene (entries 6 and 7), which



SCHEME 7
Synthesis of carbonates **4** via cross-coupling metathesis

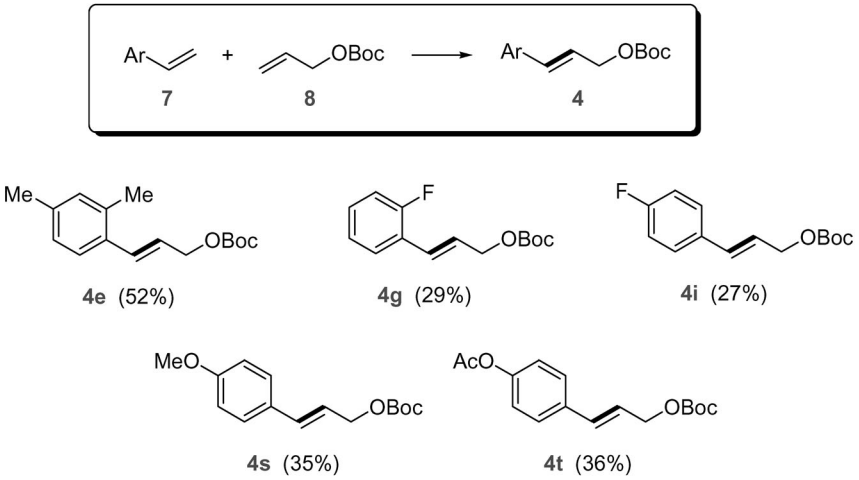
TABLE IV
Screening of the cross-metathesis reaction[a]

Entry	**7a** equiv	Catalyst mole %	Time h	Yield[b] %
1	2.0	Grubbs 1st (5.6)	12	17
2	2.0	Grubbs 2nd (2.7)	2	36
3	0.5	Grubbs 2nd (0.7)	2	21
4	0.4	Grubbs 2nd (0.8)	2	23
5	0.2	Grubbs 2nd (0.4)	2	16
6	5.0	Grubbs 2nd (2.4)	2	37
7	10.0	Grubbs 2nd (2.7)	2	43

[a] Reactions were performed on 1 mmol scale; conditions: DCM (2 ml), 40 °C, all the equivalents are based on allyl carbonate. [b] Isolated yields.

is an acceptable scenario in the case of cheap, commercially available vinyl aromatics.

Various vinyl aromatics were then submitted to the optimized cross-metathesis protocol (Scheme 8). The reaction showed reversed electronic demands to the Suzuki–Miyaura coupling and did not work for electronically poor substrates, such as nitrostyrene or pentafluorostyrene, and for vinyl pyridines. On the other hand, the reaction proceeded successfully with *ortho*-substituted styrenes to produce **4e** and **4g**.

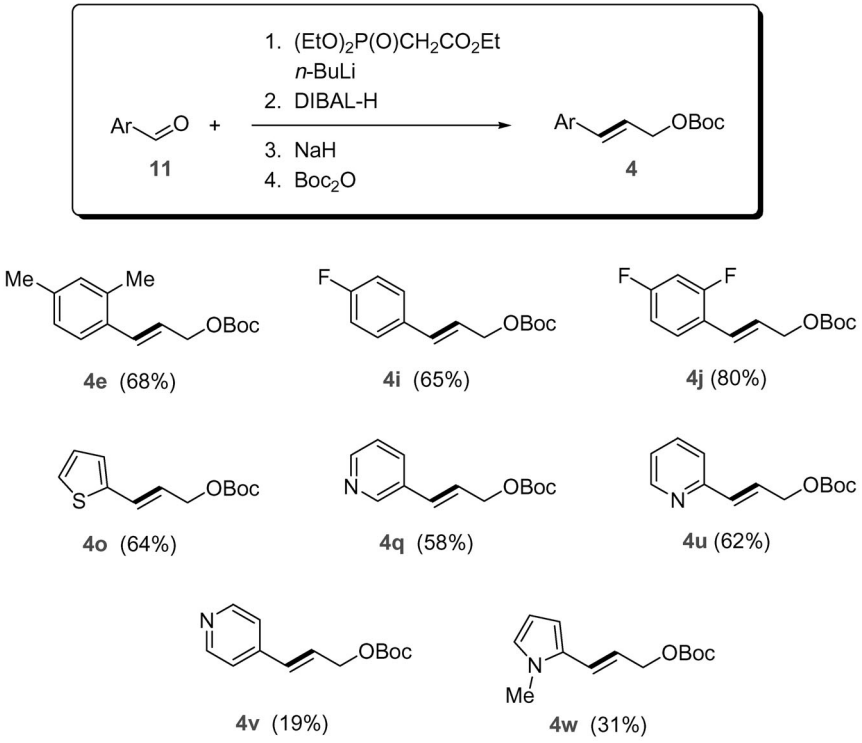


SCHEME 8
Rh-catalysed cross metathesis of styrenes **7** with allyl carbonate **8**

Horner–Wadsworth–Emmons Reaction

Optimization of the conventional synthetic approach[24] to carbonates **4** was also investigated (Schemes 2 and 9). Commercially available aryl aldehydes **11** were reacted with phosphonate **12** to afford the corresponding ethyl acrylates **10**. The reaction proved to be clean and highly stereoselective, no (*Z*)-isomers were detected by ^{1}H NMR spectroscopy[25]. The acrylates **10** were then reduced with DIBAL-H directly after the aqueous work-up without further purification. The resulting aryl propenols **9** were obtained again in sufficient purity and were directly transformed into the desired Boc derivatives **4**, using our optimized protocol (vide supra), the crude products were then subjected to the only purification (by chromatography), required in this sequence.

This classical synthetic approach proved to be very robust in a number of structural patterns (Scheme 9). The only difficulties were encountered in the reaction sequences of aldehydes **11v** and **11w**. The γ-picolinic aldehyde **11v** reacted well in the HWE reaction but subsequent reduction at room temperature resulted in the formation of intractable products only. Reduction at low temperature (–80 °C) gave propenol **9v** in about 40% yield (over two steps) but additional purification of the propenol **9v** was necessary. Carbonate **4v** was obtained from the latter product (48%) by using the standard procedure. The *N*-methylpyrrole carbonate **4w** was prepared by the standard reaction sequence. The problematic part here was the final purification, due to the low stability of the pyrrole moiety[26]. Even if the chro-



SCHEME 9
Horner–Wadsworth–Emmons approach to carbonate **4**

matography was carried out on a column of neutral alumina and with triethylamine as co-eluent, the blue color of pyrrole-based oligomers was observed upon the stationary phase. Furthermore, the final pyrrole carbonate **4w** proved unstable at room temperature, as it underwent spontaneous polymerization. Despite these particular problems, this optimized HWE approach proved to be a very convenient method for a gram scale (all reactions were carried out on 20 mmol scale) synthesis of carbonates **4** bearing various structural patterns including the *ortho* substituents and aromatic/heteroaromatic moieties with diverse electronic properties.

CONCLUSIONS

We have systematically investigated new synthetic approaches to *tert*-butyl (*E*)-3-arylprop-2-enol carbonates **4a**–**4w** and compared them with an optimized conventional approach. All these three approaches proved to be to be complementary. The Suzuki–Miyaura coupling reaction is a versatile method for aryls lacking an *ortho* substituent and for non-coordinating heterocycles, bearing preferentially electron-withdrawing functionalities. This method employs a wide range of commercially available aryl iodides and its main advantage relates to polyfunctional substrates, such as methyl acetylsalicylate (**5r** → **4r**). The cross-metathesis is a universal method with preference for electronically neutral or electron-donating groups, highlighted by the tolerance to *ortho* substituents[27]. Both these methods give moderate and reproducible yields within the limitations spelt out here. These one-step reactions are fast and atom-economic, yielding relatively clean products that are easy to purify, which makes them amenable to the use in parallel synthesis of large sets of derivatives with diverse functionality. The HWE-based reaction sequence, optimized to a three-step-one-purification protocol, represents a robust method for the standard preparation of carbonates **4** that can be easily scaled up. Comparing the three methods shows that each has its merit so that they are complementary and none is a clear, general winner. Thus, for instance, the synthesis of **4r** would be rather difficult via the classical HWE approach in view of the required protection-deprotections step, selective reactivity, etc. On the other hand, some of the low yields obtained in the Suzuki–Miyaura coupling (e.g., **4e**) would direct the strategy either toward the cross-metathesis or HWE approach.

EXPERIMENTAL

General Methods

Melting points were determined on a Kofler block and are uncorrected. The NMR spectra were measured in chloroform-d_1 (δ 7.26, ^{1}H; δ 77.00, ^{13}C) and CCl_3F (δ 0.00, ^{19}F) as internal standards unless otherwise indicated. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Complete assignment of all NMR signals was performed using a combination of H,HCOSY, H,CHSQC and H,CHMBC experiments. The IR spectra (ν in cm^{-1}) were recorded for a thin film between NaCl plates or for $CHCl_3$ solutions. The mass spectra (EI or CI-isobutane, unless otherwise specified) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. All reactions were performed under an atmosphere of dry, oxygen-free argon in oven-dried glassware three times evacuated and backfilled with the argon three times. Reaction temperature –83 °C refers to the cooling bath filled with an ethyl acetate–liquid nitrogen mixture. Solvents and solutions were transferred by syringe-septum and cannula techniques. All solvents for the reactions were of reagent grade and were dried and distilled immediately before use as follows: tetrahydrofuran (THF) from sodium/benzophenone, dichloromethane from calcium hydride. Solvents for the palladium- and ruthenium-catalyzed reactions were degassed in vacuo and stored over molecular sieves (4 Å) under argon atmosphere. Yields are given for isolated products showing one spot on a TLC plate and no impurities detectable in the NMR spectrum. The identity of the products prepared by different methods was checked by comparison of their NMR, IR, and MS data and by the TLC behavior.

General Procedure A: *tert*-Butyloxycarbonylation of Alcohols to Produce Carbonates **4**

An alcohol (100.0 mmol, neat or 5 M solution in THF if solid) was slowly added to a suspension of sodium hydride (6.0 g, 150 mmol, 60% suspension in mineral oil, 3 × washed with dry THF) in THF (100 ml) at room temperature and the mixture was stirred for 1 h. The resulting solution was slowly added to a solution of *tert*-butoxy- (*tert*-butoxycarbonyloxy)-methanone (Boc anhydride, 25.0 g, 115.0 mmol) in THF (400 ml) at room temperature and the mixture was stirred at room temperature overnight. The reaction was quenched with brine (100 ml) and the product was extracted into ether (500 ml). The organic layer was dried (Na_2SO_4) and evaporated.

General Procedure B: Suzuki–Miyaura Coupling Reaction to Produce Carbonates **4** (for the solid iodide **5**)

A flask containing aryl iodide **5** (3.00 mmol), K_2CO_3 (415 mg, 3.00 mmol) and $(Ph_3P)_4Pd$ (60.0 mg, 0.052 mmol) was sealed and three times evacuated and backfilled with argon. Boronate **6** (neat, 280 mg, 1.00 mmol), DME (5 ml) and water (5 ml) were added and the mixture was stirred at 80 °C for 2 h. The resulting solution was cooled to room temperature, diluted with Et_2O (80 ml), washed with brine (3 × 50 ml), dried (Na_2SO_4) and evaporated.

General Procedure C: Suzuki–Miyaura Coupling Reaction to Produce Carbonates **4** (for the liquid iodide **5**)

A flask containing K_2CO_3 (415 mg, 3.00 mmol) and $(Ph_3P)_4Pd$ (60.0 mg, 0.052 mmol) was sealed and three times evacuated and backfilled with argon. Aryl halide **5** (3.00 mmol), boronate **6** (neat, 285 mg, 1.00 mmol), DME (5 ml) and water (5 ml) were added and the mixture was stirred at 80 °C for 2 h. The resulting solution was cooled to room temperature, diluted with Et_2O (80 ml), washed with brine (3 × 50 ml), dried (Na_2SO_4) and evaporated.

