3-(TRIBUTYLSTANNYL)ALLYL ALCOHOLS: USEFUL BUILDING BLOCKS FOR SOLID-PHASE SYNTHESIS OF SKIPPED DIENES AND TRIENES

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Repeated Stille coupling of 3-substituted 3-(tributylstannyl)allyl alcohols **2** on a solid support was used to synthesize a 21 × 21 library of skipped dienes and a 21 × 21 × 21 library of skipped trienes. Starting 3-(tributylstannyl)allyl alcohols were prepared by Pd-catalyzed hydrostannation of substituted prop-2-yn-1-ols, by hydroalumination by $LiAlH_4$ followed with transmetallation to tin using tributyltin methoxide, or by substitution of chlorine in (*Z*)-6-chloro-3-(tributylstannyl)hex-2-en-1-ol with appropriate nucleophile. Synthesized libraries were tested for the activity to endorphin receptors, but with negative results.

Key words: Combinatorial chemistry; Libraries of structures; Stille coupling; Stannanes; Cross-coupling reactions; Solid-phase synthesis; Hydroalumination.

Oligomers with –C(R)=CH–CH_2– repeating units can, to some extent, resemble the peptide chain containing –CO–CH(R)–NH– fragments (Fig. 1). Such oligomers may therefore interact with endorphin receptors (μ, K, σ or ρ). Combinatorial synthesis on solid support would be probably the best method to find potentially active compound of this type.

The Heck, Suzuki and Stille reactions are particularly useful for the construction of libraries[1–3] based on the C–C bond formation, as discussed in

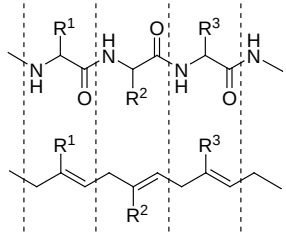


FIG. 1
Comparison of structures of the peptide chain and that of a skipped polyene

recent reviews[4]. This methodology was also used for solid-phase synthesis of dienes[5].

A possible route to skipped polyenes outlined in Fig. 1 is based on the repeated Stille coupling of 3-(tributylstannyl)allyl alcohols **2** which serve as building blocks. The polymer-attached 4-iodobenzoic acid (**1**) is first coupled with 3-substituted 3-(tributylstannyl)allyl alcohol **2**. The product **3** is then converted to the corresponding chloride **4** and coupled with another stannane **2** giving diene **5**. Repetition of the last two steps would then give higher oligomers like **6** (Scheme 1).

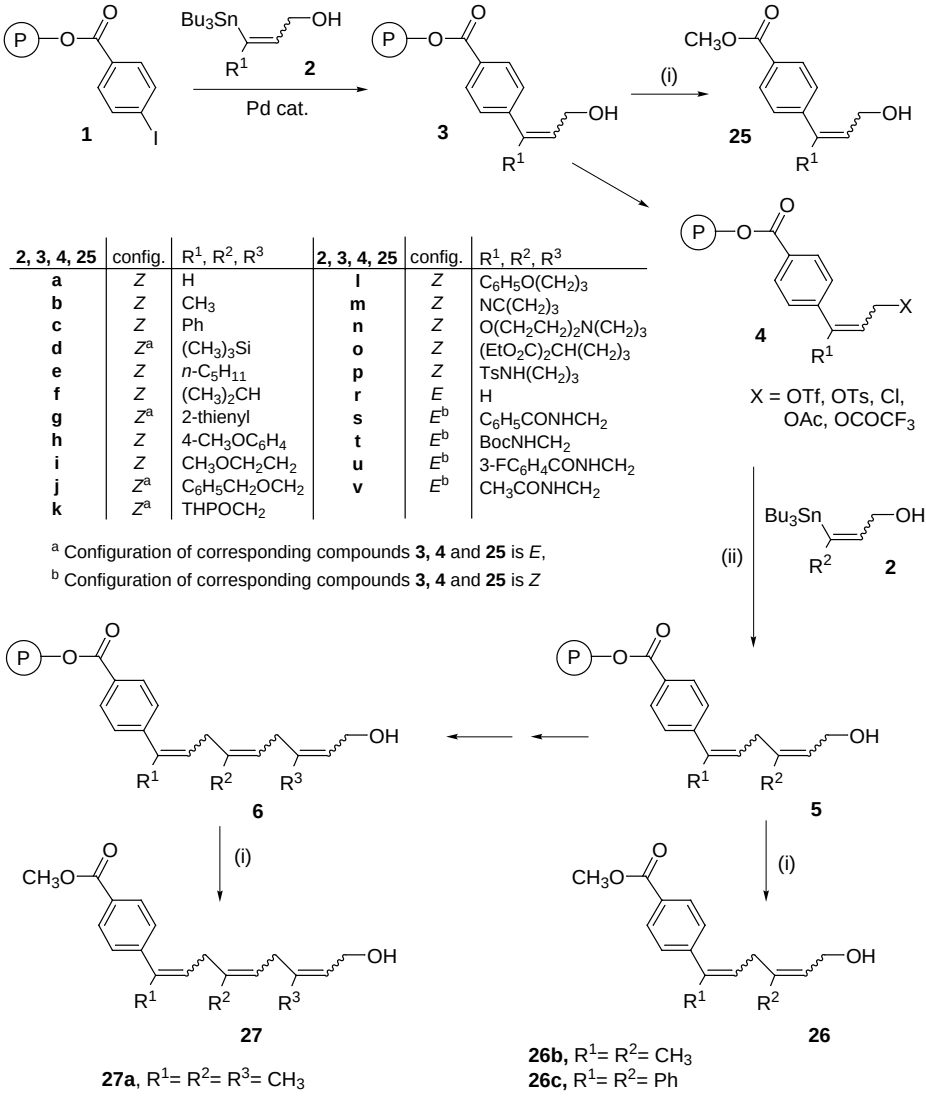
RESULTS AND DISCUSSION

The idea of repeated coupling was first tested by synthesis of dienes in solution. Thus coupling of methyl 4-iodobenzoate (**24**) with (*Z*)-3-(tributylstannyl)but-2-en-1-ol (**2b**) in the presence of $PdCl_2(PPh_3)_2$, gave cinnamyl alcohol **25b** in 53% yield. Transformation of the alcohol to the corresponding chloride with PPh_3 and CCl_4 proceeded in 80% yield. The resulting allyl chloride reacted with another (*Z*)-3-(tributylstannyl)but-2-en-1-ol (**2b**) in the presence of $Pd_2(dba)_3 \cdot CHCl_3/AsPh_3$, affording diene **26b** in 70% yield. The (*Z*)-configuration of the double bond of **2b** remains unchanged during the coupling reaction. The same reaction sequences were repeated with (*Z*)-3-phenyl-3-(tributylstannyl)prop-2-en-1-ol (**2c**). In this case the first coupling proceeds with only 35% yield using $PdCl_2(PPh_3)_2$ as a catalyst. However, when Herrmann metallacyclic catalyst[6] **7** was used, the coupling product **25c** was obtained in 65% yield (Scheme 2). Conversion of **25c** to chloride and coupling with another **2c** furnished diene **26c** in 47% overall yield, in this case as a mixture of *E* and *Z* isomers.

Synthesis of Building Blocks

For assembling the desired library, synthesis of diverse selection of stannanes **2** was crucial. Therefore stannanes **2a**–**2v** with various side-chain substituents were prepared (Scheme 1).

Stannanes **2a**–**2j** were prepared from corresponding prop-2-yn-1-ols by hydroalumination with $LiAlH_4$, followed by transmetalation to tin[7]. Due to the incompatibility of many functional groups with $LiAlH_4$, the stannanes bearing functional groups had to be prepared by different methods. The key intermediate for preparation of the stannanes **2l**–**2p** was stannane **9** which was prepared from ethyl 6-chlorohex-2-ynoate (**8**) by reaction with $Bu_3Sn(Bu)Cu(CN)Li_2$ analogous to that described for the trimethylstannyl



2, 3, 4, 25	config.	R^1, R^2, R^3	2, 3, 4, 25	config.	R^1, R^2, R^3
a	*Z*	H	**l**	*Z*	$C_6H_5O(CH_2)_3$
b	*Z*	CH_3	**m**	*Z*	$NC(CH_2)_3$
c	*Z*	Ph	**n**	*Z*	$O(CH_2CH_2)_2N(CH_2)_3$
d	*Z*[a]	$(CH_3)_3Si$	**o**	*Z*	$(EtO_2C)_2CH(CH_2)_3$
e	*Z*	*n*-C_5H_{11}	**p**	*Z*	$TsNH(CH_2)_3$
f	*Z*	$(CH_3)_2CH$	**r**	*E*	H
g	*Z*[a]	2-thienyl	**s**	*E*[b]	$C_6H_5CONHCH_2$
h	*Z*	4-$CH_3OC_6H_4$	**t**	*E*[b]	$BocNHCH_2$
i	*Z*	$CH_3OCH_2CH_2$	**u**	*E*[b]	3-$FC_6H_4CONHCH_2$
j	*Z*[a]	$C_6H_5CH_2OCH_2$	**v**	*E*[b]	$CH_3CONHCH_2$
k	*Z*[a]	$THPOCH_2$			

[a] Configuration of corresponding compounds **3, 4** and **25** is *E*,

[b] Configuration of corresponding compounds **3, 4** and **25** is *Z*

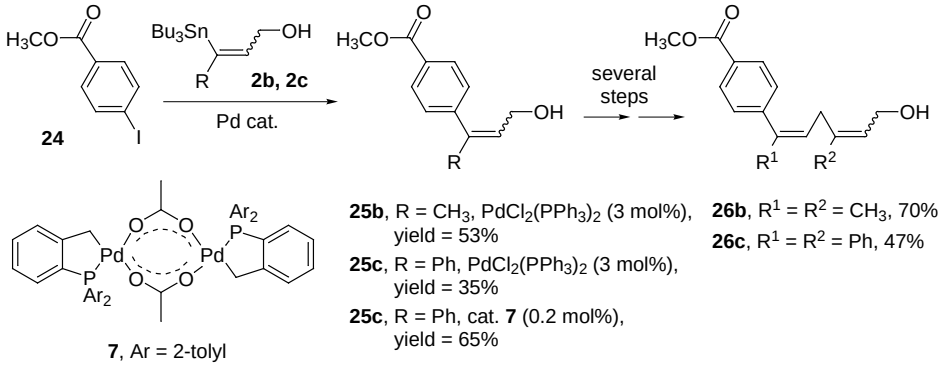
27a, $R^1 = R^2 = R^3 = CH_3$

26b, $R^1 = R^2 = CH_3$
26c, $R^1 = R^2 = Ph$

(i) CH_3ONa, CH_3OH; (ii) $Pd_2(dba)_3 \cdot CHCl_3$, P(2-tolyl)$_3$, NMP

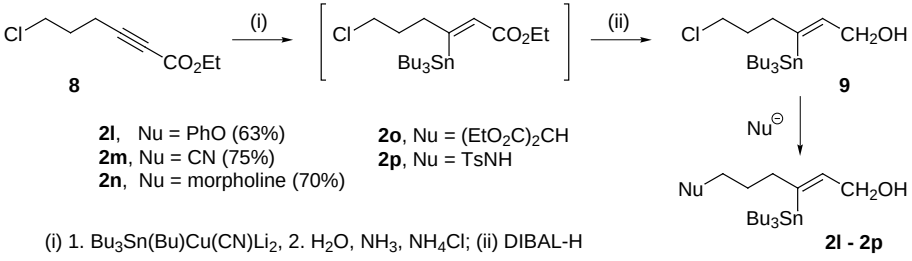
Compounds **25a-25d** and **26b, 26c** were fully characterized; compound **27a** was characterized by ^{1}H NMR and MS; compounds **25e-25v** cleaved from the polymer were of more than 78% purity (HPLC) and were not further characterized; using stannanes **2a-2v** 21 x 21 library of dienes **5** and **26** and 21 x 21 x 21 library of trienes **6** and **27** were synthetized.

