DOI: 10.1002/ejoc.200500353

The Application of [γ-(Silyloxy)allylidene]ditin to the Efficient Synthesis of the Chromophore of the Neocarzinostatin Dihydroxycyclopentene-Based Dienediyne Core

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Keywords: Allylation / Antitumour agents / Cyclisation / Diastereoselectivity / Palladium / Tin

1-(*tert*-Butyldimethylsilyl)oxy-3,3-bis(tributylstannyl)propene (**5**), a versatile *gem*-dimetallic allylic synthon accessible through various synthetic routes, has been condensed with (trimethylsilyl)propiolaldehyde to give the fully functionalised acyclic vinyltin compound **9h**, which is a precursor of the complex dihydroxycyclopentene sub-unit of neocarzinostatin chromophore (NCS) **1**. Subsequent transformation into the geminal (*E*)-α-chloro-(Z)-α-iodovinylic intermediate **20**, followed by a palladium-catalysed carbometallation/cyclisation reaction including in situ trapping with either (tributylstannyl)acetylene or the more functionalised 3,3-diethoxy-1-(tributylstannyl)prop-1-yne delivered the corresponding alkyne-substituted 4-chloro-1,2-bis(silyloxy)cyclopent-3-enes **21** or **22**, respectively. Chlorocyclopentene **21** was subsequently easily transformed into the target dienediyne adduct **23** by Sonogashira condensation with trimethylsilylacetylene. This diastereoselective process is efficient with only six steps and an overall 26 % yield from the allylic ditin precursor **5**. More than just an NCS building block, the final acyclic dihydroxycyclopentene-based dienediyne is also a *seco* analogue of the NCS chromophore.

Introduction

(Di)enediynes constitute a class of anticancer agents that include chromoproteins such as neocarzinostatin (NCS),[1] C-1027, kedarcidin or maduropeptin,[2] and non-proteinous antibiotics such as esperamycins, calicheamycins, dynemycin A, namenamycin, N1999A2 or shishijimicin.[3] In the first sub-class, the highly sensitive dienediyne chromophore is non-covalently linked to the protein counterpart in a 1:1 ratio, whereas the members of the second sub-class exist as more stable enediyne chromophores alone. NCS, the first member of this class, possesses potent antiproliferative activity with various cell-lines both in vitro and in vivo but is relatively unstable and endowed with a high toxicity profile.[4] Recent avenues for overcoming the toxicity and improving the low therapeutic indexes of these molecules involve designing enediyne analogues that are more specific for cancer DNA cells and/or to synthesise more stable molecules that retain the potent biological activity of the parent compound. A second range of approaches is concerned with a more efficient delivery of the drugs to the target cells through a tailor-made apoprotein prodrug strategy,[5] antibody-directed delivery (immunoconjugates)[6] or polymer-bound chromoproteins.[7] NCS's mechanism of action is claimed to involve, as for other enediynes, a cleavage of the DNA strand by a Bergman rearrangement of the (di)enediyne entity, which results in the formation of an activated diradical species that abstracts hydrogen atoms from the DNA deoxyribose residues. In the case of NCS, this rearrangement is triggered by an attack of a thiol group at C-12.[8]

The highly reactive strained enediyne chromophore of NCS (**1**) and congeners represents a challenging problem for organic chemists, and despite considerable achievements in the synthesis of enediynes, further synthetic developments are continuously required to find practical synthetic access to this molecule as well as to biologically significant analogues (Figure 1). To date, the very few total syntheses of the NCS chromophore – the only completely achieved synthetic work being from Myers' group[9] – clearly reflect these difficulties.

One particular non-trivial point deals with the fully functionalised *trans*-dihydroxycyclopentene part of **1**, and here again, only scarce studies have appeared for its synthesis. Strategies for the construction of this sub-unit include methylenetriphenylphosphorane homologation/condensation/cyclisation on a tartaric acid derived bis(electrophile),[10] enzymatic transformations of a *meso*-3,4,5-

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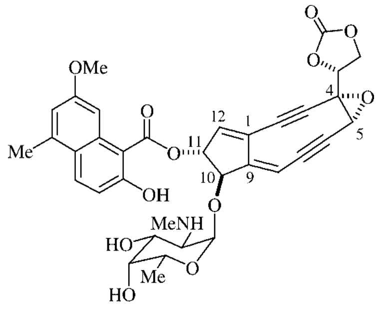


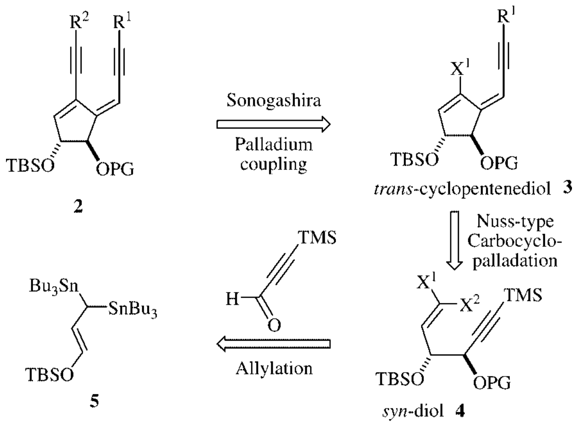
Figure 1. Neocarzinostatin chromophore **1**.

trans,*trans*-trihydroxycyclopentene precursor[11] or base-mediated isomerisation of β-pyranones.[12] Myers' strategy involves the formation of the functionalised dihydroxylated cyclopentanone ring of **1** during a late step of the synthesis through reductive deoxygenation of an intermediate epoxy alcohol. A recent paper from these authors clearly demonstrates the difficulties encountered when installing the hydroxy group at C-10 through this strategy, partly because of the rather unpredictable transformation results associated with the ultimate steps of the synthesis of such a sensitive molecule as **1**.[13]

We wish to report here our results on the diastereoselective synthesis of **2** from our previously reported [γ-(silyloxy)-allylidene]ditin building block **5**, as well as full details of the preparation of this intermediate by three alternative routes.

Results and Discussion

As summarised in Scheme 1, we planned a synthetic strategy of fully functionalised NCS cyclopentene sub-units of type **2** through a transition-metal-catalysed cyclisation reaction from a convenient acyclic precursor such as **4**, followed by a Sonogashira acetylenic coupling of the incipient activated vinyl intermediate **3**, according to a strategy already used by Torii's[14] and by Nuss' groups,[15] on monohydroxylated models. Interestingly, these authors have demonstrated that the acyclic precursor **4** can contain two identical halogen atoms ($X^1 = X^2 = Br$ for the former research group; $X^1 = X^2 = I$ for the latter) owing to the higher reactivity of the (*Z*)-vinyl halogen atom for precursors of type **4**; as claimed by Nuss and co-workers, initial complexation of the pendant alkyne by the organometallic reagent favours the subsequent formation of a transient π-complex on the (*Z*)-halogen atom that results in the high stereoselectivity observed. The more successful strategy involving diiodides that resulted in fewer uncyclised coupling products than their dibromo analogues, led to an elegant construction of cyclic monohydroxylated precursors of type **2**, in a one-pot process when $R^1 = R^2 = Br$, or a two-step process in the case of differently substituted alkynyl appendages ($R^1 \neq R^2$).[15b]



Scheme 1. Retrosynthetic approach for the preparation of the *seco* analogue **2**.

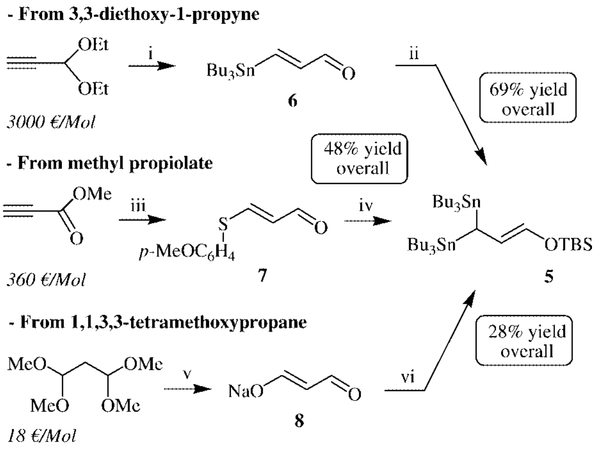
Another attractive, although apparently more complex, solution to the chemoselectivity problem will address differently functionalised *gem*-diactivated species **4** where X^1 is different from X^2. This route has been tentatively explored here.

One key feature of the strategy developed here is the use of the *gem*-distannylallyl ether **5** as starting material for the preparation of **4**. Previous results from our laboratories have shown some relevant aspects of the preparation of **5**, which can be regarded as a potential 1,3-allylic dianion,[16] as well as some examples of its synthetic potential, including preliminary results on the reaction of **5** with various aldehydes.[17]

Curiously, only a few examples of *gem*-dimetallic allylic species have been hitherto described despite their high synthetic potentialities. Beside **5**, other *gem*-homodimetallic allylic species such as other ditin[18] as well as dizinc[19] and more recently diindium compounds[20] have been described to date.

Preparation of *gem*-Distannylallyl Ether 5

Several routes from commercial materials have been explored for the synthesis of **5**, as summarised in Scheme 2. Obviously, the Quintard–Normant methodology involving an initial addition of the higher order cuprate [$Bu_3Sn(Bu)Cu(CN)Li_2$] to propiolaldehyde diethyl acetal to afford the stannylpropenal intermediate **6**,[21] followed by a second cuprate addition/silyl trapping procedure, has been shown to be the most efficient way to prepare **5** (69% overall yield), although it is also the most expensive. According to this route, we carried out the synthesis of **5** on a 20-g scale without problems. An alternative approach involves a conjugate addition of a heteronucleophile such as *p*-methoxythiophenol to methyl propiolate to give the β-hetero-substituted aldehyde **7**, which, interestingly, can be crystallised. This aldehyde was, in turn, subjected to a one-pot conjugate addition/elimination/conjugate addition/silyl trapping sequence to give **5** in 48% overall yield from methyl propiolate. An apparently less efficient route involves the very cheap malonaldehyde bis(dimethyl) acetal as starting material. The latter acetal was easily transformed into the known sodium salt **8**, which, in a one-pot procedure, was converted into the corresponding tosylate, which, in turn, was submitted to the same cuprate addition/silyl trapping procedure as above to give **5** in 28% overall yield. The purified ditin synthon **5** is rather stable and can be stored under nitrogen for months in a freezer without significant degradation.