General Procedure D: Cross-Metathesis Reaction to Carbonates **4**

A flask containing benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(tricyclohexylphosphine)ruthenium (2nd generation Grubbs catalyst, 23.9 mg, 0.028 mmol) was sealed and three times evacuated and backfilled with argon. Dichloromethane (2.0 ml), neat allyl carbonate **8** (1.00 mmol) and neat vinyl aromate **7** (0.40 to 5.00 mmol) were added and the mixture was stirred at 40 °C for 2 h. The resulting solution was cooled to room temperature and evaporated.

General Procedure E: Horner–Wadsworth–Emmons Based Reaction Sequence to Carbonates **4**

n-BuLi (11 ml, 22 mmol, 2 M solution in pentane) was slowly added to a solution of triethylphosphonoacetate **12** (4.49 g, 20.0 mmol) in THF (20 ml) at –83 °C. After 5 min, aldehyde **11** (20.0 mmol) was slowly added and the resulting mixture was stirred at –83 °C for 10 min and then at room temperature for 2 h. The reaction was quenched with brine (10 ml), the mixture was diluted with ether (100 ml), washed with brine (3 × 50 ml), dried (Na_2SO_4), and evaporated. The crude ethyl ester **10** was dissolved in THF (20 ml), cooled to 0 °C and DIBAL-H (40 ml, 60 mmol, 1.5 M solution in toluene) was slowly added at this temperature. The resulting mixture was stirred at room temperature for an additional 2 h and than the reaction was quenched with a saturated aqueous solution of potassium-sodium tartrate (50 ml). The resulting solution was stirred at 40 °C and a solid potassium-sodium tartrate (approximately 15 g) was added in portions, until the solution became homogeneous. The resulting mixture was diluted with ether (300 ml), washed with a saturated aqueous solution of potassium-sodium tartrate (3 × 100 ml), dried (Na_2SO_4), and evaporated. The crude allyl alcohol **9** was dissolved in THF (20 ml) and slowly added to a suspension of sodium hydride (1.21 g, 30.3 mmol, 60% suspension in mineral oil, 3 × washed with dry THF) in THF (20 ml) at room temperature and the mixture was stirred for 1 h. The resulting solution was slowly added to a solution of Boc anhydride (4.84 g, 22.2 mmol) in THF (50 ml) at room temperature and the mixture was stirred at room temperature overnight. The reaction was quenched with brine (10 ml) and the mixture diluted with ether (250 ml), washed with brine (3 × 50 ml), dried (Na_2SO_4), and evaporated.

tert-Butyl (E)-3-phenylprop-2-en-1-yl carbonate (**4a**). Fraction distillation of the crude product obtained by procedure A produced **4a** as a colorless oil (34.07 g, 73%): b.p. 114 °C at 270 Pa. ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.54 (s, 9 H, *t*-Bu), 4.76 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.5, $^4J_{1\text{-H},3\text{-H}}$ = 1.1, 2 H, 1-H), 6.33 (dt, ^3J = 15.9, $^3J_{2\text{-H},1\text{-H}}$ = 6.5, 1 H, 2-H), 6.71 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.9, $^4J_{3\text{-H},1\text{-H}}$ = 1.1, 1 H, 3-H), 7.27–7.32 (m, 1 H, H-arom), 7.33–7.38 (m, 2 H, H-arom), 7.43 (dd, $J_{H,H}$ = 7.2 and 1.5, 2 H, H-arom). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.65 ($C(CH_3)_3$), 67.32 (CH_2-1), 82.03 ($C(CH_3)_3$), 122.74 (CH-2), 126.51, 127.94 and 128.46 (CH-arom), 134.25 (CH-3), 136.03 (C-arom), 153.21 (CO carbonate). MS (CI-NH_3), *m/z* (%): 252 ($M + NH_4^+$, 2), 151 (1), 134 (3),

117 (2), 88 (3). IR (KBr, $CHCl_3$): 2980 (m), 1740 (s), 1449 (w), 1369 (m), 1275 (s), 1254 (s), 1163 (s), 1117 (m), 1085 (w), 967 (m). For $C_{14}H_{18}O_3$ calculated: 71.77% C, 7.74% H; found: 71.93% C, 7.78% H.

tert-Butyl (E)-3-(2′,3′-dimethoxyphenyl)prop-2-en-1-yl carbonate (**4b**). The crude product obtained by procedure A was chromatographed on a column of silica gel (5 × 10 cm) with a mixture of hexanes and AcOEt (90:10) to afford **4b** as a yellow oil (1064 mg, 49% of theory, 62% based on recovered allylic alcohol). Continued elution with a mixture of hexanes and AcOEt (80:20) gave the starting allylic alcohol **9b** (272 mg, 19% recovered). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.49 (s, 9 H, *t*-Bu), 3.79 (s, 3 H, CH_3O-2′), 3.84 (s, 3 H, CH_3O-3′), 4.73 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.5, $^4J_{1\text{-H},3\text{-H}}$ = 1.2, 2 H, 1-H), 6.31 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 16.1, $^3J_{2\text{-H},1\text{-H}}$ = 6.5, 1 H, 2-H), 6.82 (dd, $^3J_{4'\text{-H},5'\text{-H}}$ = 8.0, $^4J_{4'\text{-H},6'\text{-H}}$ = 1.4, 1 H, 4′-H), 6.98 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 16.1, $^4J_{3\text{-H},1\text{-H}}$ = 1.2, 1 H, 3-H), 7.00 (t, $^3J_{5'\text{-H},4'\text{-H}}$ = 8.0, $^3J_{5'\text{-H},6'\text{-H}}$ = 8.0, 1 H, 5′-H), 7.07 (dd, $^3J_{6'\text{-H},5'\text{-H}}$ = 8.0, $^4J_{6'\text{-H},4'\text{-H}}$ = 1.4, 1 H, 6′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.71 ($C(\mathbf{C}H_3)_3$), 55.70 (CH_3O-3′), 60.87 (CH_3O-2′), 67.75 (CH_2-1), 82.05 ($\mathbf{C}(CH_3)_3$), 111.74 (CH-4′), 118.26 (CH-6′), 123.96 (CH-5′), 124.19 (CH-2), 128.72 (CH-3), 130.29 (C-1′), 146.84 (C-2′), 152.89 (C-3′), 153.27 (CO carbonate). IR (neat): 2979 (w), 2835 (w), 1740 (s, CO carbonate), 1478 (m), 1369 (m), 1272 (s), 1255 (s), 1161 (s), 1117 (m), 1090 (m), 1070 (m), 1008 (m). MS (EI, 150 °C), *m/z* (%): 294 (M^+, 15), 238 ($M^+ - (CH_3)_2C{=}CH_2$, 100), 194 ($M^+ - (CH_3)_2C{=}CH_2 - CO_2$, 5), 177 ($MH^+ - (CH_3)_2C{=}CH_2 - CO_2 - H_2O$, 85). HRMS (EI): 294.1469 ($C_{16}H_{22}O_5$ (M^+) requires 294.1467). For $C_{16}H_{22}O_5$ calculated: 65.29% C, 7.53% H; found: 65.14% C, 7.66% H.

tert-Butyl (E)-3-(3′,4′-dimethoxyphenyl)prop-2-en-1-yl carbonate (**4c**). The crude product obtained by procedure A was chromatographed on a column of silica gel (5 × 10 cm) with a mixture of hexanes and AcOEt (90:10) to furnish **4c** as a yellow oil (638 mg, 33% of theory, 52% based on recovered allylic alcohol). Continued elution with a mixture of hexanes and AcOEt (75:25) gave the starting allylic alcohol **9c** (440 mg, 35% recovered). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.49 (s, 9 H, *t*-Bu), 3.86 (s, 3 H, CH_3O), 3.87 (s, 3 H, CH_3O), 4.69 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.6, $^4J_{1\text{-H},3\text{-H}}$ = 1.1, 2 H, 1-H), 6.15 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.8, $^3J_{2\text{-H},1\text{-H}}$ = 6.6, 1 H, 2-H), 6.59 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.8, $^4J_{3\text{-H},1\text{-H}}$ = 1.1, 1 H, 3-H), 6.80 (d, $^3J_{5'\text{-H},6'\text{-H}}$ = 8.1, 1 H, 5′-H), 6.91 (dd, $^3J_{6'\text{-H},5'\text{-H}}$ = 8.1, $^4J_{6'\text{-H},2'\text{-H}}$ = 1.9, 1 H, 6′-H), 6.93 (d, $^4J_{2'\text{-H},6'\text{-H}}$ = 1.9, 1 H, 2′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.71 ($C(\mathbf{C}H_3)_3$), 55.73 and 55.81 (CH_3O), 67.56 (CH_2-1), 82.07 ($\mathbf{C}(CH_3)_3$), 108.81 (CH-2′), 110.94 (CH-5′), 119.97 (CH-6′), 120.78 (CH-2), 129.16 (C-1′), 134.39 (CH-3), 148.93 and 149.12 (C-arom), 153.30 (CO carbonate). IR (neat): 2979 (w), 1739 (s, CO carbonate), 1515 (m), 1369 (m), 1269 (s), 1256 (s), 1160 (s), 1027 (m), 966 (m), 856 (m). MS (EI, 150 °C), *m/z* (%): 295 (MH^+, 10), 294 (M^+, 50), 238 ($M^+ - (CH_3)_2C{=}CH_2$, 100), 224 (32), 193 ($MH^+ - (CH_3)_2C{=}CH_2 - CO_2$, 15), 177 ($MH^+ - (CH_3)_2C{=}CH_2 - CO_2 - H_2O$, 100). HRMS (EI): 294.1466 ($C_{16}H_{22}O_5$ (M^+) requires 294.1467). For $C_{16}H_{22}O_5$ calculated: 65.29% C, 7.53% H; found: 65.14% C, 7.67% H.

tert-Butyl (E)-3-(4′-methylphenyl)prop-2-en-1-yl carbonate (**4d**). A flask containing 4-iodotoluene (109 mg, 0.50 mmol), boronic acid **15** (151 mg, 0.75 mmol), K_2CO_3 (187 mg, 1.35 mmol) and $(PPh_3)_4Pd$ (57.0 mg, 0.049 mmol) was sealed, three times evacuated and backfilled with argon. DME (5 ml) and water (0.7 ml) were then added and the reaction mixture was stirred at 85 °C for 20 h. The resulting solution was co-distilled three times with toluene and the residue was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (100:0 to 97:3) to afford **4d** as a colorless oil (76 mg, 61%). The crude product obtained using procedure B was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (100:0 to 97:3) to furnish **4d** as a colorless oil (89 mg, 36%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.51 (s, 9 H, *t*-Bu), 2.34 (s, 3 H, CH_3), 4.71 (dd, $^3J_{1\text{-H},2\text{-H}}$ =

6.6, $^4J_{1\text{-H},3\text{-H}}$ = 1.3, 2 H, 1-H), 6.25 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.9, $^3J_{2\text{-H},1\text{-H}}$ = 6.6, 1 H, 2-H), 6.64 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.9, $^4J_{3\text{-H},1\text{-H}}$ = 1.3, 1 H, 3-H), 7.13 (d, $^3J_{3'\text{-H},2'\text{-H}}$ = 8.1, 2 H, 3′-H), 7.29 (d, $^3J_{2'\text{-H},3'\text{-H}}$ = 8.1, 2 H, 2′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.22 (CH_3), 27.76 ($C(\mathbf{C}H_3)_3$), 67.63 (CH_2-1), 82.16 ($\mathbf{C}(CH_3)_3$), 121.73 (CH-2), 126.54 (CH-2′), 129.26 (CH-3′), 133.36 (C-1′), 134.48 (CH-3), 137.97 (C-4′), 153.33 (CO carbonate). IR (neat): 2979 (m), 1736 (s, CO carbonate), 1453 (m), 1368 (m), 1273 (s), 1155 (s). MS (CI-NH_3, 150 °C), *m/z* (%): 266 (M + NH_4^+, 35), 165 ([M + NH_4^+] – Boc, 30), 148 (M + H^+ – Boc, 45), 131 (40), 52 (100). For $C_{15}H_{20}O_3$ calculated: 72.55% C, 8.12% H; found: 72.25% C, 7.98% H.