SCHEME 1



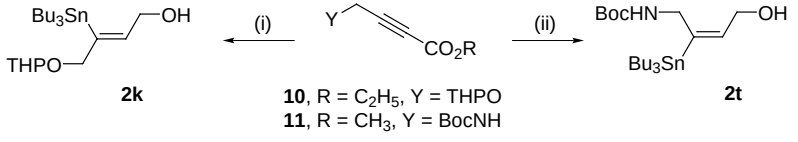
SCHEME 2

derivative[8] and subsequent reduction[9] with DIBAL-H. Nucleophilic displacement of the chlorine atom by appropriate nucleophile then furnished the desired substituted stannanes **2l**–**2p** (Scheme 3).



SCHEME 3

Stannanes **2k** and **2t** were prepared by reaction of corresponding alkynoates with tributylstannylcuprate[10] followed by reduction of the ester group with DIBAL-H (Scheme 4). The starting ester **11** was prepared by dilithiation of 3-(*N*-*tert*-butoxycarbonylamino)prop-1-yne[11] followed by reaction with carbon dioxide and esterification with diazomethane.

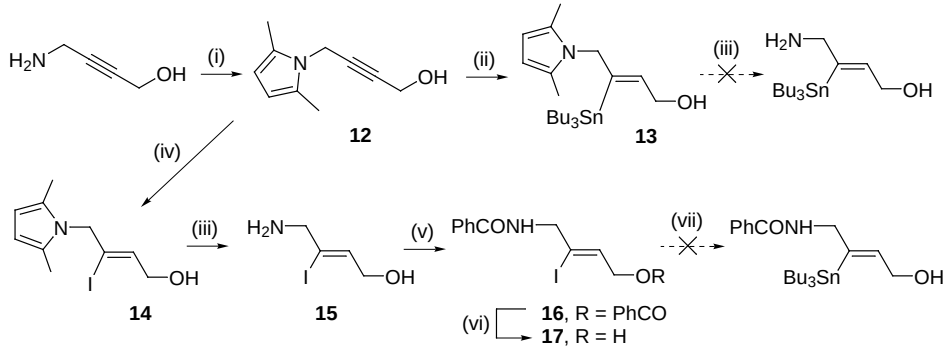


(i) 1. $Bu_3Sn(Bu)Cu(CN)Li_2$, $BF_3 \cdot Et_2O$; 2. H_2O, NH_3, NH_4Cl; 3. DIBAL-H

(ii) 1. $Bu_3Sn(Bu)Cu(CN)Li_2$, MeOH; 2. H_2O, NH_3, NH_4Cl; 3. DIBAL-H

SCHEME 4

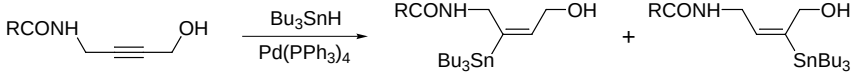
Preparation of stannanes bearing the amide group started from 4-aminobut-2-yn-1-ol with the amino group protected as 2,5-dimethylpyrrole derivative[12] **12**. Hydroalumination followed by reaction with tributyltin methoxide afforded the desired pyrrolylstannane **13** in 42% yield[7]. However, all attempts to remove the 2,5-dimethylpyrrolo group without splitting the tributylstannyl group failed. Therefore, the pyrrolylalkynol **12** was converted to iodo derivatives **16** and **17** with the aim to replace the halogen by tributylstannyl group by Pd-catalyzed reaction with hexabutyldistannane[13]. To our disappointment, this approach also failed giving only products of dimerization (Scheme 5).



(i) $(CH_3COCH_2)_2$, 96%; (ii) 1. $LiAlH_4$, 2. EtOAc, 3. Bu_3SnOCH_3, 4. H_2O; (iii) NH_2OH; (iv) 1. $LiAlH_4$, 2. EtOAc, 3. I_2; (v) PhCOCl; (vi) CH_3ONa, CH_3OH; (vii) $(Bu_3Sn)_2$, Pd cat.

SCHEME 5

The amidostannanes **2s**, **2u**, **2v** and **21**–**23** were finally prepared by Pd-catalyzed hydrostannation[14] of the corresponding amidopropynols **18**–**20**. This method gives a mixture of 2- and 3-(tributylstannyl)-propen-1-ols in roughly 1 : 1 ratio (Scheme 6). The regioisomers were separated by chromatography and their structures were determined using selectively decoupled ^1H NMR.



18, R = Ph
19, R = 3-FC_6H_4
20, R = CH_3

2s, R = Ph
2u, R = 3-FC_6H_4
2v, R = CH_3

21, R = Ph
22, R = 3-FC_6H_4
23, R = CH_3

SCHEME 6

Solid-Phase Synthesis

4-Iodobenzoic acid attached to the hydroxy-functionalized Tenta Gel resin (**1**) (diisopropylcarbodiimide, 1-hydroxybenzotriazole, 4-(dimethylamino)-pyridine, dichloromethane) was subjected to coupling reactions with an excess of 3-(tributylstannyl)allyl alcohols **2a**–**2d** under the conditions described earlier for the reaction of vinyl- and aryltin reagents (NMP, $Pd_2(dba)_3 \cdot CHCl_3$, $AsPh_3$, 45 °C)[3a] (Scheme 1). The cross-coupled products were then cleaved from the polymer by treatment with MeONa in MeOH–THF and the yields of **25a**–**25d** were determined by HPLC (Table I). Standards of the products for the HPLC determination were prepared by coupling reaction in solution (see Experimental).

As can be seen from Table I, conversion of **1** was not complete under these conditions. There is a significant difference between the reaction in solution and on a solid support. Thus the coupling of **2d** with methyl 4-iodobenzoate in solution ($Pd_2(dba)_3/AsPh_3$) gave 90% yield of the coupling product **25d**, while on a solid support the yield was only 31% under otherwise identical conditions. Increase in temperature did not improve yields and therefore the influence of various ligands was examined next using **2b** as a model compound. The best results were finally achieved using Herrmann catalyst **7** in concentration of 0.3 mol% at 100 °C. Under these conditions, not only high yield of the coupling product was obtained, but also the conversion of starting iodobenzoate was quantitative (Table I).

TABLE I
Coupling of 4-iodobenzoic acid attached to polymeric support **1** with stannanes[a] **2a**–**2d** (Scheme 1) catalyzed with $Pd_2(dba)_3 \cdot CHCl_3/AsPh_3$ and Herrmann catalyst **7**

R	Stannane	Product	$Pd_2(dba)_3/AsPh_3$[a]		Catalyst **7**[b]	
			Yield[c], %	Unreacted **1**, %	Yield[c], %	Unreacted **1**, %
H	**2a**	**25a**	90	0	89	0
Me	**2b**	**25b**	80	5	78	0
Ph	**2c**	**25c**	71	20	91	0
Me_3Si	**2d**	**25d**	50	trace	74	0

[a] Reaction conditions: $Pd_2(dba)_3 \cdot CHCl_3$ (12 mol%) : $AsPh_3$ (48 mol%), NMP, 45 °C, 20 h. [b] Reaction conditions: **7** (0.3 mol%), NMP, 100 °C, 14 h. [c] HPLC yield.

For coupling with another stannane, activation of the polymer-attached allyl alcohol obtained in the previous step was necessary. Conversion to the corresponding chloride, acetate, tosylate, trifluoroacetate and triflate was examined. Due to high reactivity of these derivatives, it was not possible to obtain the yields of the polymer-attached activated products directly. The yields were therefore determined after the second coupling step in which the polymer-bound alcohol **3b**, stannane **2b** and catalyst **7** were used. Chlorides, prepared from the alcohols by the reaction with PPh_3 and CCl_4, were found to give generally the best results.

The coupling of such prepared polymer-bound allyl chloride with the next stannane was optimized in the preparation of the dienes **26b** and **26c**. In this case $Pd_2(dba)_3 \cdot CHCl_3$/tris(2-tolyl)phosphine (PdL_2) in NMP at 80 °C gave the best results affording dienes **26b** and **26c** in 55 and 50% overall yields, respectively, based on the starting iodobenzoate **1** (Scheme 1). Synthesis of triene **27** by extension of this method was also successful. Triene **27** was obtained as a mixture of inseparable isomers in 95% purity (HPLC).