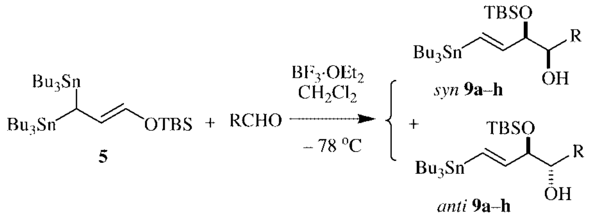


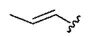
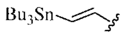
Scheme 2. Preparation of *gem*-distannylallyl ether **5**: (i) a. [$Bu_3Sn(Bu)Cu(CN)Li_2$], b. MeOH, –78 °C to room temp., c. SiO_2, $(COOH)_2$, CH_2Cl_2, 96%; (ii) [$Bu_3Sn(Bu)Cu(CN)Li_2$], THF, –78 °C, HMPA, TBSCl, 72%; (iii) a. *p*-methoxythiophenol, Et_3N, b. DIBAL-H, c. 2-iodoxybenzoic acid (IBX), DMSO then Py, AcOH and crystallisation, 88%; (iv) [$Bu_3Sn(Bu)Cu(CN)Li_2$], THF, –78 °C, HMPA, TBSCl, 54%; (v) a. Dowex 50X8–200, b. 5 N NaOH, 80%; (vi) a. TsCl, 18-crown-6, THF, b. [$Bu_3Sn(Bu)Cu(CN)Li_2$], THF, –78 °C, HMPA, TBSCl, 35%.

Access to the Acyclic Vinyl Intermediate 4

Reactions of **5** with several aldehydes have been shown to occur at –78 °C in the presence of an excess of boron trifluoride–diethyl ether to give preferentially the corresponding *syn*-diol allylation products with an exclusive (*E*) configuration of the vinyltin double bond, as shown in Table 1.[22] The best *syn*/*anti* ratio was obtained for the sterically most demanding α-sp^3 aldehydes **9a**–**c** (>95:5 to 87:13), whereas the ratios for α-sp^2 aldehydes **9d**–**f** range from 95:5 to 88:12, and for α-sp aldehydes **9g**,**h** from 75:25 to 67:33, the latter, less satisfactory, result being unfortunately obtained for the (trimethylsilyl)propiolaldehyde required for the NCS intermediate **2**. The (*E*) configuration of the double bond as well as the major *syn* configuration of the diol moiety is in agreement with an opened $S_{E'}$ antiperiplanar transition state where most steric strains are minimised (Scheme 3).[23] The diastereoselectivities observed for the distannylallyl ethers are slightly lower than in the case of the equivalent monostannylallyl ethers, probably due to supplementary conflicting steric interactions between the second tributyltin residue and the aldehyde R group, thus making formation of the antiperiplanar $S_{E'}$ transition state more difficult than the synclinal one. The lower stereoselectivity in the case of the (trimethylsilyl)acetylenic derivative **9h** is due to the less discriminating steric contribution of this group.

Table 1. Reactions of **5** with various aldehydes.

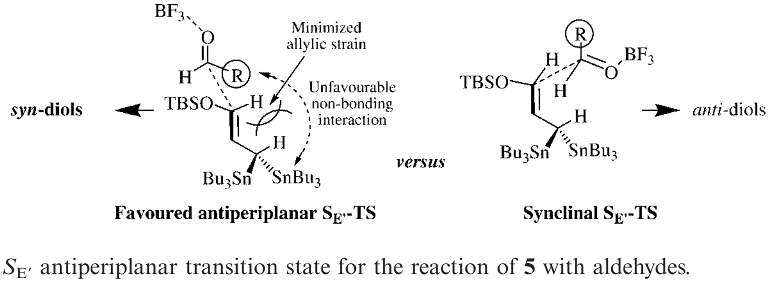


R	Product	Yield (%) [a]	Diastereomeric ratio *syn/anti* (%) [b]
*i*Pr	**9a**	100	>95:5
C_6H_{11}	**9b**	95	93:7
Et	**9c**	100	87:13
Ph	**9d**	96	95:5
	**9e**	90	90:10
	**9f**	97	88:12
*n*Bu—≡—ξ	**9g**	96	75:25
TMS—≡—ξ	**9h**	97	67:33

[a] Isolated yields. [b] Determined by ^1H NMR spectroscopy.

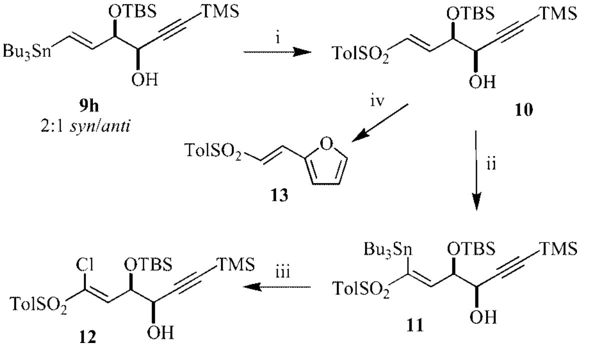
Anyway, the yield of the addition adducts is excellent in all cases tested, and is 97% in the case of (trimethylsilyl)propiolaldehyde, which furnished **9h** as a 2:1 *syn*/*anti* mixture of diastereoisomers. It is worth noting that at this stage, the possibility of protecting the incipient secondary hydroxy group in a manner different from the pre-existing OTBS group could be a great tactical advantage in light of the synthesis of **1**, where these two groups have to be differently substituted.

Having the required vinyltin adduct **9h** in hand, we now had to transform the residual stannyl group of the incipient (*E*)-vinylstannane into a functional group compatible with the subsequent cyclisation step to deliver the intermediate



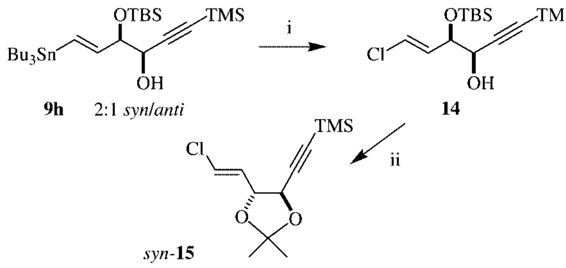
Scheme 3. Preferred opened $S_{E'}$ antiperiplanar transition state for the reaction of **5** with aldehydes.

3. Several transformations were tested on the non-separated mixture of *syn* and *anti* diastereoisomers **9h**. From a synthetic point of view, we will see below that the presence of the minor *anti* diastereoisomer is not detrimental for the final steps of the synthesis of the required cyclopentenediol **3**. A first set of reactions involved the transformation of **9h** into the (*Z*)-chloro-(*E*)-sulfonylvinyl compound **11**, which was regarded as a convenient precursor for **3** with X^1 as a tolylsulfonyl group, as well as a potential synthon for other current synthetic projects in our laboratories. Transformation of **9h** into the vinyl sulfone **10** under Labadie's conditions turned out to be totally stereoselective, as expected.[24] The metallation/stannylation of **10**,[25] followed by tin/chloride exchange according to the conditions of Takeda et al.,[26] afforded the (*Z*)-chloro-(*E*)-sulfonylvinyl adduct **12** in good yield (Scheme 4). Interestingly, attempts at hydroxy group desilylation of **10** under acidic catalysis only gave the sulfonyl-substituted furan **13**.



Scheme 4. Transformation of allylation product **9h**: (i) $[Pd(PPh_3)_4]$, TsCl, THF, reflux, 47%; (ii) MeLi, Bu_3SnCl, THF, –78 °C, 82%; (iii) $CuCl_2$, THF, 76%; (iv) *p*TsA, EtOH, reflux, 50%.

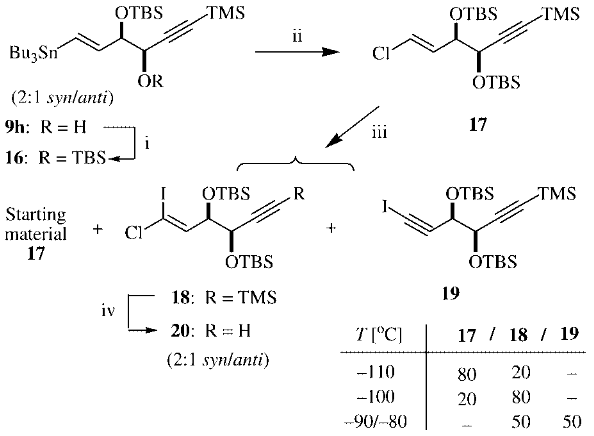
In a second set of reactions, **9h** was treated with $CuCl_2$ in THF to deliver the (*E*)-chlorovinyl derivative **14** in 87% yield (Scheme 5). At this stage, in order to ascertain the stereochemical bias of the addition reaction, **14** was converted into the corresponding diol. Therefore, treatment of **14** (*syn*/*anti* = 2:1) under mild acidic conditions cleanly delivered the required corresponding vicinal diol mixture without formation of furan **13**.[27] This diol mixture was then transformed into the corresponding acetonides from which *syn*-**15** was separated from *anti*-**15** by chromatography in 51% yield. NMR analysis of the vicinal coupling constants was in full agreement with the *syn* geometry of this major adduct.[28]



Scheme 5. Preparation of acetonide *syn*-**15**: (i) $CuCl_2$, THF, 87%; (ii) a. *p*TsA, EtOH, 55 °C, b. DMP, *p*TsA, room temp., separation, 51% (+27% *anti*-**15**).