tert-Butyl (E)-3-(2′,4′-dimethylphenyl)prop-2-en-1-yl carbonate (**4e**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (95:5) to give **4e** as a yellowish oil (27 mg, 11%). The crude product obtained by procedure D was chromatographed on a column of silica gel (3 × 10 cm) with hexanes to yield the corresponding stilbene derivate (123 mg); continued elution with a mixture of hexanes and AcOEt (98.5:1.5) gave **4e** as a colorless oil (150 mg, 52%). The crude product obtained by procedure E was chromatographed on a column of silica gel (5 × 15 cm) with a mixture of hexanes and AcOEt (98.5:1.5) to produce **4e** as a colorless oil (3.60 g, 68%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 2.30 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 4.72 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.6, $^4J_{1\text{-H},3\text{-H}}$ = 1.2, 2 H, 1-H), 6.14 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.7, $^3J_{2\text{-H},1\text{-H}}$ = 6.6, 1 H, 2-H), 6.85 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.7, $^4J_{3\text{-H},1\text{-H}}$ = 1.2, 1 H, 3-H), 6.97 (s, 1 H, 3′-H), 6.98 (d, J_{HH} = 7.6, H-arom), 7.34 (d, J_{HH} = 7.6, H-arom). ^{13}C NMR (100.6 MHz, $CDCl_3$): 19.63 (CH_3), 21.06 (CH_3), 27.78 ($C(\mathbf{C}H_3)_3$), 67.84 (CH_2-1), 82.12 ($\mathbf{C}(CH_3)_3$), 123.19 (CH-2), 125.79 and 126.83 (CH-arom), 131.04 (CH-3′), 132.41 (CH-3), 132.44, 135.53 and 137.74 (C-arom), 153.35 (CO carbonate). IR (neat): 2980 (m), 2932 (m), 1742 (s, CO carbonate), 1613 (w), 1369 (s), 1276 (s), 1254 (s), 1162 (s), 1089 (m), 858 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 508 (2), 468 ([2 M + NH_4^+] – *t*-BuOH, 5), 386 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 4), 280 ([M + NH_4^+], 3), 179 ([M + NH_4^+] – Boc, 3), 162 (MH^+ – Boc, 5), 145 (MH^+ – Boc – OH, 42), 52 (100). For $C_{16}H_{22}O_3$ calculated: 73.25% C, 8.45% H; found: 73.18% C, 8.48% H.

tert-Butyl (E)-3-(4′-bromophenyl)prop-2-en-1-yl carbonate (**4f**). The crude product obtained by procedure B was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99:1) to afford **4f** as white crystals (113 mg, 33%): m.p. 57–58 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 4.70 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.4, $^4J_{1\text{-H},3\text{-H}}$ = 1.3, 2 H, 1-H), 6.28 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.9, $^3J_{2\text{-H},1\text{-H}}$ = 6.4, 1 H, 2-H), 6.60 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.9, $^4J_{3\text{-H},1\text{-H}}$ = 1.3, 1 H, 3-H), 7.24 (d, $^3J_{\text{a-H,b-H}}$ = 8.4, 2 H, H_a-arom), 7.44 (d, $^3J_{\text{b-H,a-H}}$ = 8.4, 2 H, H_b-arom). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.75 ($C(\mathbf{C}H_3)_3$), 67.13 (CH_2-1), 82.30 ($\mathbf{C}(CH_3)_3$), 121.88 (C-4′), 123.73 (CH-2), 128.10 (C_aH-arom), 131.68 (C_bH-arom), 132.98 (CH-3), 135.10 (C-1′), 153.24 (CO carbonate). IR ($CHCl_3$): 2983 (m), 1740 (s, CO carbonate), 1487 (m), 1370 (m), 1277 (s), 1256 (s), 1216 (s), 1157 (s), 1073 (m), 845 (m), 755 (s). MS (CI-NH_3, 150 °C), *m/z* (%): 642/644/646 ([2 M + NH_4^+], 10), 524/526/528 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 65), 330/332 ([M + NH_4^+], 100), 229/231 ([M + NH_4^+] – Boc, 35), 212/214 (MH^+ – Boc, 15), 195/197 (MH^+ – Boc – OH, 4), 52 (43). For $C_{14}H_{17}BrO_3$ calculated: 53.69% C, 5.47% H; found: 53.60% C, 5.47% H.

tert-Butyl (E)-3-(2′-fluorophenyl)prop-2-en-1-yl carbonate (**4g**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (100:00 to 98.5:1.5) to give **4g** as a colorless oil (25 mg, 10%). The crude product obtained by procedure D was chromatographed on a column of silica gel (3 × 10 cm) with hexanes to yield the corresponding stilbene derivate (17 mg); continued elution with a mixture of hexanes and AcOEt (98.5:1.5) provided **4g** as a colorless oil (70 mg, 29%).

^{1}H NMR (400.1 MHz, $CDCl_3$): 1.51 (s, 9 H, *t*-Bu), 4.74 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.3, $^4J_{1\text{-H},3\text{-H}}$ = 1.4, 2 H, 1-H), 6.38 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 16.1, $^3J_{2\text{-H},1\text{-H}}$ = 6.3, 1 H, 2-H), 6.82 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 16.1, $^4J_{3\text{-H},1\text{-H}}$ = 1.4, 1 H, 3-H), 7.03 (ddd, $^3J_{HF}$ = 10.7, $^3J_{3'\text{-H},4'\text{-H}}$ = 8.2, $^4J_{3'\text{-H},5'\text{-H}}$ = 1.2, 1 H, 3′-H), 7.10 (dt, $^3J_{5'\text{-H},4'\text{-H}}$ = 7.6, $^3J_{5'\text{-H},6'\text{-H}}$ = 7.6, $^4J_{5'\text{-H},3'\text{-H}}$ = 1.2, 1 H, 5′-H), 7.22 (ddd, $^3J_{4'\text{-H},3'\text{-H}}$ = 8.2, $^3J_{4'\text{-H},5'\text{-H}}$ = 7.6, $^4J_{4'\text{-H},6'\text{-H}}$ = 1.8, 1 H, 4′-H), 7.45 (dd, $^3J_{6'\text{-H},5'\text{-H}}$ = 7.6, $^4J_{6'\text{-H},4'\text{-H}}$ = 1.8, 1 H, 6′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.76 ($C(\mathbf{C}H_3)_3$), 67.47 (CH_2-1), 82.30 ($\mathbf{C}(CH_3)_3$), 115.75 (d, $^2J_{CF}$ = 22.1, CH-3′), 123.97 (d, $^2J_{CF}$ = 12.1, C-1′), 124.10 (d, $^4J_{CF}$ = 3.6, CH-5′), 125.55 (d, $^4J_{CF}$ = 5.1, CH-2), 126.63 (d, $^3J_{CF}$ = 3.6, CH-3), 127.61 (d, $^3J_{CF}$ = 3.6, CH-6′), 129.34 (d, $^3J_{CF}$ = 8.8, CH-4′), 153.28 (CO carbonate), 160.34 (d, $^1J_{CF}$ = 250.3, CF-2′). ^{19}F NMR (376.5 MHz, $CDCl_3$): –118.21. IR ($CHCl_3$): 2979 (m), 1743 (s, CO carbonate), 1489 (m), 1457 (m), 1370 (m), 1256 (s), 1163 (s), 969 (m), 858 (m), 755 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 522 ([2 M – NH_4^+], 1), 404 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 3), 270 ([M + NH_4^+], 95), 214 ([M + NH_4^+] – CH_2=$C(CH_3)_2$, 20), 169 ([M + NH_4^+] – Boc, 20), 152 (MH^+ – Boc, 22), 135 (MH^+ – Boc – OH, 5), 52 (100). For $C_{14}H_{17}FO_3$ calculated: 66.65% C, 6.79% H; found: 66.77% C, 6.91% H.

tert-Butyl (E)-3-(3′-fluorophenyl)prop-2-en-1-yl carbonate (**4h**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99.2:0.8) to furnish **4h** as a yellowish oil (103 mg, 40%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 4.72 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.3, $^4J_{1\text{-H},3\text{-H}}$ = 1.3, 2 H, 1-H), 6.29 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.9, $^3J_{2\text{-H},1\text{-H}}$ = 6.3, 1 H, 2-H), 6.63 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.9, $^4J_{3\text{-H},1\text{-H}}$ = 1.3, 1 H, 3-H), 6.94 (dddd, $^3J_{HF}$ = 8.5, $^3J_{4'\text{-H},5'\text{-H}}$ = 8.4, $^4J_{4'\text{-H},6'\text{-H}}$ = 2.5, $^4J_{4'\text{-H},2'\text{-H}}$ = 0.9, 1 H, 4′-H), 7.08 (ddd, $^3J_{2'\text{-H,F}}$ = 10.1, $^4J_{2'\text{-H},4'\text{-H}}$ = 2.5, $^4J_{2'\text{-H},6'\text{-H}}$ = 1.9, 1 H, 2′-H), 7.14 (ddd, $^3J_{6'\text{-H},5'\text{-H}}$ = 7.8, $^4J_{6'\text{-H},2'\text{-H}}$ = 1.9, $^4J_{6'\text{-H},4'\text{-H}}$ = 0.9, 1 H, 6′-H), 7.27 (ddd, $^3J_{5'\text{-H},4'\text{-H}}$ = 8.4, $^3J_{5'\text{-H},6'\text{-H}}$ = 7.8, $^4J_{5'\text{-H,F}}$ = 6.0, 1 H, 5′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.75 ($C(\mathbf{C}H_3)_3$), 67.02 (CH_2-1), 82.35 ($\mathbf{C}(CH_3)_3$), 113.06 (d, $^2J_{CF}$ = 21.8, CH-2′), 114.84 (d, $^2J_{CF}$ = 21.4, CH-4′), 122.50 (d, $^4J_{CF}$ = 2.8, CH-6′), 124.38 (CH-2), 130.02 (d, $^3J_{CF}$ = 8.5, CH-5′), 132.93 (d, $^4J_{CF}$ = 2.5, CH-3), 138.51 (d, $^3J_{CF}$ = 7.8, C-1′), 153.25 (CO carbonate), 163.00 (d, $^1J_{CF}$ = 245.4, CF-3′). ^{19}F NMR (376.5 MHz, $CDCl_3$): –113.84. IR ($CHCl_3$): 2980 (m), 1741 (s, CO carbonate), 1584 (m), 1370 (m), 1276 (s), 1255 (s), 1161 (s), 1117 (m), 966 (m), 859 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 522 ([2 M + NH_4^+], 15), 404 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 25), 386 (10), 310 (10), 270 ([M + NH_4^+], 100), 169 ([M + NH_4^+] – Boc, 5), 152 (MH^+ – Boc, 5), 135 (MH^+ – Boc – OH, 2), 52 (5). For $C_{14}H_{17}FO_3$ calculated: 66.65% C, 6.79% H; found: 66.49% C, 6.81% H.