The above described optimized method was used for the combinatorial synthesis using twenty-one stannanes **2a**–**2v** and the resin-bound 4-iodobenzoate (**1**). To ensure quantitative consumption of **1** in the reaction with all stannanes **2a**–**2v**, the 1 mol% of the catalyst **7** was used and the reaction temperature was increased to 110 °C. After the first coupling step, the product was cleaved from a small part of each sample and analyzed by HPLC. As evident from the HPLC data (Table II), the coupling pro-

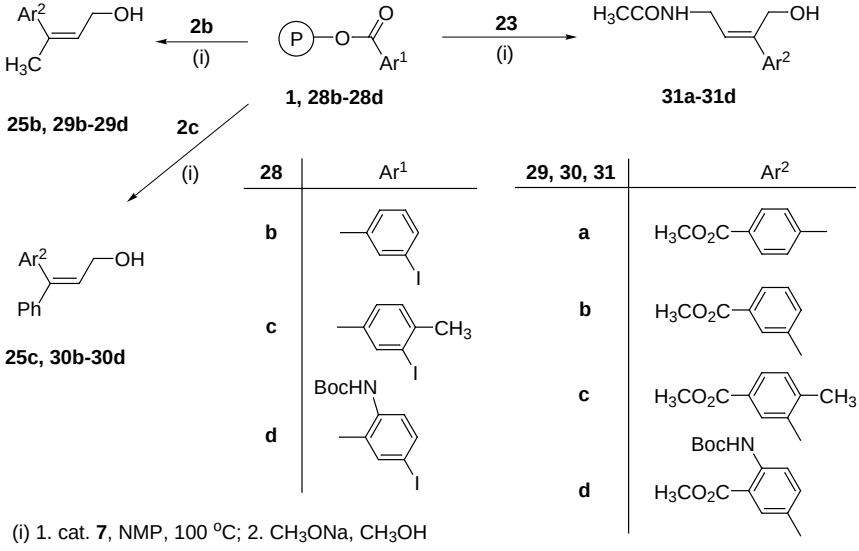
TABLE II
HPLC retention time[a] (*t*) and purity of products obtained by coupling of stannanes **2a**–**2v** with polymer-supported 4-iodobenzoate (**1**)

Stannane	*t*, min	Purity, %	Stannane	*t*, min	Purity, %	Stannane	*t*, min	Purity, %
2a	4.24	93	**2h**	9.10	94	**2o**	4.93	79
2b	4.67	93	**2i**	4.19	91	**2p**	5.54	78
2c	8.33	92	**2j**	7.16	91	**2r**	4.63	85
2d	11.71	92	**2k**	5.58	96	**2s**	3.93	95
2e	20.83	97	**2l**	16.80	95	**2t**	5.37	90
2f	9.42	83	**2m**	3.48	93	**2u**	4.36	95
2g	7.13	95	**2n**[b]	–	–	**2v**	2.96	93

[a] Reverse-phase C-18, methanol–water 76 : 24. [b] The product did not pass through the column, TLC (silica gel, $CHCl_3$–EtOH–aqueous NH_3 85 : 14 : 1) showed only one spot.

ceeds very cleanly, giving virtually single product in all cases. The samples were then mixed together, treated with PPh_3/CCl_4, divided into 21 vials, and again treated with the same set of twenty-one stannanes. Each sample was again divided into two parts and a cleavage of the products from one part afforded 21 × 21 library of dienes. With the rest, the whole process was repeated giving 21 × 21 × 21 library of trienes.

The easiest way to further increase diversity of the above libraries of dienes and trienes is to use differently substituted iodobenzoic acids. Therefore polymer-attached 3-iodobenzoic (**28b**), 3-iodo-4-methylbenzoic (**28c**) and 2-[*N*-(*tert*-butyloxycarbonyl)amino]-5-iodobenzoic (**28d**) acids were subjected to the reaction with stannanes **2b**, **2c** and **23** under the above conditions used for coupling of the polymer attached **1** (Scheme 7). As evi-



SCHEME 7

dent from HPLC analysis of the products freed from the polymer, all couplings proceeded with 100% conversion (no methyl ester of the starting substituted iodobenzoic acid was observed after methanolysis) and the products were very pure (Table III). Structure of compounds **31a**–**31d** was confirmed by ^{1}H NMR and MS.

In conclusion, the methodology suitable for the repeated Pd-catalyzed coupling of 3-(tributylstannyl)allyl alcohols on solid support was developed. This methodology was used for the combinatorial synthesis of a 21 × 21 library of skipped dienes and 21 × 21 × 21 library of skipped trienes. Both the

obtained libraries were tested for their activity to the endorphin receptors, but with negative results.

EXPERIMENTAL

All reactions were performed under dry argon atmosphere. THF was distilled from benzophenone ketyl under N_2 atmosphere just prior to use. ^{1}H NMR spectral data were recorded on a Varian Gemini spectrometer at 300 MHz, ^{13}C NMR at 100.6 MHz, chemical shifts (δ-scale) are reported in ppm and coupling constants (*J*) in Hz. IR spectra (wavenumbers in cm^{-1}) were recorded on a Nicolet 750FT-IR spectrometer. Mass spectra were recorded on a ZAB-SEQ (VG Analytical) spectrometer. HPLC analyses were run on reverse phase LiChrospher 100 RP-18, 120 mm with methanol–water 76 : 24–85 : 15 as a mobile phase. HPLC yields were

TABLE III
Coupling of polymer-supported iodobenzoic acids **1** and **28b**–**28d** with stannanes **2b**, **2c** and **23**

Polymer supported iodobenzoic acid	Stannane	Product	HPLC yield/HPLC purity %	Retention time min
1	**2b**	**25b**	78/93[a]	4.67[b]
	2c	**25c**	91/93[c]	4.24[b]
	23	**31a**	–/93[d]	3.85[b]
28b	**2b**	**29b**	88/94[e]	4.82[b]
	2c	**30b**	–/94	5.97[e]
	23	**31b**	–/87[d]	3.26
28c	**2b**	**29c**	>95/94[c]	5.95[b]
	2c	**30c**	–/83	7.15[e]
	23	**31c**	–/88	3.67[b]
28d	**2b**	**29d**	62/91[a]	7.50[f]
	2c	**30d**	–/85	12.42[f]
	23	**31d**	–/65[d]	9.56[b]

[a] Product characterized by comparison with authentic compound prepared by the same reaction in solution. [b] Methanol–water 76 : 24. [c] Product characterized by comparison with authentic compound prepared by direct Pd-catalyzed coupling of hydroaluminated alk-2-yn-1-ol with appropriate iodobenzoate in THF solution[15]. [d] Product characterized by MS and ^{1}H NMR. [e] Methanol–water 80 : 20. [f] Methanol–water 85 : 15.

obtained using authentic samples prepared by the reactions in solution with benzophenone or 2-methylnaphthalene as an internal standard. HPLC purity refers to that obtained from the peak integrals of the peaks at 254 nm. Stannanes **2a**–**2j**, **13** (ref.[7]), **2r** (ref.[14d]), ethyl-6-chlorohex-2-ynoate[9] (**8**), ethyl [(4-tetrahydropyran-2-yl)oxy]but-2-ynoate[16] (**10**), *N*-(*tert*-butyloxycarbonyl)prop-2-yn-1-ylamine[11], 4-(2,3-dimethylpyrrol-1-yl)but-2-yn-1-ol[7] (**12**), 4-benzamidobut-2-yn-1-ol[17], 4-acetamidobut-2-yn-1-ol[17] were prepared according to the reported procedures. Tenta Gel S OH (capacity 0.030 mmol/g) was purchased from RAPP Polymere GmbH. Activities of the obtained libraries were tested in the Torrey Pines Institute for Molecular Studies.

Synthesis of Cinnamyl Alcohols and Dienes in Solution

(*Z*)-3-[4-(Methoxycarbonyl)phenyl]but-2-en-1-ol (**25b**)

Methyl 4-iodobenzoate (**24**; 0.524 g, 2 mmol), (*Z*)-3-(tributylstannyl)but-2-en-1-ol (**2b**; 0.765 g, 2.1 mmol) and $PdCl_2(PPh_3)_2$ (0.042 g, 0.06 mmol) were dissolved in 3 ml of DMF and heated under argon at 100 °C for 3 h. The mixture was then poured into an aqueous solution of potassium fluoride, ether was added and the mixture was vigorously shaken to remove tributyltin iodide. The organic layer was separated and the aqueous phase was extracted with ether. The combined organic layers were dried over magnesium sulfate, ether was evaporated and the residue was chromatographed on silica (radial chromatography). Elution with petroleum ether–ether–acetone 5 : 3 : 2 afforded 0.219 g (53%) of the product as an oil. ^{1}H NMR ($CDCl_3$): 8.00 d, 2 H, J = 8.2 (Ar); 5.76 dt, 1 H, J_t = 7.0, J_d = 1.5 (=C**H**-CH_2OH); 4.05 d, 2 H, J = 7.1 (-C**H**$_2$OH); 3.91 s, 3 H ($COOCH_3$); 2.09 s, 3 H (CH_3). IR ($CHCl_3$): 3 620, 3 467, 3 018, 2 976, 2 927, 2 895, 1 713, 1 608, 1 437, 1 391, 1 284, 1 047, 877. For $C_{12}H_{14}O_3$ (206.2) calculated: 69.89% C, 6.84% H; found: 69.53% C, 6.94% H. ^{13}C NMR ($CDCl_3$): 167.6 s; 146.3 s; 139.9 s; 127.2–131.1 m; 60.8 t, J = 142; 52.8 q, J = 146; 25.7 dq, J_q = 127, J_d = 6.9 – this interaction corresponds with *cis* relation of CH_3 and =C-**H**.

(*Z*)-1-Chloro-3-[4-(methoxycarbonyl)phenyl]but-2-ene

A mixture of (*Z*)-3-[4-(methoxycarbonyl)phenyl]but-2-en-1-ol (**25b**; 0.453 g, 2.2 mmol), triphenylphosphine (0.603 g, 2.3 mmol), dichloromethane (5 ml) and tetrachloromethane (3 ml) was stirred at room temperature overnight. The solvents were then evaporated and the residue was chromatographed on silica (radial chromatography). Elution with petroleum ether–ether–acetone 8 : 1 : 1 gave 0.394 g (80%) of the desired chloride as an oil. ^{1}H NMR ($CDCl_3$): 8.03 d, 2 H, J = 8.8 (Ar); 7.26 d, 2 H, J = 8.3 (Ar); 5.77 qt, 1 H, J_1 = 8.2, J_2 = 1.7 (=CH); 3.88 d, 2 H, J = 8.8 (-CH_2Cl); 3.93 s, 3 H (-$COOCH_3$); 2.10 s, 3 H, (CH_3-C=). IR ($CHCl_3$): 3 027, 2 954, 1 720, 1 610, 1 438, 1 261, 1 117, 1 019, 864. For $C_{12}H_{13}ClO_2$ (224.7) calculated: 64.15% C, 5.83% H, 15.78% Cl; found: 63.91% C, 5.99% H, 15.41% Cl.

(*Z*,*Z*)-6-[4-(Methoxycarbonyl)phenyl]-3-methylhepta-2,5-dien-1-ol (**26b**)

A solution of (*Z*)-1-chloro-3-[4-(methoxycarbonyl)phenyl]but-2-ene (0.113 g, 0.5 mmol), stannane **2b** (0.180 g, 0.5 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.007 g, 1.5 mole %) and triphenylarsine (0.009 g, 6 mol%) in 1-methylpyrrolidin-2-one (2 ml) was heated under argon at 40 °C for 24 h and worked up as described above for the preparation of **25b**. The crude product was purified by preparative HPLC (reverse phase C-18). The product was obtained as

a colorless oil (0.092 g, 70%). ^{1}H NMR ($CDCl_3$): 7.96 d, 2 H, *J* = 8.3 (Ar); 7.41 d, 2 H (Ar); 5.77 t, 1 H, *J* = 7.4 (=CH-); 5.49 t, 1 H, *J* = 6.9 (=CH-); 4.17–4.23 m, 2 H (-C**H**$_2$OH); 3.90 s, 3 H ($COOCH_3$); 2.98 d, 2 H, *J* = 7.1 (=CH-C**H**$_2$-C=); 2.09 s, 3 H (CH_3); 1.77 s, 3 H (CH_3); 1.38–1.45 m, 1 H (OH). The compound contained about 5% of isomer, δ: 8.02, 5.36, 2.71, 2.03, 1.66. IR ($CHCl_3$): 3 611, 3 018, 2 953, 1 716, 1 606, 1 437, 1 282, 1 116, 969. For $C_{12}H_{20}O_3$ (260.3) calculated: 73.82% C, 7.74% H; found: 73.69% C, 7.81% H.