The ease of preparation of **14** by a Takeda chlorination reaction led us to address this intermediate to prepare the *gem*-dihalogenated intermediate of type **4** ready to be submitted to the subsequent cyclisation/coupling sequence. As outlined before, we decided to introduce an iodine atom as the second halogen atom to facilitate the chemical differentiation between the two halogen atoms. *cis*-Iodination of chlorovinyl substrates was first described by Köbrich in the 1960s,[29] and this reaction has more recently been applied for the synthesis of *gem*-heterodihalogenated enynes from α-chloroenynes.[30] Generally, these reactions are carried out at very low temperature (typically –100 °C) in a THF/Et_2O/pentane solvent mixture (so-called Trapp mixture) for the deprotonation reaction before addition of the required electrophile. Initial iodination attempts with chloroacetonide **15** failed. Upon treatment with *n*-butyllithium, either unchanged starting material (at –100 °C) or degradation materials were isolated.

However, the use of the bis(silylated) chlorovinyl intermediate **17**, which is easily prepared in two steps from **9h** in 96% yield, was shown to be fruitful, although a careful control of the reaction temperature was required. As shown in Scheme 6, at –110 °C the starting material was mainly recovered, thus indicating an inefficient deprotonation process, while at temperatures around –90/–80 °C, a Fritsch–Buttenberg–Wiechell rearrangement occurred from the incipient α-chlorolithio carbenoid to afford the iodoacetylenic compound **19** in significant yield.[31] When formed at the intermediate temperature of –100 °C, the expected anion is sufficiently stable to be subsequently trapped by iodine, delivering the expected *gem*-chloroiodovinyl compound **18** almost exclusively, with no trace of acetylenic by-product **19**. Examination of the ^1H NMR spectroscopic data of the crude reaction product showed a final 20:80 mixture of



T [°C]	17	18	19
–110	80	20	–
–100	20	80	–
–90/–80	–	50	50

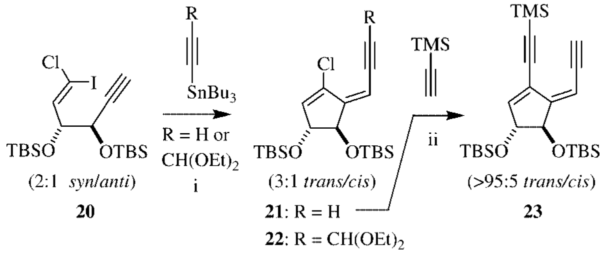
Scheme 6. Preparation of *gem*-dihalogenated enyne **20**, the precursor of the carbocyclopalladation reaction: (i) TBSCl, imidazole, DMF, quant.; (ii) $CuCl_2$, THF, 97%; (iii) a. *n*BuLi, THF/Et_2O/pentane, 1.3:1:1, –100 °C, b. I_2, THF; (iv) K_2CO_3, MeOH, ca. 75% from **17**.

starting material **17** and of *gem*-dihalogenated adduct **18** (as a 2:1 unmodified *syn*/*anti* mixture of stereoisomers). The latter mixture was directly treated with potassium carbonate in methanol to give the unprotected acetylenic derivative **20**, which is ready to be submitted to the subsequent cyclisation process.

Carbopalladation/Alkynylation Steps

This key step was carried out under Torii–Nuss conditions in THF at 60 °C using tetrakis(triphenylphosphane)palladium as a catalyst.[14,15] The alkynylation step was tested with two different known acetylenic substrates, namely (tributylstannyl)acetylene[32] and the more functionalised 3,3-diethoxy-1-(tributylstannyl)prop-1-yne.[33] The reaction with **20** was very clean, leading after 6–15h to the expected cyclopentene adducts **21** and **22**, respectively, both in 68% yield after purification and as a 3:1 mixture of *trans*/*cis* diastereoisomers. The appreciable improvement of the *trans*/*cis* ratio at the end of this reaction probably reflects the more difficult cyclisation of *anti*-**20**, whicht exhibits two bulky *cis*-*O*-TBS group interactions at the level of the transition state.

At this stage, the cyclic adduct **21** was submitted to a subsequent Sonogashira cross-coupling reaction in order to install the second acetylenic chain at C-1.[34] We were delighted to obtain the expected dienediyne **23** in 56% yield as a single *trans* diastereoisomer (Scheme 7). No trace of the corresponding *cis* isomer, reasonably expected from *cis*-**21**, could be detected by ^{1}H NMR spectroscopy. The ^{13}C NMR spectroscopic data of **23** are in agreement with those obtained by Nuss and co-workers in the case of a monohydroxylated analogue.[35] Although the reason for the absence of *cis*-**23** remains unclear, the selective formation of the expected "natural" *trans* isomer would clearly facilitate further synthetic studies of the neocarzinostatin chromophore **1**.



Scheme 7. Preparation of *seco* analogue **23** by carbocyclopalladation/alkynylation followed by Sonogashira coupling: (i) [Pd(PPh_3)$_4$], THF, 60 °C, 68% for both; (ii) [$PdCl_2(PPh_3)_2$], CuI, piperidine, THF, 60 °C, 56%.

Conclusions

We have demonstrated the possibility of applying our previously developed allylideneditin chemistry to the synthesis of a racemic fully functionalised dihydroxycyclopentene sub-unit of NCS **1**, in six steps and 26% overall yield. Interestingly, the overall sequence is stereo-discriminating, since from a *syn*/*anti* (2:1) mixture of condensation adducts **9h** it has been possible to prepare **23** as a single diastereoisomer without tedious separation steps. Furthermore, it should be emphasised that the present route allows an easy regiodifferentiation of the two secondary hydroxy groups by a judicious choice of their respective protecting groups. Finally, the dienediyne **23** cannot only be considered as an advanced precursor of **1**, but itself represents a *seco* analogue of the NCS chromophore.[36]

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker WP 200 (200 MHz) or a Bruker AM 400 (400 MHz) instrument. The chemical shifts are expressed in parts per million (ppm) referenced to residual chloroform (δ = 7.27 ppm). H,H-COSY and H,H-NOESY experiments were routinely carried out to ascertain H–H connectivity and configuration assignments, respectively. ^{13}C NMR spectra were recorded with the same instruments at 50.3 MHz and 100.6 MHz, respectively. ^{13}C NMR chemical shifts are expressed in parts per million (ppm), reported from the central peak of deuteriochloroform (δ = 77.14 ppm); *J*-modulated spin-echo technique (*J*-mod) experiments were used for evaluating CH multiplicities.[37] For Sn–^{1}H or Sn–^{13}C coupling constants, the central signal is normally associated with two close pairs of satellites corresponding to both ^{117}Sn (7.5%) and ^{119}Sn (8.6%) isotopes. When detected for large coupling constants (250–300 Hz), the two different coupling constants are reported whereas in other cases (generally for small ones, $<$ 100 Hz) average values are reported. Mass spectra were obtained with a Hewlett-Packard HP 5989B spectrometer by either direct introduction (chemical ionisation, CI; NH_3) or GC/MS coupling with a Hewlett-Packard HP 5890 chromatograph. Infrared spectra were obtained with a Perkin-Elmer FT 1600 instrument using NaCl salt plates (thin film). Microanalyses were performed by the Service de Microanalyse, Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif sur Yvette, France. Flash chromatography was performed on E. Merck silica gel Si 60 (40–63 µm). Analytical TLC was performed on Merck precoated silica 60-F$_{254}$ plates. THF was distilled from sodium/benzophenone. HMPA was distilled under vacuum in the presence of calcium hydride. All air- and/or water-sensitive reactions were carried out under argon with dry, freshly distilled solvents using standard syringe/cannula/septa techniques. All glassware was oven dried (110 °C) and/or carefully dried with a flameless heat gun.

(*E*)-3-(Tributylstannyl)prop-2-enal 6: This aldehyde was synthesised from propiolaldehyde diethyl acetal according to a slightly modified procedure from Knochel's group.[38] A solution of *n*-butyllithium in hexanes (21.70 mL, 33.6 mmol, 2.4 equiv.) was added to a suspension of CuCN (1.51 g, 16.8 mmol, 1.2 equiv.) in 100 mL of THF at –78 °C. The mixture was stirred at –78 °C for 20 min, then the temperature was allowed to rise to –40 °C for an additional 20 min. The solution was recooled to –78 °C and tributyltin hydride (9.05 mL, 33.6 mmol, 2.4 equiv.) was added dropwise. The reaction mixture was stirred at this temperature for 30 min before 3,3-diethoxyprop-1-yne (2.0 mL, 14.0 mmol) was added dropwise. The orange solution was stirred for 2 h at –78 °C, then 2 mL of methanol was added and the reaction mixture was warmed to 0 °C. A saturated aqueous $NaHCO_3$ solution (instead of NH_4Cl in the original paper; 60 mL) was added to the resulting red mixture. After decantation and separation, the aqueous layer was extracted three times with 100 mL of diethyl ether. The organic layers were washed with brine, dried with $MgSO_4$, filtered and concentrated in vacuo. The crude product was dissolved in 45 mL of CH_2Cl_2 and 33 g of silica was added. The suspension was stirred until it became homogeneous, and 3.3 mL of a 10% aqueous oxalic acid solution were added. After 15 min of stirring, the mixture was added to 1.1 g of $NaHCO_3$, and filtered. The filtrate was washed with brine, dried with $MgSO_4$, filtered again and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 80:20) to give 4.65 g of γ-stannylated aldehyde **6** (96% yield). All spectroscopic data are in agreement with those reported.