tert-Butyl (E)-3-(4′-fluorophenyl)prop-2-en-1-yl carbonate (**4i**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99:1) to give **4i** as a yellowish oil (72 mg, 29%). The crude product obtained by procedure E was chromatographed on a column of silica gel (5 × 15 cm) with a mixture of hexanes and AcOEt (100:0 to 98.5:1.5) to afford **4i** as a colorless oil (3.273 g, 65%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 4.70 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.5, $^4J_{1\text{-H},3\text{-H}}$ = 1.2, 2 H, 1-H), 6.21 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.9, $^3J_{2\text{-H},1\text{-H}}$ = 6.5, 1 H, 2-H), 6.63 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.9, $^4J_{3\text{-H},1\text{-H}}$ = 1.2, 1 H, 3-H), 6.94 (dd, $^3J_{3'\text{-H},2'\text{-H}}$ = 8.8, $^3J_{3'\text{-H,F}}$ = 8.7, 2 H, 3′-H and 5′-H), 7.28 (dd, $^4J_{2'\text{-H,F}}$ = 5.4, $^3J_{2'\text{-H},3'\text{-H}}$ = 8.8, 2 H, 2′-H and 6′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.76 ($C(\mathbf{C}H_3)_3$), 67.32 (CH_2-1), 82.26 ($\mathbf{C}(CH_3)_3$), 115.51 (d, $^2J_{CF}$ = 21.7, CH-3′), 122.64 (d, $^6J_{CF}$ = 2.2, CH-2), 128.19 (d, $^3J_{CF}$ = 8.1, CH-2′), 132.34 (d, $^4J_{CF}$ = 3.2, C-1′), 133.23 (CH-3), 153.30 (CO carbonate), 162.56 (d, $^1J_{CF}$ = 247.6, CF-4′). ^{19}F NMR (376.5 MHz, $CDCl_3$): –114.15. IR (neat): 2981 (m), 2936 (w), 1740 (s, CO carbonate), 1601 (m), 1510 (s, CF), 1370 (m), 1275 (s), 1255 (s), 1159 (s), 850 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 522 ([2 M + NH_4^+], 10), 404 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 100), 348 (10), 270 ([M + NH_4^+], 40), 169 ([M + NH_4^+] – Boc, 7), 152 (MH^+ – Boc, 9), 135 (MH^+ – Boc – OH, 8), 52 (1). For $C_{14}H_{17}FO_3$ calculated: 66.65% C,

6.79% H; found: 66.39% C, 6.95% H. The crude product obtained by procedure D was chromatographed on a column of silica gel (3 × 10 cm) with hexanes to yield the corresponding stilbene derivate (73 mg); continued elution with a mixture of hexanes and AcOEt (100:0 to 98.5:1.5) gave **4i** as a colorless oil (65 mg, 27%).

tert-Butyl (E)-3-(2′,4′-difluorophenyl)prop-2-en-1-yl carbonate (**4j**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99:1 to 98.5:1.5) to afford **4j** as a yellowish oil (31 mg, 11%). The crude product obtained by procedure E was chromatographed on a column of silica gel (5 × 15 cm) with a mixture of hexanes and AcOEt (100:0 to 98.5:1.5) to furnish **4j** as a colorless oil (4.32 g, 80%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 4.72 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.3, $^4J_{1\text{-H},3\text{-H}}$ = 1.1, 2 H, 1-H), 6.31 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 16.1, $^3J_{2\text{-H},1\text{-H}}$ = 6.3, 1 H, 2-H), 6.74 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 16.1, $^4J_{3\text{-H},1\text{-H}}$ = 1.1, 1 H, 3-H), 6.79 (ddd, $^3J_{HF}$ = 11.4 and 10.8, $^4J_{3'\text{-H},5'\text{-H}}$ = 2.4, 1 H, 3′-H), 6.84 (dddd, $^3J_{HF}$ = 11.3, $^3J_{5'\text{-H},6'\text{-H}}$ = 8.7, $^4J_{5'\text{-H},3'\text{-H}}$ = 2.4, $^5J_{HF}$ = 1.0, 1 H, 5′-H), 7.41 (ddd, $^3J_{6'\text{-H},5'\text{-H}}$ = 8.7, $^4J_{HF}$ = 8.5 and 6.4, 1 H, 6′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.77 ($C(\mathbf{C}H_3)_3$), 67.35 (CH_2-1), 82.37 ($\mathbf{C}(CH_3)_3$), 104.09 (t, $^2J_{CF}$ = 25.6, CH-3′), 111.52 (dd, $^2J_{CF}$ = 21.5, $^4J_{CF}$ = 3.6, CH-5′), 125.23 (dd, $^4J_{CF}$ = 5.1, $^6J_{CF}$ = 2.1, CH-2), 125.74 (dd, $^3J_{CF}$ = 2.9, $^5J_{CF}$ = 1.5, C-3), 128.48 (dd, $^3J_{CF}$ = 9.5 and 5.2, CH-6′), 137.50 (d, $^2J_{CF}$ = 25.6, C-1′), 153.26 (CO carbonate), 162.40 (d, $^1J_{CF}$ = 250.1, CF), 162.52 (d, $^1J_{CF}$ 250.2, CF). ^{19}F NMR (376.5 MHz, $CDCl_3$): –110.66 (d, $^4J_{FF}$ = 7.9), –113.92 (d, $^4J_{FF}$ = 7.9). IR (neat): 2981 (m), 2934 (m), 1742 (s, CO carbonate), 1615 (m), 1503 (s, CF), 1370 (m), 1275 (s), 1255 (s), 1161 (s), 966 (m), 853 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 288 ([M + NH_4^+], 30), 187 ([M + NH_4^+] – Boc, 5), 170 ([M + NH_4^+] – *t*-BuOH – CO_2, 5), 153 ([M + NH_4^+] – *t*-BuOH – CO_2 – NH_3, 5), 52 (100). For $C_{14}H_{16}F_2O_3$ calculated: 62.22% C, 5.97% H; found: 62.35% C, 6.15% H.

tert-Butyl (E)-3-(3′-methoxyphenyl)prop-2-en-1-yl carbonate (**4k**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99.2:0.8) to give iodo-3-methoxybenzene **5k** (366 mg, 51% recovered). Continued elution with a mixture of hexanes and AcOEt (98.5:1.5) furnished **4k** as a yellowish oil (73 mg, 25%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 3.81 (s, 3 H, CH_3O), 4.72 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.4, $^4J_{1\text{-H},3\text{-H}}$ = 1.3, 2 H, 1-H), 6.29 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.9, $^3J_{2\text{-H},1\text{-H}}$ = 6.4, 1 H, 2-H), 6.64 (d, $^3J_{3\text{-H},2\text{-H}}$ = 15.9, 1 H, 3-H), 6.82 (ddd, $^3J_{4'\text{-H},5'\text{-H}}$ = 8.1, $^4J_{4'\text{-H},2'\text{-H}}$ = 2.5, $^4J_{4'\text{-H},6'\text{-H}}$ = 0.9, 1 H, 4′-H), 6.92 (dd, $^4J_{2'\text{-H},4'\text{-H}}$ = 2.5, $^4J_{2'\text{-H},6'\text{-H}}$ = 1.7, 1 H, 2′-H), 6.98 (ddd, $^3J_{6'\text{-H},5'\text{-H}}$ = 7.9, $^4J_{6'\text{-H},2'\text{-H}}$ = 1.7, $^4J_{6'\text{-H},4'\text{-H}}$ = 0.9, 1 H, 6′-H), 7.24 (dd, $^3J_{5'\text{-H},4'\text{-H}}$ = 8.1, $^3J_{5'\text{-H},6'\text{-H}}$ = 7.9, 1 H, 5′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.77 ($C(\mathbf{C}H_3)_3$), 55.18 (CH_3O), 67.35 (CH_2-1), 82.22 ($\mathbf{C}(CH_3)_3$), 111.83 (CH-2′), 113.77 (CH-4′), 119.30 (CH-6′), 123.22 (CH-2), 129.54 (CH-5′), 134.22 (CH-3), 137.62 (C-1′), 153.31 (CO carbonate), 159.76 (CH-3′). IR (neat): 2979 (m), 2938 (m), 1740 (s, CO carbonate), 1598 (m), 1580 (m), 1369 (m), 1275 (s), 1255 (s), 1159 (s), 857 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 546 ([2 M + NH_4^+], 18), 428 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 63), 282 ([M + NH_4^+], 100), 181 ([M + NH_4^+] – Boc, 45), 164 (MH^+ – Boc, 40), 147 (MH^+ – Boc – OH, 10), 52 (25). For $C_{15}H_{20}O_4$ calculated: 68.16% C, 7.63% H; found: 68.03% C, 7.80% H.

tert-Butyl (E)-3-(3′-nitrophenyl)prop-2-en-1-yl carbonate (**4l**). The crude product obtained by procedure B was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (98.5:1.5) to afford iodo-3-nitrobenzene **5l** (562 mg, 73% recovered). Continued elution with a mixture of hexanes and AcOEt (97.5:2.5) furnished **4l** as a yellowish oil (134 mg, 43% of theory, 57% based on the recovered iodide): ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.49 (s, 9 H, *t*-Bu), 4.74 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.0, $^4J_{1\text{-H},3\text{-H}}$ = 1.4, 2 H, 1-H), 6.42 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 16.0, $^3J_{2\text{-H},1\text{-H}}$ = 6.0, 1 H, 2-H), 6.70 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 16.0, $^4J_{3\text{-H},1\text{-H}}$ = 1.4, 1 H, 3-H),

7.48 (dd, $^3J_{5'\text{-H},4'\text{-H}}$ = 8.1, $^3J_{5'\text{-H},6'\text{-H}}$ = 7.8, 1 H, 5′-H), 7.67 (ddd, $^3J_{6'\text{-H},5'\text{-H}}$ = 7.8, $^4J_{6'\text{-H},2'\text{-H}}$ = 1.8, $^4J_{6'\text{-H},4'\text{-H}}$ = 0.9, 1 H, 6′-H), 8.08 (ddd, $^3J_{4'\text{-H},5'\text{-H}}$ = 8.1, $^4J_{4'\text{-H},2'\text{-H}}$ = 2.2, $^4J_{4'\text{-H},6'\text{-H}}$ = 0.9, 1 H, 4′-H), 8.21 (dd, $^4J_{2'\text{-H},4'\text{-H}}$ = 2.2, $^4J_{2'\text{-H},6'\text{-H}}$ = 1.8, 1 H, 2′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.69 ($C(\mathbf{C}H_3)_3$), 66.53 (CH_2-1), 82.45 ($\mathbf{C}(CH_3)_3$), 121.14 (CH-2′), 122.49 (CH-4′), 126.40 (CH-2), 129.48 (C-5′), 131.23 (CH-3), 132.27 (C-6′), 137.93 (C-1′), 148.52 (C-3′), 153.13 (CO carbonate). IR (neat): 2981 (m), 2935 (m), 1742 (s, CO carbonate), 1531 (s, C-N), 1369 (m, N-O), 1351 (s, N-O), 1276 (s), 1255 (s), 1160 (s), 966 (m), 859 (m), 732 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 576 ([2 M + NH_4^+], 5), 458 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 1), 297 ([M + NH_4^+], 100), 241 (3), 52 (23). For $C_{14}H_{17}NO_5$ calculated: 60.21% C, 6.14% H, 5.02% N; found: 60.13% C, 6.15% H, 4.88% N.