(*Z*)-3-[4-(Methoxycarbonyl)phenyl]-3-phenylprop-2-en-1-ol (**25c**)

Methyl 4-iodobenzoate (**24**; 0.131 g, 0.5 mmol), (*Z*)-3-phenyl-3-(tributylstannyl)prop-2-en-1-ol (**2c**; 0.223 g, 0.53 mmol) and the Herrmann catalyst (**7**; 1 mg, 0.001 mmol) were dissolved in 1-methylpyrrolidin-2-one (3 ml) and heated under argon at 110 °C for 3 h. The reaction mixture was worked up as described for the preparation of **25b**. Chromatography on silica gel (radial chromatography, petroleum ether–acetone 95 : 5) gave 0.132 g (73%) of an oily product. ^{1}H NMR ($CDCl_3$): 8.05 d, 2 H, *J* = 8.2 (Ar); 7.19–7.34 m, 7 H (Ar); 6.30 t, 1 H, *J* = 6.9 (=C**H**-CH_2OH); 4.21 d, 2 H, *J* = 6.6 (-C**H**$_2$OH); 3.94 s, 3 H (-OCH_3). IR ($CHCl_3$): 3 022, 2 955, 1 721, 1 664, 1 487, 1 263, 1 116, 1 020. HR MS (EI), for $C_{17}H_{15}O_2$ (M^+ – OH) calculated: 251.1072; found: 251.1177.

(*Z*)-3-Chloro-1-[4-(methoxycarbonyl)phenyl]-1-phenylprop-1-ene

A mixture of (*Z*)-3-[4-(methoxycarbonyl)phenyl]-3-phenylprop-2-en-1-ol (**3c**; 0.170 g, 0.63 mmol), triphenylphosphine (0.190 g, 0.72 mmol), dichloromethane (2 ml) and tetrachloromethane (1.5 ml) was stirred at room temperature overnight and then heated at 35 °C until the conversion was complete. The solvents were then evaporated and the product (0.132 g, 73%) was obtained by preparative TLC on silica gel (petroleum ether–acetone 95 : 5). ^{1}H NMR ($CDCl_3$): 8.08 d, 2 H, *J* = 8.2 (Ar); 7.18–6.78 m, 7 H (Ar); 6.29 t, 1 H, *J* = 8.2 (=CH); 4.09 d, 2 H, *J* = 8.2 (-CH_2Cl); 3.95 s, 3 H ($COOCH_3$). IR ($CHCl_3$): 3 029, 2 954, 1 721, 1 610, 1 437, 1 263, 1 116. For $C_{17}H_{15}ClO_2$ (286.8) calculated: 71.21% C, 5.27% H, 12.36% Cl; found: 70.97% C, 5.49% H, 12.33% Cl.

6-[4-(Methoxycarbonyl)phenyl]-3,6-diphenylhexa-2,5-dien-1-ol (**26c**)

(*Z*)-3-Chloro-1-[4-(methoxycarbonyl)phenyl]-1-phenylprop-1-ene (0.100 g, 0.35 mmol), stannane **2c** (0.184 g, 0.4 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.005 g, 1.5 mol%) and tris(2-tolyl)-phosphine (0.006 g, 6 mole %) were dissolved in 1-methylpyrrolidin-2-one (2 ml). The mixture was heated under argon at 40 °C for 24 h and then worked up as described for preparation of **25b**. Chromatography on silica (radial chromatography, petroleum ether–ether–acetone 8 : 1 : 1) afforded 0.063 g (47%) of the product as a mixture of *E*/*Z* isomers. ^{1}H NMR ($CDCl_3$): 8.05 d + 7.87 d (9 : 5), 2 H, *J* = 8.2, 8.8 (Ar); 7.02–7.23 m, 12 H (Ar); 5.87–6.09 m, 2 H (=CH); 4.20 d + 4.18 d, 2 H, *J* = 6.6, 5.5 (-C**H**$_2$OH); 3.95 s + 3.88 s, 3 H ($COOCH_3$); 3.37 d + 3.33 d, 2 H, *J* = 7.2, 7.2 (=CH-C**H**$_2$-C=). IR ($CHCl_3$): 3 020, 2 954, 1 721, 1 438, 1 283, 1 116, 1 020. HR MS (EI), for $C_{26}H_{23}O_2$ (M^+ – OH) calculated: 367.1698; found: 367.1606.

(*Z*)-3-[4-(Methoxycarbonyl)phenyl]prop-2-en-1-ol (**25a**)

Methyl 4-iodobenzoate (**24**; 0.131 g, 0.5 mmol), (*Z*)-3-(tributylstannyl)allyl alcohol (**2a**) and the Herrmann palladium catalyst (**7**; 1 mg, 0.001 mmol) were dissolved in 1-methylpyrrolidin-2-one (3 ml). The mixture was heated under argon at 110 °C for 3 h and was worked up as described for preparation of **25b**. Chromatography on silica (radial chromatography, petroleum ether–acetone 7 : 3) afforded 0.061 g (64%) of the product. ^{1}H NMR ($CDCl_3$): 8.01 d, 2 H, *J* = 8.4 (Ar); 7.28 d, 2 H, *J* = 8.3 (Ar); 6.60 d, 1 H, *J* = 12.0 (Ar-C**H**=CH-CH_2OH); 5.99 td, 1 H, J_1 = 11.8, J_2 = 6.3 (Ar-CH=C**H**-CH_2OH); 4.44 dd , 2 H, J_1 = 6.5, J_2 = 1.7 (-C**H**$_2$OH); 3.93 s, 3 H (OCH_3). IR ($CHCl_3$): 3 615, 3 022, 2 954, 1 718, 1 610, 1 437, 1 285, 1 181, 1 111, 1 017, 866. For $C_{11}H_{12}O_3$ (192.2) calculated: 68.74% C, 6.29% H; found: 68.48% C, 6.33% H.

(*Z*)-3-[3-Methoxycarbonyl-4-(*tert*-butyloxycarbonylamino)phenyl]but-2-en-1-ol

Methyl 2-(*tert*-butoxycarbonylamino)-3-iodobenzoate (0.188 g, 0.5 mmol), (*Z*)-3-(tributylstannyl)but-2-en-1-ol (**2b**; 0.161 g, 0.5 mmol) and the Herrmann palladium catalyst (**7**; 1 mg, 0.001 mmol) were dissolved in 1-methylpyrrolidin-2-one (2 ml). The mixture was heated under argon at 110 °C for 3 h and then worked up as described for **25b**. Chromatography on silica (radial chromatography, petroleum ether–ether–acetone 8 : 1 : 1) afforded 0.114 g (71%) of the product. ^{1}H NMR ($CDCl_3$): 10.23 s, 1 H (NH); 8.42 d, 1 H, *J* = 8.8 (Ar); 7.8 d, 1 H, *J* = 2.2 (Ar); 7.33 dd, 1 H, J_1 = 8.8, J_2 = 2.2 (Ar); 5.72 t, 1 H, *J* = 6.9 (=C**H**-CH_2OH); 4.07 t, 2 H, *J* = 6.0 (-C**H**$_2$OH); 3.92 s, 3 H ($COOCH_3$); 2.06 s, 3 H (-CH_3); 1.53 s, 9 H (-C(CH_3)$_3$). IR ($CHCl_3$): 3 324, 3 017, 2 983, 1 724, 1 694, 1 582, 1 518, 1 369, 1 310, 1 249, 1 157. For $C_{17}H_{23}NO_5$ (321.4) calculated: 64.54% C, 7.21% H, 4.36% N; found: 64.82% C, 7.74% H, 4.30% N.

(*E*)-3-[4-(Methoxycarbonyl)phenyl]-3-trimethylsilylprop-2-en-1-ol (**25d**)

Methyl 4-iodobenzoate (**24**; 0.131 g, 0.5 mmol), (*Z*)-3-(tributylstannyl)allyl alcohol (**2d**; 0.5 g, 1.19 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.012 g, 0.011 mmol) and $AsPh_3$ (0.0153 g, 0.050 mmol) were dissolved in 1-methylpyrrolidin-2-one (6 ml). The mixture was heated under argon at 110 °C for 3 h and worked up as described for preparation of **25b**. Chromatography on silica (radial chromatography, petroleum ether–ether–acetone 80 : 10 : 10) afforded 0.109 g (78%) of the product. ^{1}H NMR ($CDCl_3$): 7.97 d, 2 H, *J* = 8.2 (Ar); 7.0 d, 2 H, *J* = 8.2 (Ar); 6.15 t, 1 H, *J* = 6.0 (=C**H**-CH_2OH); 3.99 d, 2 H, *J* = 6.0 (-C**H**$_2$OH); 3.91 s, 3 H (CH_3); 0.07 s, 9 H (-Si(CH_3)$_3$). IR ($CHCl_3$): 3 615, 3 014, 2 956, 1 718, 1 605, 1 437, 1 287, 1 115, 1 019, 914, 839. For $C_{14}H_{20}O_3Si$ (264.4) calculated: 63.60% C, 7.62% H; found: 63.19% C, 7.85% H.