1-(*tert*-Butyldimethyl)silyloxy-3,3-bis(tributylstannyl)propene 5. From (*E*)-3-(Tributylstannyl)prop-2-enal (6): The preparation of 20.3 g of **5** from 13 g of the above aldehyde **6** has already been described.[17] **From (*E*)-3-[(4-Methoxyphenyl)sulfanyl]prop-2-enal (7):** The same procedure as for **6** was carried out with (*E*)-3-(4-methoxyphenylsulfanyl)prop-2-enal (**7**;[39] 194 mg, 1 mmol) to give, after trapping the reaction mixture with *tert*-butyldimethylsilyl chloride (452 mg, 3 mmol, 3 equiv.) and silica gel column chromatography, 403 mg of the *gem*-distannylated silyl enol ether **5** (54% yield, (*E*)/(*Z*) = 95:5). **From the Sodium Salt of Malonaldehyde (8):** The salt **8** was prepared according to Gomez-Sanchez et al.[40] Commercially available malonaldehyde bis(dimethylacetal) (8.2 g, 50 mmol) was stirred with Dowex 50X8-200 resin (40 g) in water (100 mL) for 1 h. The resin was filtered off and the filtrate adjusted to pH = 8.0 with 5 M aqueous NaOH solution. The solution was concentrated and the syrupy residue triturated with acetone to yield a solid, which was filtered off. Recrystallisation from an acetone/water mixture afforded 4.48 g of **8** (80% yield, all data are in agreement with those reported by the authors). Crystalline **8**, known to be associated with 1 equiv. of H_2O, was then transformed into the corresponding tosylate according to David et al.,[41] then directly transformed into **5**. Thus, *p*-toluenesulfonyl chloride (1.81 g, 9.5 mmol, 0.95 equiv.) and 18-crown-6 (30 mg) were added to a suspension of **8** (1.12 g, 10 mmol, 1 equiv.) in 20 mL of THF. The mixture was stirred at room temperature for 2 h. In a second flask, a suspension of CuCN (2.69 g, 30 mmol, 3 equiv.) in 200 mL of THF at –78 °C was added dropwise to a 1.55 M solution of *n*-butyllithium in hexanes (38.7 mL, 60 mmol, 6 equiv.). The mixture was stirred at –40 °C for 30 min and then cooled to –78 °C. Tributyltin hydride (16.2 mL, 60 mmol, 6 equiv.) was added dropwise to the pale-yellow solution and the resultant dark yellow mixture was stirred at –40 °C for 30 min, then cooled to –78 °C. The preceding β-tosyloxyacrolein solution was then added dropwise with a cannula. The resulting red solution was stirred at –78 °C for 1 h and then HMPA (17.4 mL, 0.1 mol, 10 equiv.) was added dropwise. After stirring at –78 °C for a further 15 min, a solution of *tert*-butyldimethylsilyl chloride (6.0 g, 40 mmol, 4 equiv.) in 20 mL of THF was added dropwise. After 1 h at –78 °C, 100 mL of a saturated aqueous $NaHCO_3$ solution was added and the mixture was warmed to room temperature. The organic layer was separated and the aqueous layer was extracted three times with 200 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by two successive silica gel flash chromatography columns (100% petroleum ether) to give 2.5 g of **5** [35% yield, (*E*)/(*Z*) = 95:5].

General Procedure for the Condensation Reactions of 1-[(*tert*-Butyldimethyl)silyloxy]-3,3-bis(tributylstannyl)propene (5) with Aldehydes:[17] $BF_3{\cdot}OEt_2$ (40 µL, 0.29 mmol, 1.1 equiv.) was added dropwise to a solution of aldehyde (0.29 mmol, 1.1 equiv.) in dichloromethane (3 mL) at –78 °C. The mixture was stirred at –78 °C for 5 min and then a solution of 1-[(*tert*-butyldimethyl)silyloxy]-3,3-bis(tributylstannyl)propene (**5**; 200 mg, 0.27 mmol) in dichloromethane (2 mL) and $BF_3{\cdot}OEt_2$ (100 µL, 0.80 mmol, 3.0 equiv.) were added successively. The reaction mixture was stirred at –78 °C for 15 min and quenched at this temperature by addition of 5 mL of a saturated aqueous $NaHCO_3$ solution. The resulting mixture was warmed to room temperature and, after decantation, the aqueous layer was extracted three times with 15 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 95:5) to give the corresponding allylation product **9a**–**h**.

(1*E*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-5-methyl-1-(tributylstannyl)hex-1-ene-4-ol (9a):** The $BF_3{\cdot}OEt_2$-promoted condensation of **5** with isobutyraldehyde was carried out according to the general procedure to afford 141 mg of *syn*-**9a** (quantitative yield). ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.20 (d, J = 19.1 Hz, 1 H, $J_{^{117}Sn,H}$ = 70.9, $J_{^{119}Sn,H}$ = 72.8 Hz, H-1), 5.95 (dd, J = 19.1, 6.8 Hz, 1 H, $J_{^{117}Sn,H}$ = 60.0, $J_{^{119}Sn,H}$ = 62.8 Hz, H-2), 4.02 (dd, J = 6.8, 5.8 Hz, 1 H, H-3), 3.17 (dt, J = 5.8, 4.3 Hz, 1 H, H-4), 2.46 (d, J = 4.3 Hz, 1 H, OH), 1.74 (m, 1 H, H-5), 1.46 (m, 6 H, $3\times CH_3CH_2C\mathit{H}_2CH_2$), 1.32 (m, 6 H, $3\times CH_3C\mathit{H}_2CH_2CH_2$), 0.92 [m, 30 H, $(CH_3)_2CH$ + $3\times C\mathit{H}_3CH_2CH_2C\mathit{H}_2$ + $(CH_3)_3CSi$], 0.09, 0.06 [2 s, 2 × 3 H, $(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 149.0 (C-2), 131.3 (C-1), 79.4, 78.9 (C-3, C-4), 29.6 (C-5), 29.3 ($J_{Sn,C}$ = 20 Hz, $3\times CH_3CH_2\mathit{C}H_2CH_2$), 27.9 ($J_{Sn,C}$ = 53 Hz, $3\times CH_3\mathit{C}H_2CH_2CH_2$), 26.1 [$(\mathit{C}H_3)_3CSi$], 20.3 (C-6), 18.3 [$(CH_3)_3\mathit{C}Si$], 16.7 (C-6), 13.8 ($3\times \mathit{C}H_3CH_2CH_2CH_2$), 9.7 ($J_{^{117}Sn,C}$ = 320, $J_{^{119}Sn,C}$ = 342 Hz, $3\times CH_3CH_2CH_2\mathit{C}H_2$), –3.6, –4.6 [$(CH_3)_2Si$] ppm. MS (CI, NH_3): *m*/*z* (%) = 535 [M^+ + 1], 494, 477, 420, 403, 364, 308 (100), 291, 266, 132. IR (neat): $\tilde{\nu}$ = 3582, 2956, 2927, 2870, 2855, 2360, 1463, 1253, 1084, 836, 777 cm^{-1}. $C_{25}H_{54}O_2SiSn$ (533.47): calcd. C 56.28, H 10.20; found C 56.34, H 10.17.

(3*E*,1*R,2*R**)-2-[(*tert*-Butyldimethylsilyl)oxy]-1-cyclohexyl-4-(tributylstannyl)but-3-en-1-ol (9b):** The $BF_3{\cdot}OEt_2$-promoted condensation of **5** with cyclohexanecarboxaldehyde was carried out according to the general procedure to afford 145 mg of a 93:7 mixture of *syn* and *anti* isomers of **9b** (95% yield). ^1H NMR ($CDCl_3$, 400 MHz, 93:7 *syn*/*anti* mixture): *syn* isomer: δ = 6.20 (d, J = 19.2 Hz, 1 H, $J_{Sn,H}$ = 71.0 Hz, H-4), 5.96 (dd, J = 19.2, 6.7 Hz, 1 H, $J_{Sn,H}$ = 63.0 Hz, H-3), 4.07 (t, J = 6.5 Hz, 1 H, H-2), 3.16 (dt, J = 6.3, 4.4 Hz, 1 H, H-1), 2.41 (d, J = 4.4 Hz, 1 H, OH), 1.77 (m, 1 H, CH), 1.48 (m, 6 H, $3\times CH_3CH_2C\mathit{H}_2CH_2$), 1.32 (m, 6 H, $3\times CH_3C\mathit{H}_2CH_2CH_2$), 1.70–1.15 (m, 10 H, $5\times CH_2$), 0.97–0.87 [m, 24 H, $3\times C\mathit{H}_3CH_2CH_2C\mathit{H}_2$ + $(CH_3)_3CSi$], 0.09, 0.06 [2 s, 2 × 3 H, $(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 93:7 *syn*/*anti* mixture): *syn* isomer: δ = 149.1 (C-3), 131.2 ($J_{Sn,C}$ = 379 Hz, C-4), 78.9 ($J_{Sn,C}$ = 64 Hz, C-2), 78.4 (C-1), 39.7 (CH), 30.6 (CH_2), 29.3 ($J_{Sn,C}$ = 19 Hz, $3\times CH_3CH_2\mathit{C}H_2CH_2$), 27.4 ($J_{Sn,C}$ = 47 Hz, $3\times CH_3\mathit{C}H_2CH_2CH_2$), 26.7 ($CH_2$), 26.5 ($CH_2$), 26.0 [$(\mathit{C}H_3)_3CSi$], 18.3 [$(CH_3)_3\mathit{C}Si$], 13.8 ($3\times \mathit{C}H_3CH_2CH_2CH_2$), 9.7 ($J_{Sn,C}$ = 343 Hz, $3\times CH_3CH_2CH_2\mathit{C}H_2$), –3.6, –4.6 [$(CH_3)_2Si$] ppm. MS (CI, NH_3): *m*/*z* (%) = 575 [M^+ + 1], 517, 443, 291 (100), 95, 58. IR (neat): $\tilde{\nu}$ = 3582, 2955, 2926, 2868, 2853, 2351, 1600, 1463, 1253, 1088, 836, 777 cm^{-1}. $C_{28}H_{58}O_2SiSn$ (573.53): calcd. C 58.63, H 10.19; found C 59.23, H, 10.31.