tert-Butyl (E)-3-(3′,5′-dimethylphenyl)prop-2-en-1-yl carbonate (**4m**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99:1) to yield 3,5-dimethyliodobenzene **5m** (252 mg, 35% recovered). Continued elution with a mixture of hexanes and AcOEt (99:1) afforded **4m** as a yellowish oil (87 mg, 33%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.51 (s, 9 H, *t*-Bu), 2.31 (s, 6 H, CH_3), 4.71 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.5, $^4J_{1\text{-H},3\text{-H}}$ = 1.2, 2 H, 1-H), 6.27 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.9, $^3J_{2\text{-H},1\text{-H}}$ = 6.5, 1 H, 2-H), 6.61 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.9, $^4J_{3\text{-H},1\text{-H}}$ = 1.2, 1 H, 3-H), 6.91 (s, 1 H, 4′-H), 7.02 (s, 2 H, 2′-H and 6′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.19 (CH_3), 27.76 ($C(\mathbf{C}H_3)_3$), 67.55 (CH_2-1), 82.09 ($\mathbf{C}(CH_3)_3$), 122.44 (CH-2′), 124.52 (CH-2′ and CH-6′), 129.77 (CH-4′), 134.64 (CH-3), 136.08 (C-1′), 137.98 (C-3′ and C-5′), 153.35 (CO carbonate). IR (neat): 2979 (m), 2920 (w), 1740 (s, CO carbonate), 1602 (w), 1369 (m), 1274 (s), 1254 (s), 1163 (s), 853 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 542 ([2 M + NH_4^+], 15), 424 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 100), 280 ([M + NH_4^+], 42), 179 ([M + NH_4^+] – Boc, 40), 162 (MH^+ – Boc, 52), 145 (MH^+ – Boc – OH, 30), 52 (30). For $C_{16}H_{22}O_3$ calculated: 73.25% C, 8.45% H; found: 73.06% C, 8.39% H.

tert-Butyl (E)-3-(naphthalen-1′-yl)prop-2-en-1-yl carbonate (**4n**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99:1) to give 1-iodonaphthalene **5n** (629 mg, 81% recovered). Continued elution with a mixture of hexanes and AcOEt (98.5:1.5) afforded **4n** as a yellowish oil (93 mg, 32% of theory, 56% based on the recovered iodide). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.54 (s, 9 H, *t*-Bu), 4.85 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.4, $^4J_{1\text{-H},3\text{-H}}$ = 1.3, 2 H, 1-H), 6.34 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.6, $^3J_{2\text{-H},1\text{-H}}$ = 6.4, 1 H, 2-H), 7.44 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.6, $^4J_{3\text{-H},1\text{-H}}$ = 1.3, 1 H, 3-H), 7.46 (m, 1 H, 3′-H), 7.50 (m, 1 H, 6′-H), 7.52 (m, 1 H, 8′-H), 7.61 (d, J_{HH} = 7.2, 1 H, 4′-H), 7.81 (d, J_{HH} = 8.2, 1 H, 2′-H), 7.86 (dd, J_{HH} = 7.71, $^4J_{6'\text{-H},8'\text{-H}}$ = 2.0, 1 H, 6′-H), 8.11 (dd, J_{HH} = 7.2, $^4J_{8'\text{-H},6'\text{-H}}$ = 2.0, 1 H, 8′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.77 ($C(\mathbf{C}H_3)_3$), 67.52 (CH_2-1), 82.23 ($\mathbf{C}(CH_3)_3$), 123.68 (CH-7′), 124.12 (CH-4′), 125.51 (CH-2), 125.79 (CH-8′), 126.11 and 126.12 (CH-3′ and CH-6′), 128.33 (CH-2′), 128.47 (CH-5′), 131.07 (C-10′), 131.64 (CH-3), 133.50 (C-1′), 133.95 (C-9′), 153.35 (CO carbonate). IR (neat): 2979 (m), 1740 (s, CO carbonate), 1369 (m), 1276 (s), 1254 (s), 1160 (s), 857 (m), 791 (m), 777 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 586 ([2 M + NH_4^+], 10), 468 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 65), 302 ([M + NH_4^+], 30), 201 ([M + NH_4^+] – Boc, 25), 184 (MH^+ – Boc, 25), 167 (MH^+ – Boc – OH, 100), 52 (10). For $C_{18}H_{20}O_3$ calculated: 76.03% C, 7.09% H; found: 76.16% C, 6.92% H.

tert-Butyl (E)-3-(thiophen-2′-yl)prop-2-en-1-yl carbonate (**4o**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99:1) to yield **4o** as a yellowish oil (77 mg, 31%). The crude product obtained by procedure E was chromatographed on a column of silica gel (5 × 15 cm) with a mixture of hexanes and AcOEt (100:0 to 99:1) to produce **4o** as a colorless oil (3.07 g, 64%).

^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 4.67 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.5, $^4J_{1\text{-H},3\text{-H}}$ = 1.3, 2 H, 1-H), 6.12 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.7, $^3J_{2\text{-H},1\text{-H}}$ = 6.5, 1 H, 2-H), 6.79 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.7, $^4J_{3\text{-H},1\text{-H}}$ = 1.3, 1 H, 3-H), 6.96 (dd, $^3J_{4'\text{-H},5'\text{-H}}$ = 5.0, $^3J_{4\text{-H},3'\text{-H}}$ = 3.6, 1 H, 4′-H), 6.99 (dd, $^3J_{3'\text{-H},4'\text{-H}}$ = 3.6, $^4J_{3'\text{-H},5'\text{-H}}$ = 1.1, 1 H, 3′-H), 7.18 (dd, $^3J_{5'\text{-H},4'\text{-H}}$ = 5.0, $^4J_{5'\text{-H},3'\text{-H}}$ = 1.1, 1 H, 5′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.75 ($C(CH_3)_3$), 67.08 (CH_2-1), 82.23 ($C(CH_3)_3$), 122.29 (CH-2), 124.94 (CH-5′), 126.50 (CH-3′), 127.34 (CH-4′), 127.53 (CH-3), 141.13 (C-1′), 153.26 (CO carbonate). IR (neat): 2980 (m), 2933 (w), 1741 (s, CO carbonate), 1650 (w), 1369 (m), 1274 (s), 1254 (s), 1161 (s), 956 (m), 857 (m), 700 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 380 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 1), 258 ([M + NH_4^+], 5), 157 ([M + NH_4^+] – Boc, 5), 140 (MH^+ – Boc, 5), 123 (MH^+ – Boc – OH, 25), 52 (100). For $C_{12}H_{16}O_3S$ calculated: 59.97% C, 6.71% H; found: 59.75% C, 6.96% H.

tert-Butyl (E)-3-(thiophen-3′-yl)prop-2-en-1-yl carbonate (**4p**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (99:1) to afford **4p** as a yellowish oil (110 mg, 44%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 4.68 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.6, $^4J_{1\text{-H},3\text{-H}}$ = 1.3, 2 H, 1-H), 6.14 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.8, $^3J_{2\text{-H},1\text{-H}}$ = 6.6, 1 H, 2-H), 6.67 (ddt, $^3J_{3\text{-H},2\text{-H}}$ = 15.8, $^4J_{3\text{-H},1\text{-H}}$ = 1.3, $^4J_{3\text{-H},4'\text{-H}}$ = 0.6, 1 H, 3-H), 7.19 (dd, $^4J_{2'\text{-H},4'\text{-H}}$ = 2.9, $^4J_{2'\text{-H},5'\text{-H}}$ = 1.3, 1 H, 2′-H), 7.20 (dd, $^3J_{5'\text{-H},4'\text{-H}}$ = 5.1, $^4J_{5'\text{-H},2'\text{-H}}$ = 1.3, 1 H, 5′-H), 7.27 (ddd, $^3J_{4'\text{-H},5'\text{-H}}$ = 5.1, $^4J_{4'\text{-H},2'\text{-H}}$ = 2.9, $^4J_{4'\text{-H},3\text{-H}}$ = 0.6, 1 H, 4′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.73 ($C(CH_3)_3$), 67.40 (CH_2-1), 82.15 ($C(CH_3)_3$), 122.59 (CH-2), 123.10 (CH-2′), 124.91 (CH-5′), 126.13 (CH-4′), 128.62 (CH-3), 138.78 (C-3′), 153.27 (CO carbonate). IR (NaCl, neat): 2981 (m), 1741 (s, CO carbonate), 1369 (m), 1275 (s), 1254 (s), 1163 (s). MS (EI, 150 °C), *m/z* (%): 240 (M^+, 5), 205 (20), 184 (M^+ – $(CH_3)_2C{=}CH_2$, 50), 166 (M^+ – *t*-BuOH, 100), 140 (M^+ – $(CH_3)_2C{=}CH_2$ – CO_2, 20), 123 (30), 121 (40), 119 (25), 83 (40). HRMS (EI): 240.0822 ($C_{12}H_{16}O_3S$ (M^+) requires 240.0820).

tert-Butyl (E)-3-(pyridne-3′-yl)prop-2-en-1-yl carbonate (**4q**). The crude product obtained by procedure C was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (60:40) to furnish **4q** as a brown oil (44 mg, 18%). The crude product obtained by procedure E was chromatographed on a column of silica gel (5 × 15 cm) with AcOEt to afford **4q** as a brown oil (2.22 g, 48%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.45 (s, 9 H, *t*-Bu), 4.68 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.2, $^4J_{1\text{-H},3\text{-H}}$ = 1.4, 2 H, 1-H), 6.31 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 16.0, $^3J_{2\text{-H},1\text{-H}}$ = 6.2, 1 H, 2-H), 6.60 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 16.0, $^4J_{3\text{-H},1\text{-H}}$ = 1.4, 1 H, 3-H), 7.19 (dd, $^3J_{5'\text{-H},4'\text{-H}}$ = 8.0, $^3J_{5'\text{-H},6'\text{-H}}$ = 4.8, 1 H, 5′-H), 7.64 (ddd, $^3J_{4'\text{-H},5'\text{-H}}$ = 8.0, $^4J_{4'\text{-H},2'\text{-H}}$ = 2.1, $^4J_{4'\text{-H},6'\text{-H}}$ = 1.6, 1 H, 4′-H), 8.43 (dd, $^3J_{6'\text{-H},5'\text{-H}}$ = 4.8, $^4J_{6'\text{-H},4'\text{-H}}$ = 1.6, 1 H, 6′-H), 8.55 (d, $^4J_{2'\text{-H},4'\text{-H}}$ = 2.1, 1 H, 2′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.62 ($C(CH_3)_3$), 66.77 (CH_2-1), 82.26 ($C(CH_3)_3$), 123.31 (CH-5′), 125.26 (CH-2), 130.20 (CH-3), 131.68 (C-3′), 132.87 (CH-4′), 148.34 (CH-2′), 148.93 (CH-6′), 153.08 (CO carbonate). IR (neat): 2980 (w), 1744 (s, CO carbonate), 1280 (s), 1255 (m), 1161 (m). MS (EI, 150 °C), *m/z* (%): 236 (MH^+, 100), 180 (MH^+ – $(CH_3)_2C{=}CH_2$, 20), 120 (10), 118 (MH^+ – $(CH_3)_2C{=}CH_2$ – H_2O, 10). HRMS (EI): 236.1289 ($C_{13}H_{18}O_3N$ (MH^+) requires 236.1287). For $C_{13}H_{17}NO_3$ calculated: 66.36% C, 7.28% H, 5.95% N; found: 66.03% C, 7.35% H, 5.89% N.