*Synthesis of Stannanes **2** and Their Precursors*

(*Z*)-6-Chloro-3-(tributylstannyl)hex-2-en-1-ol (**9**)

A solution of 1.6 M butyllithium (7.3 ml, 11.6 mmol) was added to a suspension of copper cyanide (0.519 g, 5.8 mmol) in tetrahydrofuran (20 ml) at –78 °C. The flask was removed from the cooling bath and stirred until all the copper cyanide was dissolved, the mixture was then again cooled to –78 °C and tributyltin hydride (3.1 ml, 11.6 mmol) was added. The

formed yellow solution was stirred at –78 °C for 10 min and boron trifluoride etherate (0.74 ml, 5.8 mmol) was added followed after 5 min with ethyl 6-chlorohex-2-enoate (**8**; 0.923 g, 5.3 mmol). The resulting mixture was stirred at –78 °C for 1 h and at –40 °C for another 1.5 h. The resulting deep red solution was poured to an aqueous ammonia and ammonium chloride. Ether was added and the mixture was shaken until the aqueous phase was deep blue. The organic layer was separated and the aqueous phase was extracted twice with ether. Combined organic layers were dried over anhydrous sodium sulfate, the solvents were removed under reduced pressure and the residue was dried in high vacuum. Then it was dissolved in anhydrous ether (70 ml), cooled to –78 °C and 1 M diisobutylaluminium hydride (18 ml, 18 mmol) in hexane was slowly added. The mixture was stirred at –78 °C for 1 h and at –40 °C for another 1.5 h. Methanol (5 ml) was added, and reaction was left to warm to 0 °C and saturated solution of ammonium chloride (5 ml) was added. After 15 min the mixture was filtered through celite, the precipitate was washed three times with ether, the solvents were removed under reduced pressure and the residue chromatographed on silica (120 g). Elution with petroleum ether–acetone 96 : 4 afforded 1.677 g (75%) of the stannane **9** as a colorless oil. ^{1}H NMR ($CDCl_3$): 6.28 t, 1 H, J = 6.6, ^3J(Sn-H,*trans*) = 126 (=CH); 4.06 t, 2 H, J = 6.6 (CH_2OH); 3.51 t, J = 6.6 (CH_2Cl); 2.36 t, 2 H, J = 7.4, ^3J(Sn-H) = 45 (CH_2C=); 1.80 quintet, 2 H, J = 7.4 ($CH_2CH_2CH_2$); 1.23–1.61 m, 12 H ($SnCH_2CH_2CH_2CH_3$); 1.16 t, 1 H, J = 5.5 (OH); 0.78–1.05 m, 15 H ($SnCH_2CH_2CH_2CH_3$). ^{13}C NMR, APT ($CDCl_3$): 147.94, 65.59, 44.97, 38.14, 33.50, 29.89, 28.06, 11.29 (CH_2, C); 140.38, 12.95 (CH_3, CH). IR ($CHCl_3$): 3 612, 3 455, 3 012, 2 958, 2 928, 2 872, 2 854, 1 462, 1 378, 1 072, 990, 864. For $C_{18}H_{37}ClOSn$ (423.6) calculated: 51.03% C, 8.80% H, 8.73% Cl; found: 51.15% C, 8.70% H, 8.31% Cl.

(*Z*)-6-Phenoxy-3-(tributylstannyl)hex-2-en-1-ol (**2l**)

Phenol (0.168 g, 2 mmol) and sodium hydride (0.060 g, 80%, 2 mmol) were mixed in DMF (3 ml). After all NaH was dissolved, a solution of stannane **9** (0.423 g, 1 mmol) in DMF (1 ml) was added. The reaction mixture was heated at 50 °C for 14 h, then poured into water, extracted with ether (3 ×) and combined ethereal layers were dried over anhydrous sodium sulfate. Chromatography on 15 g of silica (petroleum ether–acetone 96 : 4) afforded 0.303 g (63%) stannane **2l** as a colorless oil. ^{1}H NMR ($CDCl_3$): 7.24–7.32 m, 2 H (Ar); 6.86–6.97 m, 3 H (Ar); 6.28 t, 1 H, J = 6.6, ^3J(Sn-H,*trans*) = 124 (=CH); 4.05 t, 2 H, J = 5.8 (CH_2OH); 3.95 t, 2 H, J = 6.6 ($PhOCH_2$); 2.40 t, 2 H, J = 7.7 (CH_2C=); 1.82 quintet, 2 H, J = 7.1 ($CH_2CH_2CH_2$); 1.30–1.60 m, 12 H ($SnCH_2CH_2CH_2CH_3$); 1.17 t, 1 H, J = 5.5 (OH); 0.75–1.10 m, 15 H ($SnCH_2CH_2CH_2CH_3$).^{13}C NMR, APT ($CDCl_3$): 159.76, 149.00, 67.78, 65.74, 37.45, 30.45, 29.93, 28.10, 11.28 (CH_2, C); 139.80, 13.12, 121.27, 115.24, 14.37 (CH_3, CH). IR ($CHCl_3$): 3 611, 3 013, 2 959, 2 928, 2 873, 2 854, 1 600, 1 586, 1 497, 1 487, 1 377, 1 247, 1 078, 1 041, 994. MS (EI), *m*/*z*: 425.1 ($M^+ - C_4H_9$).

(*Z*)-6-Cyano-3-(tributylstannyl)hex-2-en-1-ol (**2m**)

Stannane **9** (0.296 g, 0.7 mmol) and sodium cyanide (0.049 g, 1 mmol) were mixed in DMF (4 ml) and heated at 60 °C. After 14 h the reaction mixture was poured into water, extracted with ether (3 ×) and combined ethereal layers were dried over anhydrous sodium sulfate. Chromatography on 10 g of silica (petroleum ether–acetone 90 : 10) afforded 0.217 g (75%) of stannane **2m** as a colorless oil. ^{1}H NMR ($CDCl_3$): 6.28 t, 1 H, J = 6.3, ^3J(Sn-H,*trans*) = 121 (=CH); 4.07 t, 2 H, J = 5.8 (CH_2OH); 2.28–2.40 m, 4 H (CH_2CN, =C-CH_2CH_2); 1.69 quintet,

2 H, *J* = 7.3 ($CH_2C\mathbf{H}_2CH_2$); 1.25–1.53 m, 12 H ($SnCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 1.23 t, 1 H, *J* = 5.5 (OH); 0.82–1.05 m, 15 H ($SnC\mathbf{H}_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR, APT ($CDCl_3$): 147.00, 120.31, 65.44, 39.85, 29.90, 28.08, 26.14, 17.14, 11.30 (CH_2, C); 141.16, 14.36 (CH_3, CH). IR ($CHCl_3$): 3 611, 3 021, 2 959, 2 928, 2 872, 2 854, 2 250, 1 460, 1 377, 1 074, 996. For $C_{19}H_{37}NOSn$ (414.2) calculated: 55.10% C, 9.00% H, 3.38% N; found: 55.02% C, 8.77% H, 3.56% N.

(*Z*)-6-Morpholino-3-(tributylstannyl)hex-2-en-1-ol (**2n**)

Stannane **9** (0.296 g, 0.7 mmol) was dissolved in morpholine (3 ml) and the solution was heated at 60 °C for 24 h. The reaction mixture was poured into water, extracted with ether (3×) and combined ethereal layers were dried anhydrous over sodium sulfate. Chromatography on 10 g of silica (petroleum ether–ether–triethylamine 50 : 49 : 1) afforded 0.232 g (70%) of stannane **2n** as an oil. ^{1}H NMR ($CDCl_3$): 6.25 t, 1 H, *J* = 6.6, ^3J(Sn-H,*trans*) = 125 (=CH); 4.05 d, 2 H, *J* = 6.6 ($C\mathbf{H}_2OH$); 3.68–3.75 m, 4 H ($C\mathbf{H}_2$-O-$C\mathbf{H}_2$); 2.42 bs, 4 H (CH_2N); 2.31 t, 2 H, *J* = 7.4 (CH_2N); 2.22 t, 2 H, *J* = 7.4 (CH_2-C=); 1.22–1.58 m, 14 H ($CH_2C\mathbf{H}_2CH_2$, $SnCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 0.82–0.98 m, 15 H ($SnC\mathbf{H}_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR, APT ($CDCl_3$): 149.29, 67.71, 65.71, 59.45, 54.50, 38.99, 29.93, 28.11, 11.27 (CH_2, C); 139.42, 14.38 (CH_3, CH). IR ($CHCl_3$): 3 609, 3 014, 2 959, 2 927, 2 872, 2 857, 2 815, 1 461, 1 377, 1 116, 1 071, 1 003, 862. For $C_{22}H_{45}NO_2Sn$ (474.3) calculated: 55.71% C, 9.56% H, 2.95% N; found: 55.50% C, 9.41% H, 3.05% N.

(*Z*)-Diethyl [6-Hydroxy-4-(tributylstannyl)hex-4-en-1-yl]malonate (**2o**)

To a solution of sodium (0.12 g, 5 mmol) in anhydrous ethanol (5 ml), diethyl malonate (0.9 ml, 6 mmol) followed by stannane **9** (0.423 g, 1 mmol) were added. The resulting mixture was heated under reflux for 24 h, then poured into water and extracted three times with ether. Combined organic layers were dried over anhydrous sodium sulfate, the solvent was evaporated and chromatography of the residue on silica (petroleum ether–ether–acetone 90 : 5 : 5) afforded 0.309 g (56%) of desired stannane **2o** as a colorless oil. ^{1}H NMR ($CDCl_3$): 6.22 t, 1 H, *J* = 6.6, ^3J(Sn-H,*trans*) = 126 (=CH); 4.19 q, 4 H, *J* = 7.1 ($CH_3C\mathbf{H}_2O$); 4.03 t, 2 H, *J* = 6.1 ($C\mathbf{H}_2OH$); 3.30 t, 1 H, *J* = 7.4 ($C\mathbf{H}(COOEt)_2$); 2.23 t, 2 H, *J* = 7.4 (CH_2C=); 1.86 q, 2 H, *J* = 7.7 ($CHC\mathbf{H}_2CH_2CH_2$); 1.23–1.52 m, 14 H ($CH_2C\mathbf{H}_2CH_2$, $SnCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 1.26 t, 6 H, *J* = 7.1 ($C\mathbf{H}_3CH_2O$); 1.17 t, 1 H, *J* = 5.5 (OH); 0.82–0.95 m, 15 H ($SnC\mathbf{H}_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR, APT ($CDCl_3$): 170.13, 149.03, 65.73, 62.02, 40.67, 29.90, 29.05, 28.46, 28.08, 11.26 (CH_2, C); 139.57, 52.62, 14.80, 14.36 (CH_3, CH). IR ($CHCl_3$): 3 609, 3 016, 2 959, 2 928, 2 872, 2 855, 1 727, 1 463, 1 373, 1 294, 1 181, 1 152, 1 024. For $C_{25}H_{48}O_5Sn$ (547.3) calculated: 54.86% C, 8.84% H; found: 54.58% C, 8.81% H.

(*Z*)-*N*-[6-Hydroxy-4-(tributylstannyl)hex-4-en-1-yl]-4-methylbenzene-1-sulfonamide (**2p**)

4-Methylbenzene-1-sulfonamide (0.171 g, 1 mmol) was dissolved in 5 ml anhydrous DMF, sodium hydride (0.021 g (80% in oil), 0.7 mmol) was added and the reaction mixture was heated to 60 °C until all the sodium hydride reacted. A solution of stannane **9** (0.254 g, 0.58 mmol) in 1 ml DMF was then added to the resulting white suspension and the reaction mixture was heated to 80 °C for another 16 h. The mixture was poured into water and extracted twice with chloroform and twice with ether. Combined organic layers were dried with anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. Chromatography of the residue on 10 g of silica (petroleum ether–ether–acetone 80 : 10 : 10) afforded

0.241 g (60%) of the product **2p**. ^{1}H NMR ($CDCl_3$): 7.74 d, 2 H, *J* = 8.3 (Ar); 7.31 d, 2 H, *J* = 8.2 (Ar); 6.16 t, 1 H, *J* = 6.6, ^3J(Sn-H,*trans*) = 125 (=CH); 4.35 t, 2 H, *J* = 6.1 (CH_2OH); 4.00 t, 1 H, *J* = 6.3 (NH); 2.92 q, 2 H, *J* = 6.8 (HN-CH_2); 2.43 s, 3 H (CH_3); 2.20 t, 2 H, *J* = 7.4 (CH_2C=); 1.22–1.59 m, 14 H ($CH_2CH_2CH_2$, $SnCH_2CH_2CH_2CH_3$); 0.77–1.00 m, 15 H ($SnCH_2CH_2CH_2CH_3$). ^{13}C NMR, APT ($CDCl_3$): 148.09, 144.10, 137.70, 65.55, 43.28, 37.99, 30.37, 29.88, 28.07, 11.25 (CH_2, C); 140.31, 130.43, 127.84, 22.25, 14.37 (CH_3, CH). IR ($CHCl_3$): 3 609, 3 027, 3 015, 2 958, 2 927, 2 872, 2 854, 1 599, 1 463, 1 409, 1 377, 1 331, 1 160, 1 094, 1 076, 987, 814. For $C_{25}H_{45}NO_3SSn$ (558.4) calculated: 53.78% C, 8.12% H, 2.51% N, 5.74% S; found: 53.83% C, 7.96% H, 2.57% N, 6.41% S.