(1*E*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-(tributylstannyl)-hex-1-ene-4-ol (9c):** The $BF_3{\cdot}OEt_2$-promoted condensation of **5** with propionaldehyde was carried out according to the general procedure to afford 139 mg of an inseparable 87:13 mixture of *syn* and *anti* isomers of **9c** (quantitative yield). ^1H NMR ($CDCl_3$, 400 MHz, 87:13 *syn*/*anti* mixture): *syn* isomer: δ = 6.18 (dd, J = 19.1, 0.7 Hz, 1 H, $J_{^{117}Sn,H} = J_{^{119}Sn,H}$ = 70.6 Hz, H-1), 5.93 (dd, J = 19.1, 6.5 Hz, 1 H, $J_{^{117}Sn,H}$ = 60.6, $J_{^{119}Sn,H}$ = 63.6 Hz, H-2), 3.85 (t, J = 6.4 Hz, 1 H, H-3), 3.32 (m, J = 8.5 Hz, 1 H, 6.4, 3.7 Hz, H-4), 3.02 (d, J = 3.7 Hz, 1 H, OH), 1.66 (q, J = 7.6 Hz, 2 H, H_2-5), 1.48 (m, 6 H, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 1.30 (m, 6 H, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 0.99 (t, J = 7.5 Hz, 3 H, H_3-6), 0.96–0.80 [m, 24 H, $3\times \mathit{CH_3}CH_2CH_2\mathit{CH_2}$ + $(CH_3)_3CSi$], 0.10, 0.05 [2 s, 2 × 3 H, $(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 87:13 *syn*/*anti* mixture): *syn* isomer: δ = 148.6 (C-2), 131.6 ($J_{Sn,C}$ = 365 Hz, C-1), 80.8 ($J_{Sn,C}$ = 68 Hz, C-3), 76.1 (C-4), 29.3 ($J_{Sn,C}$ = 23 Hz, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 27.3 ($J_{Sn,C}$ = 57 Hz, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 26.0 [$(\mathit{CH_3})_3CSi$], 25.7 (C-5), 18.3 [$(CH_3)_3\mathit{C}Si$], 13.8 ($3\times \mathit{CH_3}CH_2CH_2CH_2$), 10.3 (C-6), 9.6 ($J_{^{117}Sn,C}$ = 320, $J_{^{119}Sn,C}$ = 342 Hz, $3\times CH_3CH_2CH_2\mathit{CH_2}$), –3.8, –4.7 [$(CH_3)_2Si$] ppm. MS (CI, NH_3): m/z (%) = 521 [M^+ + 1], 480, 308 (100), 291, 250, 213, 132. IR (neat): $\tilde{\nu}$ = 3581, 2955, 2927, 2869, 2855, 1601, 1463, 1253, 1083, 837, 777 cm^{-1}. $C_{24}H_{52}O_2SiSn$ (519.44): calcd. C 55.49, H 10.09; found C 55.89, H 10.21.

(3*E*,1*R,2*R**)-2-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyl-3-(tributylstannyl)but-3-en-1-ol (9d):** The $BF_3\cdot OEt_2$-promoted condensation of **5** with benzaldehyde was carried out according to the general procedure to afford 145 mg of a 95:5 mixture of *syn* and *anti* isomers of **9d** (96% yield). ^1H NMR ($CDCl_3$, 400 MHz, 95:5 *syn*/*anti* mixture): *syn* isomer: δ = 7.50–7.20 (m, 5 H, H_{ar}), 6.03 (dd, J = 19.1, 0.6 Hz, 1 H, $J_{^{117}Sn,H}$ = 66.4, $J_{^{119}Sn,H}$ = 87.5 Hz, H-4), 5.89 (dd, J = 19.1, 5.9 Hz, 1 H, $J_{^{117}Sn,H}$ = 57.4, $J_{^{119}Sn,H}$ = 60.4 Hz, H-3), 4.48 (dd, J = 6.4, 3.1 Hz, 1 H, H-1), 4.09 (dd, J = 6.4, 5.9 Hz, 1 H, H-2), 3.09 (d, J = 3.1 Hz, 1 H, OH), 1.43 (m, 6 H, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 1.30 (m, 6 H, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 0.93–0.86 [m, 24 H, $3\times \mathit{CH_3}CH_2CH_2\mathit{CH_2}$ + $(CH_3)_3CSi$], 0.01, –0.01 [2 s, 2 × 3 H, $(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 95:5 *syn*/*anti* mixture): *syn* isomer: δ = 147.8 (C-3), 141.2 (C_{ar}), 131.8 ($J_{Sn,C}$ = 375 Hz, C-4), 128.0, 127.7, 127.4 ($5\times CH_{ar}$), 82.1 ($J_{Sn,C}$ = 83 Hz, C-2), 77.9 (C-1), 29.3 ($J_{Sn,C}$ = 20 Hz, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 27.3 ($J_{Sn,C}$ = 42 Hz, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 26.1 [$(\mathit{CH_3})_3CSi$], 18.5 [$(CH_3)_3\mathit{C}Si$], 13.7 ($3\times \mathit{CH_3}CH_2CH_2CH_2$), 9.8 ($J_{Sn,C}$ = 332 Hz, $3\times CH_3CH_2CH_2\mathit{CH_2}$), –4.0, –4.7 [$(CH_3)_2Si$] ppm. MS (CI, NH_3): m/z (%) = 569 [M^+ + 1], 528, 308 (100), 291, 132. IR (neat): $\tilde{\nu}$ = 3564, 3086, 3063, 3031, 2955, 2927, 2869, 2855, 2359, 2341, 1602, 1463, 1253, 1081, 881, 778, 698 cm^{-1}.

(1*E*,5*E*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-(tributylstannyl)hepta-1,5-dien-4-ol (9e):** The $BF_3\cdot OEt_2$-promoted condensation of **5** with (*E*)-crotonaldehyde was carried out according to the general procedure to afford 128 mg of a 90:10 mixture of *syn* and *anti* isomers of **9e** (90% yield). ^1H NMR ($CDCl_3$, 200 MHz, 90:10 *syn*/*anti* mixture): *syn* isomer: δ = 6.19 (d, J = 19.2 Hz, 1 H, $J_{^{117}Sn,H}$ = 69.1, $J_{^{119}Sn,H}$ = 71.0 Hz, H-1), 5.93 (dd, J = 19.2, 5.8 Hz, 1 H, $J_{^{117}Sn,H}$ = 53.8, $J_{^{119}Sn,H}$ = 57.6 Hz, H-2), 5.72 (dq, J = 15.4, 6.4 Hz, 1 H, H-6), 5.44 (ddq, J = 15.4, 4.6, 1.3 Hz, 1 H, H-5), 3.90 (m, 2 H, H-3 + H-4), 2.59 (d, J = 3.0 Hz, 1 H, OH), 1.70 (d, J = 6.4 Hz, 3 H, H_3-7), 1.45 (m, 6 H, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 1.30 (m, 6 H, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 0.94–0.86 [m, 24 H, $3\times \mathit{CH_3}CH_2CH_2\mathit{CH_2}$ + $(CH_3)_3CSi$], 0.09, 0.06 [2 s, 2 × 3 H, $(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 90:10 *syn*/*anti* mixture): *syn* isomer: δ = 147.0 (C-2), 131.4 ($J_{Sn,H}$ = 358 Hz, C-1), 130.1, 128.3 (C-5, C-6), 80.8 ($J_{Sn,C}$ = 69 Hz, C-3), 75.8 (C-4), 29.2 ($J_{Sn,C}$ = 23 Hz, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 27.3 ($J_{Sn,C}$ = 57 Hz, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 26.0 [$(\mathit{CH_3})_3CSi$], 18.3 [$(CH_3)_3\mathit{C}Si$], 17.8 (C-7), 13.7 ($3\times \mathit{CH_3}CH_2CH_2CH_2$), 9.6 ($J_{^{117}Sn,C}$ = 323, $J_{^{119}Sn,C}$ = 346 Hz, $3\times CH_3CH_2CH_2\mathit{CH_2}$), –3.9, –4.7 [$(CH_3)_2Si$] ppm. MS (CI, NH_3): m/z (%) = 533 [M^+ + 1], 308 (100), 291, 225, 132. IR (neat): $\tilde{\nu}$ = 3565, 2956, 2928, 2868, 2854, 1677, 1601, 1463, 1376, 1252, 1084, 837, 777 cm^{-1}. $C_{25}H_{52}O_2SiSn$ (531.45): calcd. C 56.50, H 9.86; found C 56.57, H 9.74.