Methyl 2-acetoxy-5-(E)-3′-tert-butoxycarbonyloxyprop-1′-en-1′-yl benzoate (**4r**). The crude product obtained by procedure B was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (98.5:1.5) to yield the deacetylated iodide (192 mg); continued elution with a 95:5 mixture gave the starting iodide **5r** (195 mg, 20% recovered). Finally elution with a 90:10 mixture afforded **4r** (84 mg, 22%) as a yellow oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.48 (s, 9 H, *t*-Bu), 2.32 (s, 3 H, CH_3CO), 3.85 (s, 3 H, CH_3O), 4.70 (dd, $^3J_{3'\text{-H},2'\text{-H}}$ = 6.2, $^4J_{3'\text{-H},1'\text{-H}}$ = 1.0, 2 H, 3′-H), 6.29 (dt, $^3J_{2'\text{-H},1'\text{-H}}$ = 15.9, $^3J_{2'\text{-H},3'\text{-H}}$ = 6.2, 1 H,

2′-H), 6.64 (dt, $^3J_{1'\text{-H},2'\text{-H}}$ = 15.9, $^4J_{1'\text{-H},3'\text{-H}}$ = 1.0, 1 H, 1′-H), 7.04 (d, $^3J_{3\text{-H},4\text{-H}}$ = 8.4, 1 H, 3-H), 7.54 (dd, $^3J_{4\text{-H},3\text{-H}}$ = 8.4, $^4J_{4\text{-H},6\text{-H}}$ = 2.2, 1 H, 4-H), 8.01 (d, $^4J_{6\text{-H},4\text{-H}}$ = 2.2, 1 H, 6-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 20.86 ($\mathbf{C}H_3CO$), 27.67 ($C(\mathbf{C}H_3)_3$), 52.15 (CH_3O), 66.88 (CH_2-3), 82.26 ($\mathbf{C}(CH_3)_3$), 123.12 (C-1), 123.19 (CH-3), 124.53 (CH-2′), 129.79 (CH-6), 131.46 (CH-4), 132.00 (CH-1′), 134.28 (C-5), 150.07 (C-2), 153.16 (CO carbonate), 164.54 (CO benzoate), 169.55 (CO acetate). IR (NaCl, $CHCl_3$): 2980 (m), 1740 (s), 1731 (s), 1369 (s), 1275 (s), 1187 (s), 1081 (s). MS (EI, 150 °C), *m/z* (%): 350 (M^+, 1), 319 (4), 294 ($M^+ - (CH_3)_2C{=}CH_2$, 14), 252 (100), 220 (30), 191 (30), 159 (25), 158 (18), 103 (15). HRMS (EI): 350.1367 ($C_{18}H_{22}O_7$ (M^+) requires 350.1366). For $C_{17}H_{22}O_7$ calculated: 61.71% C, 6.33% H; found: 61.53% C, 6.47% H.

tert-Butyl (E)-3-(4′-methoxyphenyl)prop-2-en-1-yl carbonate (**4s**). The crude product obtained by procedure D was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (98.5:1.5) to give **4s** as a colorless oil (88 mg, 35%), followed by the corresponding stilbene derivative (21 mg). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 3.81 (s, 3 H, CH_3O), 4.70 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.7, $^4J_{1\text{-H},3\text{-H}}$ = 1.2, 2 H, 1-H), 6.16 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.8, $^3J_{2\text{-H},1\text{-H}}$ = 6.7, 1 H, 2-H), 6.62 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.8, $^4J_{3\text{-H},1\text{-H}}$ = 1.2, 1 H, 3-H), 6.85 (d, $^3J_{3'\text{-H},2'\text{-H}}$ = 8.8, 2 H, 3′-H), 7.33 (d, $^3J_{2'\text{-H},3'\text{-H}}$ = 8.8, 2 H, 2′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.78 ($C(\mathbf{C}H_3)_3$), 55.26 (CH_3O), 67.74 (CH_2-1), 82.11 ($\mathbf{C}(CH_3)_3$), 113.97 (CH-3′), 120.54 (CH-2), 127.88 (CH-2′), 128.93 (C-1′), 134.25 (CH-3), 153.37 (CO carbonate), 159.56 (C-4′). IR (neat): 2979 (m), 1742 (s, CO carbonate), 1610 (m), 1514 (m), 1370 (m), 1275 (s), 1253 (s), 1164 (s), 1034 (m), 849 (m). MS (CI-NH_3, 150 °C), *m/z* (%): 282 ([M + NH_4^+], 0.5), 264 (M^+, 1), 208 (5), 175 (20), 147 ([M + NH_4^+] – NH_3 – *t*-BuOH – CO_2, 100). For $C_{15}H_{20}O_4$ calculated: 68.16% C, 7.63% H; found: 68.32% C, 7.89% H.

tert-Butyl (E)-3-(4′-acetyloxyphenyl)prop-2-en-1-yl carbonate (**4t**). The crude product obtained by procedure D was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (98.5:1.5) to yield the starting acetate **7t** (46 mg, 28% recovered). Continued elution with a 92.5:7.5 mixture afforded **4t** (75 mg, 36% based on the recovered starting acetate) as a colorless oil, the corresponding stilbene derivative (8 mg) was eluted with an 85:15 mixture. ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.50 (s, 9 H, *t*-Bu), 2.29 (s, 3 H, CH_3CO_2), 4.70 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.4, $^4J_{1\text{-H},3\text{-H}}$ = 1.2, 2 H, 1-H), 6.24 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.9, $^3J_{2\text{-H},1\text{-H}}$ = 6.4, 1 H, 2-H), 6.64 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.9, $^4J_{3\text{-H},1\text{-H}}$ = 1.2, 1 H, 3-H), 7.04 (d, $^3J_{3'\text{-H},2'\text{-H}}$ = 8.6, 2 H, 3′-H), 7.39 (d, $^3J_{2'\text{-H},3'\text{-H}}$ = 8.6, 2 H, 2′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.06 ($\mathbf{C}H_3CO_2$), 27.73 ($C(\mathbf{C}H_3)_3$), 67.25 (CH_2-1), 82.19 ($\mathbf{C}(CH_3)_3$), 121.67 (CH-3′), 123.13 (CH-2), 127.57 (CH-2′), 133.27 (CH-3), 133.94 (C-1′), 150.34 (C-4′), 153.26 (CO carbonate), 169.28 (CO acetate). IR (neat): 2981 (m), 1740 (s, CO carbonate), 1507 (m), 1370 (m), 1275 (s), 1255 (s), 1194 (s), 1164 (s). MS (CI-NH_3, 150 °C), *m/z* (%): 602 ([2 M + NH_4^+], 1), 484 ([2 M + NH_4^+] – *t*-BuOH – CO_2, 2), 310 ([M + NH_4^+], 10), 175 ([M + NH_4^+] – NH_3 – *t*-BuOH – CO_2, 100). For $C_{16}H_{20}O_5$ calculated: 65.74% C, 6.90% H; found: 65.60% C, 7.02% H.

tert-Butyl (E)-3-(pyridin-2′-yl)prop-2-en-1-yl carbonate (**4u**). The crude product obtained by procedure E was chromatographed on a column of silica gel (5 × 15 cm) with AcOEt to afford **4u** as a brown oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.46 (s, 9 H, *t*-Bu), 4.74 (d, $^3J_{1\text{-H},2\text{-H}}$ = 4.7, 2 H, 1-H), 6.69 (d, $^3J_{3\text{-H},2\text{-H}}$ = 15.8, 1 H, 3-H), 6.75 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.8, $^3J_{2\text{-H},1\text{-H}}$ = 4.7, 1 H, 2-H), 7.09 (ddd, $^3J_{5'\text{-H},4'\text{-H}}$ = 7.6, $^3J_{5'\text{-H},6'\text{-H}}$ = 4.8, $^4J_{5'\text{-H},3'\text{-H}}$ = 1.0, 1 H, 5′-H), 7.24 (ddd, $^3J_{3'\text{-H},4'\text{-H}}$ = 7.8, $^4J_{3'\text{-H},5'\text{-H}}$ = 1.0, $^5J_{3'\text{-H},6'\text{-H}}$ = 0.9, 1 H, 3′-H), 7.58 (ddd, $^3J_{4'\text{-H},3'\text{-H}}$ = 7.8, $^3J_{4'\text{-H},5'\text{-H}}$ = 7.6, $^4J_{4'\text{-H},6'\text{-H}}$ = 1.8, 1 H, 4′-H), 8.51 (ddd, $^3J_{6'\text{-H},5'\text{-H}}$ = 4.8, $^4J_{6'\text{-H},4'\text{-H}}$ = 1.8, $^5J_{6'\text{-H},3'\text{-H}}$ = 0.9, 1 H, 6′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.66 ($C(\mathbf{C}H_3)_3$), 66.57 (CH_2-1), 82.13 ($\mathbf{C}(CH_3)_3$), 121.74 (CH-3′), 122.37 (CH-5′), 127.49 (CH-3), 132.66 (CH-2), 136.37 (CH-4′), 149.46

(CH-6′), 153.15 (CO carbonate), 154.48 (C-2′). IR (neat): 2980 (w), 1741 (s, CO carbonate), 1278 (s), 1254 (s), 1161 (s). MS (CI-isobutane, 150 °C), *m/z* (%): 236 (MH^+, 100), 180 (MH^+ – $(CH_3)_2C{=}CH_2$, 20), 120 (MH^+ – $(CH_3)_2C{=}CH_2$ – H_2O, 40). HRMS (CI-isobutane): 236.1289 ($C_{13}H_{18}O_3N$ (MH^+) requires 236.1287). For $C_{13}H_{17}NO_3$ calculated: 66.36% C, 7.28% H, 5.95% N; found: 66.22% C, 7.27% H, 6.07% N.

tert-Butyl (E)-3-(pyridin-4′-yl)prop-2-en-1-yl carbonate (**4v**). A solution of the allyl alcohol **9v** (60 mg, 0.44 mmol) in THF (2 ml) was slowly added to a suspension of sodium hydride (54 mg, 1.30 mmol, 60% suspension in mineral oil, 3 × washed with dry THF) in THF (3 ml) at room temperature and the mixture was stirred for 1 h. The resulting solution was slowly added to a solution of Boc anhydride (226 mg, 1.04 mmol) in THF (7 ml) at room temperature and the mixture was stirred at room temperature overnight. The reaction was quenched with brine (5 ml), the mixture was diluted with ether (100 ml), washed with brine (3 × 50 ml), dried (Na_2SO_4), and evaporated. The residue was chromatographed on a column of silica gel (3 × 10 cm) with a mixture of hexanes and AcOEt (60:40) to furnish **4v** as a yellow oil (50 mg, 48%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.49 (s, 9 H, *t*-Bu), 4.73 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 5.7, $^4J_{1\text{-H},3\text{-H}}$ = 1.2, 2 H, 1-H), 6.48 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 16.0, $^3J_{2\text{-H},1\text{-H}}$ = 5.7, 1 H, 2-H), 6.59 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 16.0, $^4J_{3\text{-H},1\text{-H}}$ = 1.2, 1 H, 3-H), 7.22 (d, $^3J_{3'\text{-H},2'\text{-H}}$ = 6.0, 2 H, 3′-H and 5′-H), 8.54 (d, $^3J_{2'\text{-H},3'\text{-H}}$ = 6.0, 2 H, 2′-H and 6′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.71 ($C(CH_3)_3$), 66.47 (CH_2-1), 82.53 ($C(CH_3)_3$), 120.96 (CH-3′ and CH-5′), 127.94 (CH-2), 131.01 (CH-3), 143.47 (C-4′), 150.16 (CH-2′ and CH-6′), 153.11 (CO carbonate). IR (neat): 2980 (m), 1742 (s, CO carbonate), 1596 (m), 1369 (m), 1277 (s), 1255 (s), 1162 (s), 1119 (m), 849 (m). MS (EI, 150 °C), *m/z* (%): 235 (M^+, 10), 179 (M^+ – $(CH_3)_2C{=}CH_2$, 45), 135 (M^+ – $(CH_3)_2C{=}CH_2$ – CO_2, 10), 118 (MH^+ – $(CH_3)_2C{=}CH_2$ – CO_2 – H_2O, 30), 28 (100). HRMS (EI): 235.1207 ($C_{13}H_{17}NO_3$ (M^+) requires 235.1208). For $C_{13}H_{17}NO_3$ calculated: 66.36% C, 7.28% H, 5.95% N; found: 66.20% C, 7.34% H, 5.81% N.