(*Z*)-4-[(Tetrahydropyran-2-yl)oxy]-3-(tributylstannyl)but-2-en-1-ol[7] (**2k**)

A solution of 1.6 M butyllithium (1.4 ml, 2.2 mmol) was added to a suspension of copper cyanide (0.098 g, 1.1 mmol) in tetrahydrofuran (3 ml) at –78 °C. The flask was removed from the cooling bath and stirred until all the copper cyanide dissolved. The reaction mixture was then cooled again to –78 °C and tributyltin hydride (0.58 ml, 2.2 mmol) was added followed, after 10 min, by boron trifluoride diethyl etherate (0.14 ml, 1.1 mmol) and a solution of ethyl 4-[(tetrahydropyran-2-yl)oxy]but-2-ynoate[16] (**10**; 0.212 g, 1 mmol) in THF after another 5 min. The mixture was stirred at –78 °C for 1 h and then at –40 °C for 1.5 h. The resulting deep red solution was poured to an aqueous ammonia and ammonium chloride. Ether was added and the mixture was shaken until the aqueous phase was deep blue. The organic layer was separated and the aqueous phase was extracted twice with ether. Combined organic layers were dried over anhydrous sodium sulfate, the solvents were removed under reduced pressure and the residue was dried in high vacuum. Then it was dissolved in anhydrous ether (70 ml), cooled to –78 °C and 1 M diisobutylaluminium hydride (3.5 ml, 3.5 mmol) in hexane was added slowly. The mixture was stirred at 0 °C for 2 h and then a saturated aqueous solution of ammonium chloride (1 ml) was added. After 15 min, the mixture was filtered through celite and the precipitate was washed three times with ether. The solvent was removed under reduced pressure and the crude product was purified by chromatography on 30 g of silica (petroleum ether–acetone 95 : 5) furnishing 0.160 g (35%) of stannane **2k** as a colorless oil. The ^{1}H NMR was identical with that described in ref.[7].

Methyl 4-(*tert*-Butoxycarbonylamino)but-2-ynoate[10] (**11**)

A solution of 1.6 M butyllithium (7.5 ml, 12 mmol) was added to a solution of 3-(*tert*-butoxycarbonylamino)prop-1-yne[11] (0.7785 g, 5 mmol) in THF (10 ml) at –78 °C. The mixture was allowed to warm to room temperature, poured into a dry ice–THF mixture and left standing overnight. The reaction mixture was then diluted with water, acidified with dilute hydrochloric acid and extracted three times with ether. Combined organic layers were dried over anhydrous magnesium sulfate and the solvents were evaporated in vacuum. Pure acid (0.663 g, 67%) was obtained by chromatography on silica (petroleum ether–acetone 80 : 20). Esterification with diazomethane in ethereal solution furnished alkyne **11** (0.670 g, 63%). The ^{1}H NMR spectrum of the obtained product was identical with that described in ref.[10].

(*E*)-4-(*tert*-Butoxycarbonylamino)-3-(tributylstannyl)but-2-en-1-ol (**2t**)

This compound was synthesized by the procedure used for synthesis of **2k** except that boron trifluoride etherate was not used. A solution of ester **11** (0.213 g, 1 mmol) and methanol

(0.2 ml) in THF was added to a solution of stannylcuprate prepared from CuCN (0.098 g, 1.1 mmol), 1.6 M solution of butyllithium (1.4 ml, 2.2 mmol) and tributyltin hydride (0.58 ml, 2.2 mmol). After reduction of the intermediate with a 1 M solution of diisobutylaluminium hydride in toluene and chromatography of the crude product on 30 g of silica (petroleum ether–triethylamine 92 : 8), 0.106 g (23%) of stannane **2t** was obtained as colorless oil. ^{1}H NMR ($CDCl_3$): 5.95 t, 1 H, J = 6.6, ^3J(Sn-H,*cis*) = 64 (=CH); 4.62 bs, 1 H (NH); 4.22 d, 2 H, J = 6.6 (C**H**$_2$OH); 3.93 d, 2 H, J = 6.1, ^3J(Sn-H) = 48 (C**H**$_2$NH); 1.43 s, 9 H ((CH$_3$)$_3$C-); 1.25–1.60 m, 12 H (SnCH$_2$C**H**$_2$C**H**$_2$CH$_3$); 0.82–1.05 m, 15 H (SnC**H**$_2$CH$_2$CH$_2$C**H**$_3$). ^{13}C NMR, APT ($CDCl_3$): 156.79, 145.75, 58.93, 42.97, 29.96, 28.09, 10.20, 9.95 (CH_2, C); 141.77, 29.11, 13.38 (CH_3, C). IR ($CHCl_3$): 3 614, 3 452, 3 010, 2 959, 2 928, 2 873, 2 855, 1 704, 1 502, 1 458, 1 367, 1 278, 1 185, 1 007. For $C_{21}H_{43}NO_3Sn$ (476.3) calculated: 52.96% C, 9.10% H, 2.94% N; found: 53.01% C, 8.80% H, 3.06% N.

4-(2,5-Dimethylpyrrol-1-yl)-3-iodobut-2-en-1-ol (**14**)

To a solution of 4-(2,5-dimethylpyrrol-1-yl)but-2-yn-1-ol (**12**; 3.26 g, 20 mmol) in THF, 0.8 M THF solution of $LiAlH_4$ (27.5 ml, 22 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature overnight, then cooled to 0 °C, ethyl acetate (0.4 ml, 4.1 mmol) was added and the mixture was stirred for 15 min without cooling. The solution was then cooled to –78 °C and a solution of iodine (6.3 g, 25 mmol) in THF was added. After stirring at room temperature for 3 h, the mixture was poured into an aqueous solution of sodium thiosulfate and extracted with ether (3×). The combined ethereal extracts were dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuum. Chromatography of the crude product on silica (petroleum ether–ether–acetone 8 : 1 : 1) afforded 4 g (69%) of the product. ^{1}H NMR ($CDCl_3$): 5.82 s, 2 H (Ar); 5.30 tt, 1 H, J_1 = 5.8, J_2 = 1.8 (=CH); 4.59 s, 2 H (CH_2N); 4.21 bs, 2 H (C**H**$_2$OH); 2.16 s, 6 H (CH_3). IR ($CHCl_3$): 3 611, 3 451, 2 999, 2 932, 2 667, 1 647, 1 523, 1 443, 1 405, 1 297, 1 050, 1 000. For $C_{10}H_{14}INO$ (291.1) calculated: 41.26% C, 4.85% H, 43.59% I, 4.81% N; found: 39.05% C, 4.56% H, 43.51% I, 4.58 N.

(*Z*)-4-Amino-3-iodobut-2-en-1-ol (**15**)

A mixture of hydroxylamine hydrochloride (0.414 g, 6 mmol), potassium hydroxide (0.2 g, 3.5 mmol), ethanol (3.3 ml), water (1.2 ml) and compound **14** (0.350 g, 1.2 mmol) was heated under reflux for 24 h. Then another portion of potassium hydroxide (0.1 g, 1.8 mmol) and hydroxylamine hydrochloride (0.2 g, 2.9 mmol) was added and the mixture was heated for another 24 h. After cooling, the pH of the reaction mixture was adjusted to >10 by addition of a dilute solution of sodium hydroxide, the solids were filtered off and the solvent was evaporated. The residue was dissolved in ethanol, alumina (5 g) was added and ethanol was evaporated. The dry mixture was transferred onto the column filled with silica (20 g) and chromatography with a mixture of chloroform–ethanol–ammonium hydroxide (75 : 24 : 1) afforded 0.175 g (68%) of the amino alcohol **15**. ^{1}H NMR (DMSO-d_6): 6.27 t, 1 H, J = 4.9 (=CH); 3.93 d, J = 4.9 (C**H**$_2$OH); 3.73 s, 2 H (C**H**$_2$NH$_2$). IR (KBr): 3 328, 3 278, 2 902, 2 745, 1 654, 1 615, 1 439, 1 322, 1 246, 1 116, 1 077, 1 042, 954, 757. Since no satisfactory elemental analysis was obtained, the amine **15** was characterized as sulfate. The amino alcohol was dissolved in methanol and a solution of sulfuric acid in methanol was carefully added until the mixture became neutral. The sulfate (m.p. 171–175 °C) was precipitated during the neutralization (its crystallization from acidic solution was unsuccessful).

Addition of a small amount of ether aided the precipitation. ^{1}H NMR (DMSO-d_6): 6.17 t, 1 H, J = 5.2 (=CH); 3.98 d, J = 4.9 (C**H**$_2$OH); 3.58 d, 2 H, J = 1.1 (C**H**$_2$NH$_2$). IR (KBr): 3 367, 3 108, 2 882, 1 630, 1 527, 1 477, 1 429, 1 110, 1 010, 880. For $C_8H_{18}I_2N_2O_6S$ (524.1): 18.33% C, 3.46% H, 48.43% I, 5.34 % N; found: 18.37% C, 3.88% H, 48.13% I, 5.47% N.

(*Z*)-4-Benzamido-1-(benzoyloxy)-3-iodobut-2-en (**16**)
and (*Z*)-4-Benzamido-3-iodobut-2-en-1-ol (**17**)

A solution of benzoyl chloride (1.3 ml, 11 mmol) in ether (10 ml) was added dropwise to a solution of amino alcohol **15** (1.065 g, 5 mmol) in pyridine (10 ml) at 0 °C. The reaction mixture was stirred for 3 h at room temperature, then poured into water, acidified with hydrochloric acid until it became slightly acidic and extracted three times with chloroform. The organic layers were combined, dried over anhydrous $MgSO_4$ and chloroform was evaporated. Crystallization from toluene afforded 1.602 g (76%) of **16** (m.p. 92 °C). ^{1}H NMR ($CDCl_3$): 8.02–8.09 m, 2 H (Ar); 7.79–7.85 m, 2 H (Ar); 7.41–7.62 m, 6 H (Ar); 6.46 bs, 1 H (NH); 6.35 tt, 1 H, J_1 = 5.8, J_2 = 1.5 (=CH); 4.92 d, J = 5.9 (CH_2O); 4.44 dd, 2 H, J_1 = 5.9, J_2 = 0.9 (CH_2N). IR ($CHCl_3$): 3 452, 3 026, 3 012, 1 719, 1 666, 1 516, 1 486, 1 272, 1 110. For $C_{18}H_{16}INO_3$ (421.2) calculated: 51.32% C, 3.83% H, 30.13% I, 3.33% N; found: 51.46% C, 3.94% H, 30.43% I, 3.29% N.