(1*E*,5*E*,3*R,4*R**)-4-[(*tert*-Butyldimethylsilyl)oxy]-1,6-bis(tributylstannyl)hexa-1,5-dien-3-ol (9f):** *This condensation was carried on a 2.0-g scale.* The $BF_3\cdot OEt_2$-promoted condensation of **5** with 3-(tributylstannyl)prop-2-enal was carried out according to the general procedure to afford 2.09 g of an 88:12 mixture of *syn* and *anti* isomers of **9f** (97% yield). ^1H NMR ($CDCl_3$, 400 MHz, 88:12 *syn*/*anti* mixture): *syn* isomer: δ = 6.27 (d, J = 19.1 Hz, 1 H, $J_{Sn,H}$ = 71.8 Hz, H-1), 6.19 (d, J = 19.1 Hz, 1 H, H-6), 6.01 (dd, J = 19.1, 4.4 Hz, 1 H, H-2), 5.96 (dd, J = 19.1, 5.8 Hz, 1 H, H-5), 3.93 (m, 2 H, H-3 + H-4), 2.60 (d, J = 4.4 Hz, 1 H, OH), 1.48 (m, 12 H, $6\times CH_3CH_2\mathit{CH_2}CH_2$), 1.30 (m, 12 H, $6\times CH_3\mathit{CH_2}CH_2CH_2$), 0.90 [m, 39 H, $6\times \mathit{CH_3}CH_2CH_2\mathit{CH_2}$ + $(CH_3)_3CSi$], 0.09, 0.06 [2 s, 2 × 3 H, $(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 88:12 *syn*/*anti* mixture): *syn* isomer: δ = 148.0 (C-2), 147.1 ($J_{Sn,C}$ = 39 Hz, C-5), 131.2 (C-6), 129.6 (C-1), 80.4 ($J_{Sn,C}$ = 64 Hz, C-4), 77.8 ($J_{Sn,C}$ = 43 Hz, C-3), 29.2 ($J_{Sn,C}$ = 19 Hz, $6\times CH_3CH_2\mathit{CH_2}CH_2$), 27.4 ($J_{Sn,C}$ = 54 Hz, $6\times CH_3\mathit{CH_2}CH_2CH_2$), 26.0 [$(\mathit{CH_3})_3CSi$], 18.3 [$(CH_3)_3$-$\mathit{C}Si$], 13.8 ($6\times \mathit{CH_3}CH_2CH_2CH_2$), 9.6 ($J_{^{117}Sn,C}$ = 329, $J_{^{119}Sn,C}$ = 343 Hz, $6\times CH_3CH_2CH_2\mathit{CH_2}$), –3.9, –4.7 [$(CH_3)_2Si$] ppm. MS (CI, NH_3): m/z (%) = 791 [M^+ + 1 – 18], 777, 749, 675, 617, 443, 405, 347, 291 (100), 235, 57. IR (neat): $\tilde{\nu}$ = 3568, 2955, 2926, 2869, 2854, 1602, 1463, 1376, 1251, 1080, 991, 863, 778 cm^{-1}. $C_{36}H_{76}O_2SiSn_2$ (806.45): calcd. C 53.62, H 9.50; found C 53.74, H 9.51.

(1*E*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-(tributylstannyl)dec-1-en-5-yn-4-ol (*syn* Isomer) (9g):** The $BF_3\cdot OEt_2$-promoted condensation of **5** with hex-2-ynal was carried out according to the general procedure to afford 146 mg of a 75:25 mixture of *syn* and *anti* isomers of **9g** (96% yield). ^1H NMR ($CDCl_3$, 400 MHz, 75:25 *syn*/*anti* mixture): *syn* isomer: δ = 6.28 (dd, J = 19.1, 0.9 Hz, 1 H, $J_{Sn,H}$ = 69.4 Hz, H-1), 6.02 (dd, J = 19.1, 6.0 Hz, 1 H, $J_{^{117}Sn,H}$ = 59.1, $J_{^{119}Sn,H}$ = 62.0 Hz, H-2), 4.12 (ddt, J = 6.0, 4.9, 2.0 Hz, 1 H, H-4), 4.06 (td, J = 6.0, 0.9 Hz, 1 H, H-3), 2.60 (d, J = 4.9 Hz, 1 H, OH), 2.21 (m, J = 5.1 Hz, 2 H, 2.0 Hz, H_2-7), 1.60–1.20 (m, 16 H, $3\times CH_3\mathit{CH_2}\mathit{CH_2}CH_2$ + H_2-8 + H_2-9), 0.93–0.86 [m, 27 H, $3\times \mathit{CH_3}CH_2CH_2\mathit{CH_2}$ + H-3–10 + $(CH_3)_3CSi$], 0.08 [s, 6 H, $(CH_3)_2Si$] ppm; *anti* isomer: δ = 6.27 (dd, J = 19.1, 1.0 Hz, 1 H, $J_{Sn,H}$ = 69.4 Hz, H-1), 6.08 (dd, J = 19.1, 5.9 Hz, 1 H, $J_{^{117}Sn\text{-}H}$ = 61.2, $J_{^{119}Sn,H}$ = 65.9 Hz, H-2), 4.16 (m, 2 H, H-3 + H-4), 2.33 (d, J = 6.6 Hz, 2 H, OH), 2.22 (td, J = 6.8, 1.9 Hz, 2 H, H_2-7), 1.52 (m, 6 H, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 1.33 (m, 6 H, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 1.60–1.20 (m, 4 H, H_2-8 + H_2-9), 0.91 [m, 27 H, $3\times \mathit{CH_3}CH_2CH_2\mathit{CH_2}$ + H_3-10 + $(CH_3)_3CSi$], 0.12 [s, 6 H, $(CH_3)_2$-Si] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 75:25 *syn*/*anti* mixture): *syn* isomer: δ = 147.0 (C-2), 131.8 ($J_{Sn,C}$ = 349 Hz, C-1), 86.5 (C-6), 80.3 ($J_{Sn,H}$ = 70 Hz, C-3), 79.4 (C-5), 66.7 (C-4), 30.8 (C-8), 29.2 ($J_{Sn,C}$ = 18 Hz, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 27.9 ($J_{Sn,C}$ = 56 Hz, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 26.0 [$(\mathit{CH_3})_3CSi$], 22.1 (C-9), 18.6 (C-7), 18.4 [$(CH_3)_3\mathit{C}Si$], 13.8 ($3\times \mathit{CH_3}CH_2CH_2CH_2$), 13.7 (C-10), 9.6 ($J_{^{117}Sn,C}$ = 331, $J_{^{119}Sn,C}$ = 349 Hz, $3\times CH_3CH_2CH_2\mathit{CH_2}$), –4.1, –4.7 [$(CH_3)_2Si$] ppm; *anti* isomer: δ = 146.5 (C-2), 132.0 (C-1), 86.8 (C-6), 78.6 (C-3), 77.8 (C-5), 66.6 (C-4), 30.8 (C-8), 29.2 ($J_{Sn,C}$ = 18 Hz, $3\times CH_3CH_2\mathit{CH_2}CH_2$), 27.9 ($J_{Sn,C}$ = 56 Hz, $3\times CH_3\mathit{CH_2}CH_2CH_2$), 26.0 [$(\mathit{CH_3})_3CSi$], 22.1 (C-9), 18.6 (C-7), 18.4 [$(CH_3)_3\mathit{C}Si$], 13.8 ($3\times \mathit{CH_3}CH_2CH_2CH_2$), 13.7 (C-10), 9.6 ($J_{^{117}Sn,C}$ = 331, $J_{^{119}Sn,C}$ = 349 Hz, $3\times CH_3CH_2CH_2\mathit{CH_2}$), –4.1, –4.7 [$(CH_3)_2Si$] ppm. MS (CI, NH_3): m/z (%) = 573 [M^+ + 1], 532, 441, 308 (100), 291, 132. IR (neat): $\tilde{\nu}$ = 3463, 2956, 2927, 2869, 2855, 2232, 1602, 1463, 1252, 1098, 837, 778 cm^{-1}. $C_{28}H_{56}O_2SiSn$ (571.52): calcd. C 58.84, H 9.88; found C 58.63, H 10.01.

(1*E*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-(tributylstannyl)-6-(trimethylsilyl)hex-1-en-5-yn-4-ol (*syn* Isomer) (9h):** The $BF_3\cdot OEt_2$-