tert-Butyl (E)-3-(N-methylpyrrol-2′-yl)prop-2-en-1-yl carbonate (**4w**). The crude product obtained by procedure E was chromatographed on a column of neutral alumina (3 × 15 cm) with a mixture of hexanes, AcOEt and Et_3N (74:25:1) to give **4w** as a brown oil (200 mg, 31%). ^{1}H NMR (400.1 MHz, C_6D_6): 1.35 (s, 9 H, *t*-Bu), 2.72 (s, 3 H, CH_3), 4.60 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 6.6, $^4J_{1\text{-H},3\text{-H}}$ = 1.2, 2 H, 1-H), 5.94 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 15.7, $^3J_{2\text{-H},1\text{-H}}$ = 6.6, 1 H, 2-H), 6.16 (dd, $^3J_{4'\text{-H},3'\text{-H}}$ = 3.7, $^3J_{4'\text{-H},5'\text{-H}}$ = 2.6, 1 H, 4′-H) 6.20 (dd, $^3J_{5'\text{-H},4'\text{-H}}$ = 2.6, $^4J_{5'\text{-H},3'\text{-H}}$ = 1.6, 1 H, 5′-H), 6.31 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 15.7, $^4J_{3\text{-H},1\text{-H}}$ = 1.2, 1 H, 3-H), 6.41 (dd, $^3J_{3'\text{-H},4'\text{-H}}$ = 3.7, $^4J_{3'\text{-H},5'\text{-H}}$ = 1.6, 1 H, 3′-H). ^{13}C NMR (100.6 MHz, C_6D_6): 27.76 ($C(CH_3)_3$), 33.32 (CH_3), 67.92 (CH_2-1), 81.16 ($C(CH_3)_3$), 108.30 (CH-3′), 108.47 (CH-4′), 119.72 (CH-2), 123.58 (CH-5′), 123.85 (CH-3), 130.53 (C-2′), 154.17 (CO carbonate). MS (EI, 150 °C), *m/z* (%): 237 (M^+, 80), 181 (M^+ – $(CH_3)_2C{=}CH_2$, 80), 137 (M^+ – $(CH_3)_2C{=}CH_2$ – CO_2, 52), 120 (80), 57 (100). HRMS (EI): 237.1362 ($C_{13}H_{19}NO_3$ (M^+) requires 237.1365).

Pinacolyl 1-(tert-butyloxycarbonyl)prop-2-en-1-ol-3-yl boronate (**6**). Cyclohexene (164 mg, 2.00 mmol) was added to a mixture of a 1 M solution of borane in THF (1.0 ml, 1.0 mmol) and THF (1 ml) at 0 °C and the mixture was stirred for 1.5 h. The resulting solution was evaporated in vacuum to form a white solid, to which neat pinacolborane (1.41 g, 11.0 mmol) was added. Carbonate **13** (1.56 g, 10.0 mmol) was then slowly added and the reaction mixture heated spontaneously. The resulting mixture was stirred at room temperature overnight, the reaction was quenched with water (2 ml) and the mixture was stirred for 1 h. The resulting suspension was extracted with AcOEt (3 × 20 ml), the combined organic layers were dried (Na_2SO_4) and evaporated, yielding boronate **6** (2.70 g, 95%): b.p. 110–111 °C at 270 Pa. ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.20 (s, 12 H, CH_3), 1.42 (s, 9 H, *t*-Bu), 4.58 (dd,

$^3J_{1\text{-H},2\text{-H}}$ = 4.8, $^4J_{1\text{-H},3\text{-H}}$ = 1.8, 2 H, 1-H), 5.63 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 18.1, $^4J_{3\text{-H},1\text{-H}}$ = 1.8, 1 H, 3-H), 6.55 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 18.1, $^3J_{2\text{-H},1\text{-H}}$ = 4.8, 1 H, 2-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 24.65 ($C(\mathbf{C}H_3)_2$), 27.65 ($C(\mathbf{C}H_3)_3$), 67.76 (CH_2-1), 82.03 ($\mathbf{C}(CH_3)_3$), 83.27 ($\mathbf{C}(CH_3)_2$), 120.25 (CH-3), 145.66 (CH-2), 153.13 (CO carbonate). IR ($CHCl_3$): 2980 (s), 1744 (s), 1648 (m), 1458 (w), 1370 (m), 1350 (m), 1329 (m), 1278 (s), 1255 (s), 1165 (m), 1145 (s), 1118 (m). MS (CI), *m/z* (%): 285 (M + H^+, 9), 284 (M^+, 2), 229 (M + H^+ – *t*-Bu, 100), 228 (M^+ – *t*-Bu, 25), 185 (M + H^+ – *t*-Bu – CO_2, 7), 119 (20), 101 (35). HRMS (CI): 285.1871 ($C_{14}H_{26}BO_5$ (M + H)$^+$ requires 285.1873). For $C_{14}H_{25}BO_5$ calculated: 59.18% C, 8.87% H; found: 59.32% C, 8.83% H.

tert-Butyl prop-2-en-1-yl carbonate (**8**)[28]. Fraction distillation of the crude product obtained by procedure A yielded **8** as a colorless oil (7.89 g, 50%): b.p. 40 °C at 270 Pa. ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.46 (s, 9 H, *t*-Bu), 4.53 (ddd, $^3J_{1\text{-H},2\text{-H}}$ = 5.8, $^4J_{1\text{-H},3\text{-Ha}}$ = 1.4, $^4J_{1\text{-H},3\text{-Hb}}$ = 1.3, 2 H, 1-H), 5.22 (ddd, $^3J_{3\text{-Hb},2\text{-H}}$ = 10.5, $^2J_{3\text{-Hb},3\text{-Ha}}$ = 2.8, $^4J_{3\text{-Hb},1\text{-H}}$ = 1.3, 1 H, 3-Hb), 5.31 (ddd, $^3J_{3\text{-Ha},2\text{-H}}$ = 17.2, $^2J_{3\text{-Ha},3\text{-Hb}}$ = 2.8, $^4J_{3\text{-Ha},1\text{-H}}$ = 1.4, 1 H, 3-Ha), 5.90 (ddt, $^3J_{2\text{-H},3\text{-Ha}}$ = 17.2, $^3J_{2\text{-H},3\text{-Hb}}$ = 10.5, $^3J_{2\text{-H},1\text{-H}}$ = 5.8, 1 H, 2-H). For $C_8H_{14}O_3$ calculated: 60.74% C, 8.92% H; found: 60.70% C, 8.96% H.

(E)-3-(Pyridin-4′yl)prop-2-en-1-ol (**9v**). *n*-BuLi (1.1 ml, 2.2 mmol, 2 M solution in pentane) was slowly added to a solution of triethyl phosphonoacetate **12** (450 mg, 2.01 mmol) in THF (5 ml) at –83 °C. After stirring for 5 min, pyridin-4-carbaldehyde **11v** (214 mg, 2.00 mmol) was slowly added and the resulting mixture was stirred at –83 °C for an additional 10 min and then at room temperature for 2 h. The reaction was quenched with brine (5 ml), the mixture was diluted with ether (100 ml) and washed with brine (3 × 50 ml), dried (Na_2SO_4), and evaporated. The crude ethyl ester **10v** was dissolved in THF (5 ml), cooled to –83 °C and DIBAL-H (3.2 ml, 4.8 mmol, 1.5 M solution in toluene) was slowly added and the resulting mixture was stirred at this temperature for an additional 2 h. The reaction was quenched with MeOH (5 ml) and then a saturated aqueous solution of potassium-sodium tartrate (10 ml) was added. The resulting mixture was stirred at 40 °C and a solid potassium-sodium tartrate (approximately 2 g) was added in portions, until the solution became homogeneous. The resulting mixture was diluted with ether (100 ml), washed with an aqueous saturated solution of potassium-sodium tartrate (3 × 50 ml), dried (Na_2SO_4), and evaporated. The residue was chromatographed on a column of silica gel (3 × 10 cm) with AcOEt to afford **9v** as a white solid (105 mg, 39%): m.p. 90–91 °C ($CHCl_3$). ^{1}H NMR (400.1 MHz, $CDCl_3$): 2.52 (s, 1 H, OH), 4.39 (m, 2 H, 1-H), 6.58–6.60 (m, 2 H, 2-H and 3-H), 7.24 (d, $^3J_{3'\text{-H},2'\text{-H}}$ = 6.2, 2 H, 3′-H and 5′-H), 8.52 (d, $^3J_{2'\text{-H},3'\text{-H}}$ = 6.2, 2 H, 2′-H and 6′-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 62.86 (CH_2-1), 120.95 (CH-3′ and CH-5′), 127.66 and 133.94 (CH-2 and CH-3), 144.30 (C-4′), 149.99 (CH-6′). IR ($CHCl_3$): 3019 (m), 1220 (m), 1211 (m), 784 (m). MS (EI, 150 °C), *m/z* (%): 135 (M^+, 75), 117 (M^+ – H_2O, 20), 106 (85), 93 (100). HRMS (EI): 135.0686 (C_8H_9NO (M^+) requires 135.0684).

tert-Butyl prop-2-yn-1-yl carbonate (**13**). Fraction distillation of the crude product obtained by procedure A gave **13** as a colorless liquid (25.60 g, 82%): b.p. 47–49 °C at 270 Pa. ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.47 (s, 9 H, *t*-Bu), 2.50 (t, $^4J_{3\text{-H},1\text{-H}}$ = 2.5, 1 H, 3-H), 4.64 (d, $^4J_{1\text{-H},3\text{-H}}$ = 2.5, 2 H, 1-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.6 ($C(\mathbf{C}H_3)_3$), 54.2 (CH_2-1), 75.2 (CH-3), 77.2 (C-2), 82.9 ($\mathbf{C}(CH_3)_3$), 152.6 (CO carbonate). IR ($CHCl_3$): 3296, 2983, 1747, 1395, 1371, 1280, 1256, 1158, 1097. MS (CI), *m/z* (%): 157 (M + H^+, 100), 139 (5), 119 (5), 101 (20), 81 (22). HRMS (CI): 157.0862 ($C_8H_{13}O_3$ (M + H)$^+$ requires 157.0865). For $C_8H_{12}O_3$ calculated: 61.52% C, 7.74% H; found: 61.54% C, 7.80% H.

1-(tert-Butyloxycarbonyl)prop-2-en-1-ol-3-yl boronic acid (**15**). Cyclohexene (165 mg, 2.01 mmol) was added to a mixture of a 1 M solution of borane in THF (1.0 ml, 1.0 mmol) and THF (1 ml)

at 0 °C and the mixture was stirred for 1.5 h. The resulting solution was evaporated in vacuum to form a white solid, to which neat catecholborane (1.34 g, 11.2 mmol) and then carbonate **13** (1.50 g, 9.6 mmol) were added at room temperature (spontaneous heating is desired for high yield) and the resulting mixture was stirred at room temperature overnight. The reaction was quenched with water (10 ml) and the mixture was stirred for 2 h. The resulting suspension was filtered off, yielding white solid of **15** (710 mg, 36%). The filtrate was extracted with AcOEt (3 × 20 ml). Combined organics layers were dried (Na_2SO_4) and evaporated. The residue was chromatographed on a column of silica gel (5 × 5 cm) with a mixture of hexanes and AcOEt (80:20), which eluted catechol. Continued elution with AcOEt afforded boronic acid **15** as a white foam (504 mg, 26%). The combined yield of boronic acid **15** was 1.210 g (62%). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.48 (s, 9 H, *t*-Bu), 4.69 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 4.5, $^4J_{1\text{-H},3\text{-H}}$ = 1.7, 2 H, 1-H), 5.76 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 17.9, $^4J_{3\text{-H},1\text{-H}}$ = 1.7, 1 H, 3-H), 6.91 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 17.9, $^3J_{2\text{-H},1\text{-H}}$ = 4.5, 1 H, 2-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 27.70 ($C(\mathbf{C}H_3)_3$), 67.49 (CH_2-1), 82.40 ($\mathbf{C}(CH_3)_3$), 122.45 (CH-3), 149.18 (CH-2), 153.15 (CO carbonate). IR ($CHCl_3$): 3328 (m), 2977 (w), 1748 (s), 1645 (w), 1394 (m), 1349 (m), 1279 (m), 1248 (m), 1159 (m), 1138 (m), 1113 (m), 1074 (m). MS (EI), *m/z* (%): 384 (3 ($M + H^+ - H_2O$ – *t*-Bu), 20), 322 (3 ($M + H^+ - H_2O$ – *t*-Bu – $H_2O{\cdot}CO_2$), 10), 278 (3 ($M + H^+ - H_2O$ – *t*-Bu – $H_2O{\cdot}CO_2 - CO_2$), 10), 216 (7), 177 (8). HRMS (EI): 384.0844 ($C_{12}H_{15}O_{12}B_3$ trimer ($M + H^+ - H_2O$ – *t*-Bu) requires 384.0842). For $C_8H_{15}BO_5$ calculated: 47.56% C, 7.48% H; found: 47.68% C, 7.34% H.