Alcohol **17** was obtained by sodium methoxide-catalyzed methanolysis of **16** at 40 °C overnight. After evaporation of methanol, the product was separated by chromatography on silica (radial chromatography). Elution with petroleum ether–ether–acetone (50 : 30 : 20) afforded **17** as a white solid (m.p. 80–82 °C). ^{1}H NMR ($CDCl_3$): 7.78–7.83 m, 2 H (Ar); 7.42–7.57 m, 3 H (Ar); 6.62 bs, 1 H (NH); 6.22 tt, 1 H, J_1 = 5.7, J_2 = 1.1 (=CH); 4.36 dd, 2 H, J_1 = 5.9, J_2 = 0.9 (C**H**$_2$NH); 4.22–4.25 m, (C**H**$_2$OH). Peaks were assigned according to the COSY spectrum. ^{13}C NMR, APT ($CDCl_3$): 168.97, 134.31, 104.00, 67.36, 52.19 (CH_2, C); 136.72, 132.74, 129.41, 127.90 (CH_3, CH). ^{13}C NMR, nondecoupled: 52.19 dt, J_t = 142.3, J_d = 4.6. Interaction J_d corresponds with *cis* relation of CH_2OH and C-**H**. IR ($CHCl_3$): 3 608, 3 449, 3 355, 3 011, 1 659, 1 518, 1 487, 1 292, 1 076, 1 004. For $C_{11}H_{12}INO_2$ (317.1) calculated: 41.66% C, 3.81% H, 40.02% I, 4.42% N; found: 42.09% C, 3.77% H, 40.41% I, 4.43% N.

(*E*)-4-Benzamido-3-(tributylstannyl)but-2-en-1-ol (**2s**)
and (*E*)-4-Benzamido-2-(tributylstannyl)but-2-en-1-ol (**21**)

4-Benzamidobut-2-yn-1-ol (**18**; 0.284 g, 1.5 mmol) and tetrakis(triphenylphosphine)palladium (0.035 g, 0.03 mmol) were dissolved in anhydrous THF (7 ml) under argon and tributyltin hydride (0.37 ml, 1.65 mmol) was added *via* syringe. After 10 min, the solvents were evaporated and the products were separated by chromatography (radial chromatography). Elution with petroleum ether–ether–acetone 8 : 1 : 1 afforded 0.168 g (23%) of **21** (less polar) and 0.192 g (27%) of **2s** (more polar), respectively.

Compound **21**. ^{1}H NMR ($CDCl_3$): 7.75–7.79 m, 2 H (Ar); 7.40–7.53 m, 3 H (Ar); 6.23 s, 1 H (NH); 5.62 t, 1 H, J = 6.7, ^3J(Sn-H,*cis*) = 66 (=CH); 4.46 d, 2 H, J = 5.3, ^3J(Sn-H) = 37 (C**H**$_2$OH); 4.12 t, 2 H, J = 6.2 (C**H**$_2$NH); 2.37 t, 1 H, J = 5.3 (OH); 1.25–1.60 m, 12 H ($SnCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 0.82–1.05 m, 15 H ($SnC\mathbf{H}_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR, APT ($CDCl_3$): 168.16, 151.00, 63.94, 39.23, 29.86, 28.09, 10.74 (CH_2, C); 135.02, 132.22, 129.29, 127.62 (CH_3, CH). IR ($CHCl_3$): 3 618, 3 451, 3 365, 3 010, 2 959, 2 926, 2 872, 2 853, 1 653, 1 579, 1 520, 1 496, 1 462, 1 287, 1 074, 1 026. For $C_{23}H_{39}NO_2Sn$ (480.3) calculated: 57.52% C, 8.19% H, 2.92% N; found: 57.24% C, 7.88% H, 2.78% N.

Compound **2s**. ^{1}H NMR ($CDCl_3$): 7.74–7.80 m, 2 H (Ar); 7.41–7.53 m, 3 H (Ar); 6.32 bs, 1 H (NH); 6.05 t, 1 H, *J* = 6.5, ^3J(Sn-H,*cis*) = 65 (=CH); 4.26–4.35 m, 4 H, ^3J(Sn-H) = 47 ($C\mathbf{H}_2OH$, $C\mathbf{H}_2NH$); 2.78 t, 1 H, *J* = 5.7 (OH); 1.20–1.60 m, 12 H ($SnCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 0.82–1.05 m, 15 H ($SnC\mathbf{H}_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR, APT ($CDCl_3$): 168.05, 144.73, 134.93, 59.17, 42.70, 29.83, 28.08, 10.46 (CH_2, C); 142.87, 132.31, 129.31, 127.53, 14.33 (CH_3, CH). IR ($CHCl_3$): 3 613, 3 453, 3 010, 2 959, 2 927, 2 874, 2 853, 1 656, 1 518, 1 485, 1 462, 1 340, 1 074, 1 002. For $C_{23}H_{39}NO_2Sn$ (480.3) calculated: 57.52% C, 8.19% H, 2.92% N; found: 57.56% C, 7.90% H, 2.76% N.

(*E*)-4-(3-Fluorobenzamido)-3-(tributylstannyl)but-2-en-1-ol (**2u**)
and (*E*)-4-(3-Fluorobenzamido)-2-(tributylstannyl)but-2-en-1-ol (**22**)

These stannanes were prepared as described for compounds **2s** and **2l**. From a one mmol reaction 0.224 g (45%) of **22** (less polar) and 0.193 g (38%) of **2u** (more polar) was obtained.

Compound **22**. ^{1}H NMR ($CDCl_3$): 7.45–7.53 m, 2 H (Ar); 7.36–7.45 m, 1 H (Ar); 7.15–7.24 m, 1 H (Ar); 6.26 bs, 1 H (NH); 5.61 t, 1 H, *J* = 6.6, ^3J(Sn-H,*cis*) = 66 (=CH); 4.47 d, 2 H, *J* = 5.3, ^3J(Sn-H) = 38 ($C\mathbf{H}_2OH$); 4.11 t, 2 H, *J* = 6.1 ($C\mathbf{H}_2NH$); 2.20 t, 1 H, *J* = 5.2 (OH); 1.25–1.62 m, 12 H ($SnCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 0.82–1.05 m, 15 H ($SnC\mathbf{H}_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR, APT ($CDCl_3$): 166.89, 164.70, 162.23, 151.27, 137.47, 63.90, 39.29, 29.84, 28.08, 10.72 (CH_2, C); 134.81, 131.02, 123.19, 119.25, 115.10, 14.42 (CH_3, CH). IR ($CHCl_3$): 3 617, 3 451, 3 015, 2 958, 2 927, 2 872, 1 659, 1 500, 1 520, 1 482, 1 292, 1 271, 1 023. For $C_{23}H_{38}FNO_2Sn$ (498.3) calculated: 55.47% C, 7.69% H, 2.81% N; found: 55.46% C, 7.52% H, 2.99% N.

Compound **2n**. ^{1}H NMR ($CDCl_3$): 7.45–7.53 m, 2 H (Ar); 7.35–7.45 m, 1 H (Ar); 7.15–7.24 m, 1 H (Ar); 6.34 bs, 1 H (NH); 6.05 t, 1 H, *J* = 6.6, ^3J(Sn-H,*cis*) = 66 (=CH); 4.24–4.34 m, 4 H, ^3J(Sn-H) = 48 ($C\mathbf{H}_2OH$, $C\mathbf{H}_2NH$); 2.62 t, 1 H, *J* = 5.8 (OH); 1.20–1.65 m, 12 H ($SnCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 0.80–1.05 m, 15 H ($SnC\mathbf{H}_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR, APT ($CDCl_3$): 166.64, 164.75, 162.29, 144.71, 137.28, 59.18, 42.75, 29.82, 28.07, 10.46 (CH_2, C); 142.97, 131.00, 122.96, 119.31, 115.09, 14.32 (CH_3, CH). IR ($CHCl_3$): 3 447, 3 363, 3 010, 2 959, 2 927, 2 873, 2 854, 1 658, 1 588, 1 518, 1 482, 1 468, 1 292, 1 271, 1 023, 1 001. For $C_{23}H_{38}FNO_2Sn$ (498.3) calculated: 55.47% C, 7.69% H, 2.81% N; found: 55.53% C, 7.59% H, 2.99% N.

(*E*)-4-Acetamido-3-(tributylstannyl)but-2-en-1-ol (**2v**)
and (*E*)-4-Acetamido-2-(tributylstannyl)but-2-en-1-ol (**23**)

These stannanes were prepared as described for compounds **2s** and **2l**. Two mmol scale reaction afforded **23** (0.282 g, 34%) as a less polar fraction and **2v** (0.219 g, 26%) as a more polar fraction after chromatography on alumina (50 g) using gradient elution with petroleum ether–ether–acetone 55 : 40 : 5, 50 : 40 : 10 and 40 : 40 : 20.

Compound **23**. ^{1}H NMR ($CDCl_3$): 5.61 bs, 1 H (NH); 5.501 tt, 1 H, J_1 = 6.9, J_2 = 1.9, ^3J(Sn-H,*cis*) = 64 (=CH); 4.38 d, 2 H, *J* = 5.0, ^3J(Sn-H) = 38 ($C\mathbf{H}_2OH$); 3.89 t, 2 H, *J* = 6.0 ($C\mathbf{H}_2NH$); 2.29 t, 1 H, *J* = 5.2 (OH); 1.98 s, 3 H (CH_3CO); 1.24–1.60 m, 12 H ($SnCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 0.80–1.02 m, 15 H ($SnC\mathbf{H}_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR, APT ($CDCl_3$): 170.76, 150.66, 63.84, 38.89, 29.84, 28.08, 10.71 (CH_2, C); 135.04, 24.01, 14.42 (CH_3, CH). IR ($CHCl_3$): 3 450, 3 335, 3 008, 2 959, 2 927, 2 872, 2 854, 1 662, 1 519, 1 463, 1 376, 1 273, 1 021. For $C_{18}H_{37}NO_2Sn$ (418.2) calculated: 51.70% C, 8.92% H, 3.35% N; found: 51.52% C, 8.43% H, 3.20% N.