promoted condensation of **5** with (trimethylsilyl)propiolaldehyde was carried out according to the general procedure already described to afford 152 mg of a 66:33 mixture of *syn* and *anti* isomers of **9h** (97% yield). ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz, 66:33 *syn*/*anti* mixture): *syn* isomer: δ = 6.29 (d, J = 19.1 Hz, 1 H, $J_{^{117}\mathrm{Sn,H}} = J_{^{119}\mathrm{Sn,H}}$ = 76.4 Hz, H-1), 6.01 (dd, J = 19.2, 5.6 Hz, 1 H, $J_{^{117}\mathrm{Sn,H}}$ = 45.1, $J_{^{119}\mathrm{Sn,H}}$ = 48.6 Hz, H-2), 4.27–4.10 (m, 2 H, H-3, H-4), 2.64 (d, J = 5.6 Hz, 1 H, OH), 1.51 (m, 6 H, $3\times\mathrm{CH_3CH_2C}\mathit{H}_2\mathrm{CH_2}$), 1.30 (m, 6 H, $3\times\mathrm{CH_3C}\mathit{H}_2\mathrm{CH_2CH_2}$), 0.96–0.88 [m, 24 H, $3\times\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2C}\mathit{H}_2$ and $(\mathrm{CH_3})_3\mathrm{CSi}$], 0.17 [s, 9 H, $(\mathrm{CH_3})_3\mathrm{Si}$], 0.08 [s, 6 H, $(\mathrm{CH_3})_2\mathrm{Si}$] ppm; *anti* isomer: δ = 6.31 (d, J = 19.2 Hz, 1 H, $J_{^{117}\mathrm{Sn,H}} = J_{^{119}\mathrm{Sn,H}}$ = 76.4 Hz, H-1), 6.08 (dd, J = 19.2, 5.8 Hz, 1 H, H-2), 4.24 (m, 2 H, H-3, H-4), 2.34 (d, J = 6.6 Hz, 1 H, OH), 1.51 (m, 6 H, $3\times\mathrm{CH_3CH_2C}\mathit{H}_2\mathrm{CH_2}$), 1.30 (m, 6 H, $3\times\mathrm{CH_3C}\mathit{H}_2\mathrm{CH_2CH_2}$), 0.96–0.88 [m, 24 H, $3\times\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2C}\mathit{H}_2$ + $(\mathrm{CH_3})_3\mathrm{CSi}$], 0.13 [s, 9 H, $(\mathrm{CH_3})_3\mathrm{Si}$], 0.10 [s, 6 H, $(\mathrm{CH_3})_2\mathrm{Si}$] ppm. ^{13}C NMR ($\mathrm{CDCl_3}$, 50.3 MHz, 66:33 *syn*/*anti* mixture): *syn* isomer: δ = 146.9 (C-2), 132.5 ($J_{\mathrm{Sn,C}}$ = 360 Hz, C-1), 104.6 (C-5), 90.2 (C-6), 79.8 ($J_{\mathrm{Sn,C}}$ = 57 Hz, C-3), 66.7 (C-4), 29.2 ($J_{\mathrm{Sn,C}}$ = 23 Hz, $3\times\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2CH_2}$), 27.4 ($J_{\mathrm{Sn,C}}$ = 50 Hz, $3\times\mathrm{CH_3}\mathit{C}\mathrm{H_2CH_2CH_2}$), 26.0 [$(\mathit{C}\mathrm{H_3})_3\mathrm{CSi}$], 18.4 [$(\mathrm{CH_3})_3\mathit{C}\mathrm{Si}$], 13.8 ($3\times\mathit{C}\mathrm{H_3CH_2CH_2CH_2}$), 9.6 ($J_{^{117}\mathrm{Sn,C}}$ = 328, $J_{^{119}\mathrm{Sn,C}}$ = 340 Hz, $3\times\mathrm{CH_3CH_2CH_2}\mathit{C}\mathrm{H_2}$), 0.0 [$(\mathrm{CH_3})_3\mathrm{Si}$], –4.1, –4.6 [$(\mathrm{CH_3})_2\mathrm{Si}$] ppm; *anti* isomer: δ = 146.5 (C-2), 132.7 (C-1), 104.1 (C-5), 90.8 (C-6), 79.2 ($J_{\mathrm{Sn,C}}$ = 68 Hz, C-3), 67.0 (C-4), 29.4 ($J_{\mathrm{Sn,C}}$ = 23 Hz, $3\times\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2CH_2}$), 27.4 ($J_{\mathrm{Sn,C}}$ = 50 Hz, $3\times\mathrm{CH_3}\mathit{C}\mathrm{H_2CH_2CH_2}$), 26.0 [$(\mathit{C}\mathrm{H_3})_3\mathrm{CSi}$], 18.4 [$(\mathrm{CH_3})_3\mathit{C}\mathrm{Si}$], 13.8 ($3\times\mathit{C}\mathrm{H_3CH_2CH_2CH_2}$), 9.7 ($J_{^{117}\mathrm{Sn,C}}$ = 328, $J_{^{119}\mathrm{Sn,C}}$ = 340 Hz, $3\times\mathrm{CH_3CH_2CH_2}\mathit{C}\mathrm{H_2}$), 0.0 [$(\mathrm{CH_3})_3\mathrm{Si}$], –4.1, –4.6 [$(\mathrm{CH_3})_2\mathrm{Si}$] ppm. MS (CI, $\mathrm{NH_3}$): *m*/*z* (%) = 589 [$\mathrm{M^+}$ + 1], 308 (100), 291. IR (neat): $\tilde{\nu}$ = 3457, 2956, 2927, 2868, 2855, 2175, 1602, 1463, 1373, 1250, 1107, 1074, 1053, 989, 916, 841, 778, 760 cm^{-1}. $\mathrm{C_{27}H_{56}O_2Si_2Sn}$ (587.59): calcd. C 55.19, H 9.61; found C 55.41, H 9.87.

(1*E*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-(*p*-tolylsulfonyl)-6-(trimethylsilyl)hex-1-en-5-yn-4-ol (*syn* Isomer) (10):** A solution of vinylstannane **9h** (1.825 g, 3.11 mmol, 2:1 *syn*/*anti* mixture) in THF (4 mL) and *p*-toluenesulfonyl chloride (593 mg, 3.73 mmol, 1.2 equiv.) were added at room temperature to a solution of [$\mathrm{Pd(PPh_3)_4}$] (108 mg, 0.09 mmol, 0.03 equiv.) in THF (3 mL) and the reaction mixture was stirred at reflux for 2 h. After cooling to room temperature, the resulting mixture was poured into 20 mL of water, and 50 mL of diethyl ether was added. The phases were separated and the aqueous layer was extracted three times with 50 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous $\mathrm{MgSO_4}$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 95:5) to give 660 mg of **10** as a inseparable 2:1 mixture of *syn* and *anti* diastereoisomers (47% yield). ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz, 2:1 *syn*/*anti* mixture): *syn* isomer: δ = 7.78 (d, J = 8.3 Hz, 2 H, $2\times\mathrm{H_{ar}}$), 7.34 (d, J = 8.3 Hz, 2 H, $2\times\mathrm{H_{ar}}$), 7.00 (dd, J = 15.0, 4.6 Hz, 1 H, H-2), 6.57 (dd, J = 15.0, 1.5 Hz, 1 H, H-1), 4.39 (m, 1 H, H-3), 4.22 (dd, J = 6.4, 5.2 Hz, 1 H, H-4), 2.45 (s, 3 H, $\mathrm{CH_3\text{-}C_{ar}}$), 2.40 (d, J = 6.3 Hz, 1 H, OH), 0.89 [s, 9 H, $(\mathrm{CH_3})_3\mathrm{CSi}$], 0.15 [s, 9 H, $(\mathrm{CH_3})_3\mathrm{Si}$], 0.11 [s, 3 H, $(\mathrm{CH_3})_2\mathrm{Si}$], 0.02 [s, 3 H, $(\mathrm{CH_3})_2\mathrm{Si}$] ppm; *anti* isomer: δ = 7.79 (d, J = 8.3 Hz, 2 H, $2\times\mathrm{H_{ar}}$), 7.34 (d, J = 8.3 Hz, 2 H, $2\times\mathrm{H_{ar}}$), 7.07 (dd, J = 14.9, 4.2 Hz, 1 H, H-2), 6.58 (dd, J = 14.9, 1.6 Hz, 1 H, H-1), 4.39 (m, 2 H, H-3, H-4), 2.45 (s, 3 H, $\mathrm{CH_3\text{-}C_{ar}}$), 2.24 (d, J = 5.4 Hz, 1 H, OH), 0.89 [s, 9 H, $(\mathrm{CH_3})_3\mathrm{CSi}$], 0.15 [s, 9 H, $(\mathrm{CH_3})_3\mathrm{Si}$], 0.10 [s, 3 H, $(\mathrm{CH_3})_2\mathrm{Si}$], 0.02 [s, 3 H, $(\mathrm{CH_3})_2\mathrm{Si}$] ppm. ^{13}C NMR ($\mathrm{CDCl_3}$, 50.3 MHz, 2:1 *syn*/*anti* mixture): *syn* isomer: δ = 144.4 ($\mathit{C}_{\mathrm{ar}}\text{-}\mathrm{CH_3}$), 143.7 (C-2), 137.5 ($\mathrm{C_{ar}\text{-}SO_2}$), 132.9 (C-1), 130.0 ($2\times\mathrm{CH_{ar}}$), 127.8 ($2\times\mathrm{CH_{ar}}$), 102.8 (C-5), 92.1 (C-6), 74.3 (C-3), 66.0 (C-4), 25.8 [$(\mathit{C}\mathrm{H_3})_3\mathrm{CSi}$], 21.6 ($\mathit{C}\mathrm{H_3\text{-}C_{ar}}$), 18.2 [$(\mathrm{CH_3})_3\mathit{C}\mathrm{Si}$], –0.3 [$(\mathrm{CH_3})_3\mathrm{Si}$], –4.6 [$(\mathrm{CH_3})_2\mathrm{Si}$], –4.8 [$(\mathrm{CH_3})_2\mathrm{Si}$] ppm; *anti* isomer: δ = 144.4 ($\mathit{C}_{\mathrm{ar}}\text{-}\mathrm{CH_3}$), 143.7 (C-2), 137.5 ($\mathrm{C_{ar}\text{-}SO_2}$), 132.9 (C-1), 130.0 ($2\times\mathrm{CH_{ar}}$), 127.8 ($2\times\mathrm{CH_{ar}}$), 102.4 (C-5), 92.5 (C-6), 74.0 (C-3), 66.3 (C-4), 25.8 [$(\mathit{C}\mathrm{H_3})_3\mathrm{CSi}$], 21.6 ($\mathit{C}\mathrm{H_3\text{-}C_{ar}}$), 18.2 [$(\mathrm{CH_3})_3\mathit{C}\mathrm{Si}$], –0.3 [$(\mathrm{CH_3})_3\mathrm{Si}$], –4.6 [$(\mathrm{CH_3})_2\mathrm{Si}$], –4.8 [$(\mathrm{CH_3})_2\mathrm{Si}$] ppm. MS (CI, $\mathrm{NH_3}$): *m*/*z* (%) = 470 (100) [$\mathrm{M^+}$ + 18], 453 [$\mathrm{M^+}$ + 1], 344. IR (neat): $\tilde{\nu}$ = 3476, 2955, 2929, 2857, 2176, 1597, 1318, 1251, 1144, 1086, 841, 779 cm^{-1}. $\mathrm{C_{22}H_{36}O_4SSi_2}$: calcd. C 58.36, H 8.01; found C 58.45, H 8.14.