Prop-2-en-1-ol-3-yl boronic acid (**16**)[12]. Neat catecholborane (13.25 g, 110.49 mmol) was slowly added to neat propargyl alcohol (2.76 g, 50.80 mmol) at room temperature over a period of 15 min. After the addition has been completed, the mixture was heated at 70 °C for 1 h. White precipitate that was formed during the course of the reaction was dissolved in a small amount of a mixture of MeOH and CH_2Cl_2 (1:1) and chromatographed on a column of silica gel (5 × 5 cm): a mixture of hexanes and AcOEt (50:50) eluted catechol; continued elution with a mixture of CH_2Cl_2 and MeOH (90:10) furnished boronic acid **16** as a white foam (2.08 g, 40%). ^{1}H NMR (400.1 MHz, CD_3OD): 4.10 (dd, $^3J_{1\text{-H},2\text{-H}}$ = 4.2, $^4J_{1\text{-H},3\text{-H}}$ = 1.9, 2 H, 1-H), 5.80 (dt, $^3J_{3\text{-H},2\text{-H}}$ = 17.8, $^4J_{3\text{-H},1\text{-H}}$ = 1.9, 1 H, 3-H), 6.60 (dt, $^3J_{2\text{-H},3\text{-H}}$ = 17.8, $^3J_{2\text{-H},1\text{-H}}$ = 4.2, 1 H, 2-H). ^{13}C NMR (100.6 MHz, CD_3OD): 64.78 (CH_2-1), 123.10 (CH-3), 151.75 (CH-2).

Supporting information available. ^{1}H NMR spectra for some of the key compounds. These supplementary data are available free of charge via doi:10.1135/cccc20080705.

We thank the University of Glasgow for a studentship to J. Štambaský.

REFERENCES AND NOTES

1. For general review of palladium complexes in allylic substitution: a) Godleski S. A. in: *Comprehensive Organic Synthesis*, Vol. 4 (B. M. Trost, I. Fleming and M. F. Semmelhack, Eds), pp. 585–661. Pergamon, Oxford 1991; b) Frost C. G., Howarth J., Williams J. M. J.: *Tetrahedron: Asymmetry* **1992**, *3*, 1089; c) Trost B. M., VanVranken D. L.: *Chem. Rev.* **1996**, *96*, 395; d) Negishi E. (Ed.): *Handbook of Organopalladium Chemistry for Organic Synthesis*, Vols I and II. J. Wiley & Sons, New York 2002.
2. For reversed regioselectivity to branched products in Pd-catalyzed allylic substitution: a) Prétôt R., Pfaltz A.: *Angew. Chem. Int. Ed.* **1998**, *37*, 323; b) Hayashi T., Kawatsura M.,

Uozumi Y.: *J. Am. Chem. Soc.* **1998**, *120*, 1681; c) You S. L., Zhu X. Z., Luo Y. M., Hou X. L., Dai L. X.: *J. Am. Chem. Soc.* **2001**, *123*, 7471; d) Hou X. L., Sun N.: *Org. Lett.* **2004**, *6*, 4399; e) Zheng W. H., Sun N., Hou X. L.: *Org. Lett.* **2005**, *7*, 5151.
3. a) Dvořák D., Starý I., Kočovský P.: *J. Am. Chem. Soc.* **1995**, *117*, 6130; b) Malkov A. V., Baxendale I. R., Dvořák D., Mansfield D. J., Kočovský P.: *J. Org. Chem.* **1999**, *64*, 2737; c) Malkov A. V., Spoor P., Vinader V., Kočovský P.: *Tetrahedron Lett.* **2001**, *42*, 509; d) Glorius F., Neuburger M., Pfaltz A.: *Helv. Chim. Acta* **2001**, *84*, 3178. For a recent overview, see the following: e) Belda O., Moberg C.: *Acc. Chem. Res.* **2004**, *37*, 159.
4. Lloyd-Jones G. C., Pfaltz A.: *Angew. Chem. Int. Ed.* **1995**, *34*, 462.
5. a) Zhang S. W., Mitsudo T., Kondo T., Watanabe Y.: *J. Organomet. Chem.* **1995**, *485*, 55; b) Trost B. M., Fraisse P. L., Ball Z. T.: *Angew. Chem. Int. Ed.* **2002**, *41*, 1059.
6. a) Evans P. A., Leahy D. K.: *J. Am. Chem. Soc.* **2002**, *124*, 7882; b) Hayashi T., Okada A., Suzuka T., Kawatsura M.: *Org. Lett.* **2003**, *5*, 1713.
7. For a review, see: Takeuchi R.: *Synlett* **2002**, 1954.
8. Bricout H., Carpentier J. F., Mortreux A.: *Tetrahedron Lett.* **1996**, *37*, 6105.
9. Blacker A. J., Clarke M. l., Loft M. S., Mahon M. F., Humphries M. E., Williams J. M. J.: *Chem. Eur. J.* **2000**, *6*, 353.
10. Karlström A. S. E., Bäckvall J. E. in: *Modern Organocopper Chemistry* (M. Krause, Ed.), pp. 259–288. Wiley–VCH, Wienheim 2002.
11. a) Houlihan F., Bouchard F., Frechet J. M. J., Willson C. G.: *Can. J. Chem.* **1985**, *63*, 153; b) Chen C. T., Kuo J. H., Li C. H., Barhate N. B., Hon S. W., Li T. W., Chao S. D., Liu C. C., Li Y. C., Chang I. H., Lin J. S., Liu C. J., Chou Y. C.: *Org. Lett.* **2001**, *3*, 3729; c) Hudlicky T., Rinner U., Gonzalez D., Akgun H., Schilling S., Siengalewicz P., Martinot T. A., Pettit G. R.: *J. Org. Chem.* **2002**, *67*, 8726; d) Alonso E., Guijarro D., Martínez P., Ramón D. J., Yus M.: *Tetrahedron* **1999**, *55*, 11027; e) Basel Y., Hassner A.: *J. Org. Chem.* **2000**, *65*, 6368; f) Basel Y., Hassner A.: *Synthesis* **2001**, *4*, 550.
12. a) Roush W. R., Champoux J. A., Peterson B. C.: *Tetrahedron Lett.* **1996**, *37*, 8989; b) Frank S. A., Chen H., Kunz R. K., Schnaderbeck M. J., Roush W. R.: *Org. Lett.* **2000**, *2*, 2691.
13. a) Kobayashi Y., Murugesh M. G., Nakano M., Takahisa E., Usmani S. B., Ainai T.: *J. Org. Chem.* **2002**, *67*, 7110; b) Organ M. G., Ghasemi H.: *J. Org. Chem.* **2004**, *69*, 695.
14. Shirakawa K., Arase A., Hoshi M.: *Synthesis* **2004**, *11*, 1814.
15. We have found difficult to constantly reproduce the yield of the free boronic acid. We propose, this was caused by separation difficulties rather than by reaction parameters.
16. Frank S. A., Chen H., Kunz R. K., Schnaderbeck M. J., Roush W. R.: *Org. Lett.* **2000**, *2*, 2691.
17. No decomposition was detected when stored at room temperature up to 1 month and at 4 °C more than 1 year.
18. a) Berrée F., Bleis P. G. L., Carboni B.: *Tetrahedron Lett.* **2002**, *43*, 4935; b) Guiles J. W., Johnson S. G., Murray W. V.: *J. Org. Chem.* **1996**, *61*, 5169; c) Shimizu M., Kitagawa H., Kurahashi T., Hiyama T.: *Angew. Chem. Int. Ed.* **2001**, *40*, 4283; d) Arterburn J. B., Corona C., Rao K. V., Carlson K. E., Katzenellenbogen J. A.: *J. Org. Chem.* **2003**, *68*, 7063; e) Reed M. A., Chang M. T., Snieckus V.: *Org. Lett.* **2004**, *6*, 2297; f) Murata M., Watanabe S., Masuda Y.: *Tetrahedron Lett.* **1999**, *40*, 2585.
19. a) Pears D. A., Smith S. C.: *Aldrichimica Acta* **2005**, *38*, 23; b) Ramarao C., Ley S. V., Smith S. C., Shirley I. M., DeAlmeida N.: *Chem. Commun.* **2002**, 1132.

20. a) Barder T. E., Walker S. D., Martinelli J. R., Buchwald S. L.: *J. Am. Chem. Soc.* **2005**, *127*, 4685; b) Raheem I. T., Goodman S. N., Jacobsen E. N.: *J. Am. Chem. Soc.* **2004**, *126*, 706.
21. Filler R., Lin S., Zhang Z.: *J. Fluorine Chem.* **1995**, *74*, 69.
22. a) Chatterjee A. K., Choi T. L., Sanders D. P., Grubbs R. H.: *J. Am. Chem. Soc.* **2003**, *125*, 11360; b) Connon S. J., Blechert S.: *Angew. Chem. Int. Ed.* **2003**, *42*, 1900.
23. a) Hallberg A., Westerlund C.: *Chem. Lett.* **1982**, 1993; b) Bumagin N. A., Bumagina I. G., Beletskaya I. P.: *Dokl. Chem.* **1984**, *274*, 39; c) Bumagin N. A., Andryukhova N. P., Beletskaya I. P.: *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* **1987**, *36*, 1561; d) Mckean D. R., Parrinello G., Renaldo A. F., Stille J. K.: *J. Org. Chem.* **1987**, *52*, 422; e) Denmark S. E., Wang Z.: *Synthesis* **2000**, *7*, 999; f) Lee H. M., Nolan S. P.: *Org. Lett.* **2000**, *2*, 2053; g) Amatore M., Gosmini C., Perichon J.: *Eur. J. Org. Chem.* **2005**, *6*, 989; h) Clarke M. L.: *Adv. Synth. Catal.* **2005**, *347*, 303.
24. Takacs J. M., Helle M. A., Seely F. L.: *Tetrahedron Lett.* **1986**, *27*, 1257.
25. For the sample spectrum of a crude reaction mixture, see the Supporting Information.
26. Iwasaki M., Kobayashi Y., Li J. P., Matsuzaka H., Ishii Y., Hidai M.: *J. Org. Chem.* **1991**, *56*, 1922.
27. Large sterically demanding *ortho* substituents were not investigated.
28. Stoner E. J., Peterson M. J., Allen M. S., DeMattei J. A., Haight A. R., Leanna M. R., Patel S. R., Plata D. J., Premchandran R. H., Rasmussen M.: *J. Org. Chem.* **2003**, *68*, 8847.