Compound **2v**. ^{1}H NMR ($CDCl_3$): 6.58 t, 1 H, J = 6.6, ^3J(Sn-H,*cis*) = 64 (=CH); 5.58 bs, 1 H (NH); 6.35 t, 2 H, J = 5.8 (C**H**$_2$OH); 4.06 d, 2 H, J = 5.5, ^3J(Sn-H) = 49 (C**H**$_2$NH); 2.76 t, 1 H, J = 5.5 (OH); 1.96 s, 3 H (CH_3CO); 1.24–1.60 m, 12 H ($SnCH_2C$**H**$_2C$**H**$_2CH_3$); 0.80–1.02 m, 15 H (SnC**H**$_2CH_2CH_2C$**H**$_3$). ^{13}C NMR, APT ($CDCl_3$): 170.81, 144.47, 59.20, 42.28, 29.81, 28.08, 10.43 (CH_2, C); 142.71, 24.02, 14.37 (CH_3, CH). IR ($CHCl_3$): 3 447, 3 338, 3 008, 2 959, 2 928, 2 872, 2 855, 1 663, 1 517, 1 463, 1 375, 1 279, 1 007. For $C_{18}H_{37}NO_2Sn$ (418.2) calculated: 51.70% C, 8.92% H, 3.35% N; found: 51.81% C, 8.63% H, 3.23% N.

Solid-Phase Synthesis

General Method for the Coupling of Polymer-Attached Iodobenzoates with Stannanes **2**

The hydroxy-functionalized Tenta Gel resin was mixed with iodobenzoic acid (4 equivalents), diisopropylcarbodiimide (4 equivalents), 1-hydroxybenzotriazole (4 equivalents) and 4-(dimethylamino)pyridine (0.4 equivalents) in dichloromethane (8 ml/g of resin) and the mixture was shaken for 14 h. The polymer was then filtered off, washed with DMF (3×), dichloromethane (3×), acetone (3×) and dried under high vacuum. The amount of attached iodobenzoic acid was 0.25–0.30 mmol/g of the polymer (from the iodine content).

The above iodobenzoic acid attached to Tenta Gel (0.1 g, 0.025–0.03 mmol), stannane **2** (25–30 mg, 0.06–0.09 mmol) and 0.5 ml (0.0003 mmol) of stock solution of palladium catalyst **7** in 1-methylpyrrolidin-2-one (9 mg of catalyst in 15 ml) were heated to 110 °C under argon for 14 h. Polymer was than washed with DMF (3×), dichloromethane (3×), acetone (3×) and dried under high vacuum.

Transformation of Polymer-Supported Allyl Alcohol **3** to Supported Allyl Chloride **4**

Tenta Gel with attached allyl alcohol **3** (0.1 g) and a solution of triphenylphosphine in carbon tetrachloride–methylene chloride (1 ml) were heated to 35 °C for 14 h. The polymer was then washed with dichloromethane (3×), acetone (3×) and dried in high vacuum. The solution of triphenylphosphine was prepared by dissolving of 0.262 g (1 mmol) triphenylphosphine in the mixture of carbon tetrachloride (3 ml) and dichloromethane (4 ml) and heating at 35 °C for 0.5 h.

Coupling of Allyl Chloride **4** with Stannanes **2**

Tenta Gel with attached allyl chloride **4** (0.1 g, 0.025–0.03 mmol), stannane **2** (25–30 mg, 0.06–0.09 mmol) and 0.5 ml of the solution of palladium catalyst in 1-methylpyrrolidin-2-one (30 mg of $Pd_2(dba)_3{\cdot}CHCl_3$ and 36 mg of tris(2-tolyl)phosphine in 15 ml) were heated at 80 °C under argon for 14 h. The polymer was washed with DMF (3×), dichloromethane (3×) and acetone (3×) and dried under high vacuum.

Cleavage of Products from the Polymer Support

The substituted Tenta Gel was stirred at room temperature in a solution of sodium methoxide (0.02 mmol) in a mixture of methanol (0.5 ml) and THF (2 ml). After 40 min, the mixture was neutralized with dilute solution of acetic acid in methanol, filtered and evaporated.

(Z)-4-Acetamido-2-[4-(methoxycarbonyl)phenyl]but-2-en-1-ol (**31a**), product of coupling of polymer supported 4-iodobenzoate (**1**) with stannane **23** (Table III). ^{1}H NMR ($CDCl_3$): 7.96–8.02 m, 2 H (Ar); 7.53–7.59 m, 2 H (Ar); 6.05 bs, 1 H (NH); 5.83 t, 1 H, J = 7.7 (=CH); 4.58 d, 2 H, J = 6.6 (CH_2); 4.09 dd, 2 H, J_1 = 6.0, J_2 = 7.7 (CH_2); 3.91 s, 3 H (OCH_3); 1.99 s, 3 H (CH_3CO). HR MS (FAB), for $C_{14}H_{18}NO_4$ (M + 1) calculated: 264.1236; found: 264.1259.

(Z)-4-Acetamido-2-[3-(methoxycarbonyl)phenyl]but-2-en-1-ol (**31b**), product of coupling of polymer supported 3-iodobenzoic acid (**28b**) with stannane **23** (Table III). ^{1}H NMR ($CDCl_3$): 8.13 s, 1 H (Ar); 7.93 d, 1 H, J = 7.7 (Ar); 7.73 d, 1 H, J = 8.2 (Ar); 7.40 t, 1 H, J = 7.7 (Ar); 6.07 bs, 1 H (NH); 5.81 t, 1 H, J = 7.7 (=CH); 4.58 d, 2 H, J = 6.1 (CH_2); 4.09 dd, 2 H, J_1 = 6.6, J_2 = 7.7 (CH_2); 3.91 s, 3 H (OCH_3); 1.99 s, 3 H (CH_3CO). MS, m/z: 264.1 (M + 1).

(Z)-4-Acetamido-2-[2-methyl-5-(methoxycarbonyl)phenyl]but-2-en-1-ol (**31c**), product of coupling of polymer supported 3-iodo-4-methylbenzoic acid (**28c**) with stannane **23** (Table III). ^{1}H NMR ($CDCl_3$): 7.77–7.86 m, 2 H (Ar); 7.22–7.32 m, 1 H (Ar); 5.95 s, 1 H (NH); 5.40 t, 1 H, J = 8.0 (=CH); 4.43 d, 2 H, J = 6.0 (CH_2); 4.11 t, 2 H, J = 6.9 (CH_2); 3.89 s, 3 H (OCH_3); 2.32 s, 3 H (CH_3); 2.02 s, 3 H (CH_3). MS, m/z: 278.1 (M + 1).

(Z)-4-Acetamido-2-{4-[N-(tert-butyloxycarbonyl)amino]-3-(methoxycarbonyl)phenyl}but-2-en-1-ol (**31d**), product of coupling of polymer supported 2-[*N*-(*tert*-butyloxycarbonyl)amino]-5-iodobenzoic acid (**28d**) with stannane **23** (Table III). ^{1}H NMR ($CDCl_3$): 10.26 s, 1 H (Boc-NH); 8.38 d, 1 H, J = 8.8 (Ar); 8.18 d, 1 H, J = 2.8 (Ar); 7.60 dd, 1 H, J_1 = 8.8, J_2 = 2.2 (Ar); 6.01 s, 1 H (NH); 5.74 t, 1 H, J = 7.8 (=CH); 4.55 d, 2 H, J = 6.6 (CH_2); 4.07 dd, 2 H, J_1 = 6.6, J_2 = 8.2 (CH_2); 3.91 s, 3 H (OCH_3); 1.52 s, 9 H ((CH_3)$_3$C). MS, m/z: 379.1 (M + 1).

Triene **27**. ^{1}H NMR ($CDCl_3$): 7.95–8.03 m, 2 H (Ar); 7.23–7.47 m, 2 H (Ar); 5.80–5.88 m, 1 H (=CH); 5.33–5.53 m, 1 H (=CH); 4.95–5.20 m, 1 H (=CH); 4.16 bs, 2 H (C**H**$_2$OH); 3.92 m, 3 H (OCH_3); 2.98–3.01 m, 4 H (=CH-C**H**$_2$-CH=); 1.70–2.11 m, 9 H (=C-C**H**$_3$). MS, m/z: 314 (M + 1).

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REFERENCES

1. Yu K.-L., Desphande M. S., Vyas D. M.: *Tetrahedron Lett.* **1994**, *35*, 8919.
2. Frenette R., Friesen R. W.: *Tetrahedron Lett.* **1994**, *35*, 9177.
3. a) Desphande M. S.: *Tetrahedron Lett.* **1994**, *35*, 5613; b) Forman F. W., Sucholeiki I.: *J. Org. Chem.* **1995**, *60*, 523.
4. a) Booth S., Hermkens P. H. H., Ottenhejm H. C. J., Rees D. C.: *Tetrahedron* **1998**, *54*, 15385; b) Brown R. C. D. J.: *J. Chem. Soc., Perkin Trans. 1* **1998**, 3293; c) Lorsbach B. A., Karth M. J.: *Chem. Rev.* **1999**, *99*, 1549.
5. Blaskovich M. A., Kahn M.: *J. Org. Chem.* **1998**, *63*, 1119.
6. a) Herrmann W. A., Brossmer Ch., Ofele K., Reisinger C.-P., Priermeier T., Beller M., Fischer H.: *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844; b) Beller M., Fischer H., Herrmann W. A., Ofele K., Brossmer Ch.: *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848.
7. Havránek M., Dvořák D.: *Synthesis* **1998**, 1264.
8. Piers E., Friesen R. W., Retting S. J.: *Can. J. Chem.* **1992**, *70*, 1385.
9. Piers E., Tillyer R. D.: *J. Org. Chem.* **1988**, *53*, 5366.

10. Reginato G., Capperuci A., Degl'Innoceti A., Mordini A., Pecchi A.: *Tetrahedron* **1995**, *51*, 2129.
11. Casara P., Danzin Ch., Metcalf B., Jung M.: *J. Chem. Soc., Perkin Trans. 1* **1985**, 2201.
12. Bruekelman S. P., Leach S. E., Meakins G. D., Tirel M. D.: *J. Chem. Soc., Perkin Trans. 1* **1992**, 1089.
13. Mitchell T. N.: *Synthesis* **1992**, 803.
14. a) Zhang H. X., Guibe F., Balavoine G.: *Tetrahedron Lett.* **1988**, *29*, 619; b) Miake H., Yamakura K.: *Chem. Lett.* **1989**, 981; c) Ensley H. E., Buescher R. R., Lee K.: *J. Org. Chem.* **1982**, *47*, 404; d) Zhang H. X., Guibe F., Balavoine G.: *J. Org. Chem.* **1990**, *55*, 1857.
15. Havránek M., Dvořák D.: Unpublished results.
16. MacInnes I., Walton J. C.: *J. Chem. Soc., Perkin Trans. 2* **1987**, 1077.
17. Marszak-Feury A., Larote J.: *Bull. Soc. Chim. Fr.* **1963**, 1270.