(1*Z*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-(*p*-tolylsulfonyl)-1-(tributylstannyl)-6-(trimethylsilyl)hex-1-en-5-yn-4-ol (*syn* Isomer) (11):** A 1 M MeLi·LiBr solution in hexanes (0.45 mmol, 2.1 equiv., 460 µL) was added dropwise to a solution of vinyl sulfone **10** (100 mg, 0.22 mmol, 1.0 equiv., 2:1 *syn*/*anti* mixture) in THF (3 mL) cooled to –78 °C. The reaction mixture was stirred at this temperature for 30 min and tributyltin chloride (150 µL, 0.48 mmol, 2.2 equiv.) was added. The mixture was stirred again at –78 °C for 1 h and hydrolysed with a saturated aqueous $\mathrm{NaHCO_3}$ solution (5 mL). After warming to room temperature, the resulting mixture was diluted with 10 mL of diethyl ether. The phases were separated, and the aqueous layer was extracted three times with 20 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous $\mathrm{MgSO_4}$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether) to give 132 mg of the expected α-stannylated sulfone **11** as a 3:1 mixture of *syn* and *anti* diastereoisomers (82% yield). ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz, 3:1 *syn*/*anti* mixture): *syn* isomer: δ = 7.70 (d, J = 8.2 Hz, 2 H, $2\times\mathrm{H_{ar}}$), 7.31 (d, J = 8.2 Hz, 2 H, $2\times\mathrm{H_{ar}}$), 6.89 (d, J = 8.3 Hz, 1 H, $J_{^{117}\mathrm{Sn,H}}$ = 70.6, $J_{^{119}\mathrm{Sn,H}}$ = 73.2 Hz, H-2), 4.29 (dd, J = 8.3, 2.2 Hz, 1 H, H-3), 4.16 (dd, J = 10.0, 2.2 Hz, 1 H, H-4), 2.56 (d, J = 10.0 Hz, 1 H, OH), 2.43 (s, 3 H, $\mathrm{CH_3\text{-}C_{ar}}$), 1.60–1.40 (m, 12 H, $3\times\mathrm{CH_3C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2}$), 1.04–0.87 [m, 24 H, $3\times\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2C}\mathit{H}_2$ + $(\mathrm{CH_3})_3\mathrm{CSi}$], 0.16 [s, 9 H, $(\mathrm{CH_3})_3\mathrm{Si}$], 0.12 [s, 3 H, $(\mathrm{CH_3})_2\mathrm{Si}$], 0.04 [s, 3 H, $(\mathrm{CH_3})_2\mathrm{Si}$] ppm; *anti* isomer: δ = 7.73 (d, J = 8.2 Hz, 2 H, $2\times\mathrm{H_{ar}}$), 7.31 (d, J = 8.2 Hz, 2 H, $2\times\mathrm{H_{ar}}$), 6.80 (d, J = 8.4 Hz, 1 H, H-2), 4.24 (dd, J = 8.4, 4.7 Hz, 1 H, H-3), 4.08 (dd, J = 8.8, 4.7 Hz, 1 H, H-4), 2.43 (s, 3 H, $\mathrm{CH_3\text{-}C_{ar}}$), 2.38 (d, J = 8.8 Hz, 1 H, OH), 1.60–1.40 (m, 12 H, $3\times\mathrm{CH_3C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2}$), 1.04–0.87 [m, 24 H, $3\times\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2C}\mathit{H}_2$ + $(\mathrm{CH_3})_3\mathrm{CSi}$], 0.16 [s, 9 H, $(\mathrm{CH_3})_3\mathrm{Si}$], 0.08 [s, 3 H, $(\mathrm{CH_3})_2\mathrm{Si}$], 0.01 [s, 3 H, $(\mathrm{CH_3})_2\mathrm{Si}$] ppm. ^{13}C NMR ($\mathrm{CDCl_3}$, 200 MHz, 3:1 *syn*/*anti* mixture): *syn* isomer: δ = 153.3 (C-2), 151.0 (C-1), 143.8 ($\mathit{C}_{\mathrm{ar}}\text{-}\mathrm{CH_3}$), 137.3 ($\mathrm{C_{ar}\text{-}SO_2}$), 129.7 ($2\times\mathrm{CH_{ar}}$), 128.4 ($2\times\mathrm{CH_{ar}}$), 104.2 (C-5), 90.8 (C-6), 75.7 (C-3), 67.6 (C-4), 28.9 ($J_{\mathrm{Sn,C}}$ = 21 Hz, $3\times\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2CH_2}$), 27.3 ($J_{\mathrm{Sn,C}}$ = 70 Hz, $3\times\mathrm{CH_3}\mathit{C}\mathrm{H_2CH_2CH_2}$), 25.8 [$(\mathit{C}\mathrm{H_3})_3\mathrm{CSi}$], 21.6 ($\mathit{C}\mathrm{H_3\text{-}C_{ar}}$), 18.3 [$(\mathrm{CH_3})_3\mathit{C}\mathrm{Si}$], 13.6 ($3\times\mathit{C}\mathrm{H_3CH_2CH_2CH_2}$), 12.6 ($3\times\mathrm{CH_3CH_2CH_2}\mathit{C}\mathrm{H_2}$), –0.2 [$(\mathrm{CH_3})_3\mathrm{Si}$], –4.1 [$(\mathrm{CH_3})_2\mathrm{Si}$], –4.3 [$(\mathrm{CH_3})_2\mathrm{Si}$] ppm; *anti* isomer: δ = 152.4 (C-2), 152.0 (C-1), 143.8 ($\mathit{C}_{\mathrm{ar}}\text{-}\mathrm{CH_3}$), 137.3 ($\mathrm{C_{ar}\text{-}SO_2}$), 129.7 ($2\times\mathrm{CH_{ar}}$), 128.4 ($2\times\mathrm{CH_{ar}}$), 103.5 (C-5), 92.0 (C-6), 75.8 (C-3), 66.7 (C-4), 28.9 ($J_{\mathrm{Sn,C}}$ = 21 Hz, $3\times\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2CH_2}$), 27.3 ($J_{\mathrm{Sn,C}}$ = 70 Hz, $3\times\mathrm{CH_3}\mathit{C}\mathrm{H_2CH_2CH_2}$), 25.8 [$(\mathit{C}\mathrm{H_3})_3\mathrm{CSi}$], 21.6 ($\mathit{C}\mathrm{H_3\text{-}C_{ar}}$), 18.3 [$(\mathrm{CH_3})_3\mathit{C}\mathrm{Si}$], 13.6 ($3\times\mathit{C}\mathrm{H_3CH_2CH_2CH_2}$), 12.6 ($3\times\mathrm{CH_3CH_2CH_2}\mathit{C}\mathrm{H_2}$), –0.2 [$(\mathrm{CH_3})_3\mathrm{Si}$], –4.1 [$(\mathrm{CH_3})_2\mathrm{Si}$], –4.3 [$(\mathrm{CH_3})_2\mathrm{Si}$] ppm. MS (CI, $\mathrm{NH_3}$, 3:1 *syn*/*anti* mixture): *m*/*z* (%) = 760 [$\mathrm{M^+}$ + 18], 743 [$\mathrm{M^+}$ + 1], 685, 470 (100), 344, 308. IR (neat): $\tilde{\nu}$ = 3468, 2956, 2928, 2856, 2175, 1596, 1463, 1282, 1251, 1139, 1083, 843 cm^{-1}.

(1*Z*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-chloro-1-(*p*-tolylsulfonyl)-6-(trimethylsilyl)hex-1-en-5-yn-4-ol (*syn* Isomer) (12):** A solution of the preceding α-stannylated sulfone **11** (200 mg, 0.27 mmol, 3:1 *syn*/*anti* mixture) in THF (3 mL) was added at room temperature to a solution of anhydrous copper(II) chloride (91 mg, 0.67 mmol, 2.5 equiv.) in THF (3 mL). The reaction mixture was stirred at room temperature for 15 h and quenched at this temperature by addition of 10 mL of diethyl ether and 10 mL of a saturated aqueous NaHCO$_3$ solution. After decantation, the aqueous layer was extracted three times with 20 mL of diethyl ether and the combined organic layers were washed with brine, dried with anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 95:5) to give 100 mg of **12** as a 3:1 mixture of *syn* and *anti* diastereoisomers (76% yield). ^{1}H NMR (CDCl$_3$, 200 MHz, 3:1 *syn*/*anti* mixture): *syn* isomer: δ = 7.82 (d, J = 8.3 Hz, 2 H, 2×H$_{ar}$), 7.36 (d, J = 8.3 Hz, 2 H, 2×H$_{ar}$), 7.12 (dd, J = 8.6, 0.6 Hz, 1 H, H-2), 4.55 (dd, J = 8.6, 5.0 Hz, 1 H, H-3), 4.26 (ddd, J = 6.9, 5.0, 0.6 Hz, 1 H, H-4), 2.61 (d, J = 6.9 Hz, 1 H, OH), 2.46 (s, 3 H, CH$_3$-C$_{ar}$), 0.89 [s, 9 H, (CH$_3$)$_3$CSi], 0.12 [s, 9 H, (CH$_3$)$_3$Si], 0.08 [s, 3 H, (CH$_3$)$_2$Si], 0.04 [s, 3 H, (CH$_3$)$_2$Si] ppm; *anti* isomer: δ = 7.83 (d, J = 8.3 Hz, 2 H, 2×H$_{ar}$), 7.36 (d, J = 8.3 Hz, 2 H, 2×H$_{ar}$), 7.17 (d, J = 8.5 Hz, 1 H, H-2), 4.60 (dd, J = 8.5, 4.4 Hz, 1 H, H-3), 4.37 (dd, J = 6.0, 4.4 Hz, 1 H, H-4), 2.51 (d, J = 6.0 Hz, 1 H, OH), 2.46 (s, 3 H, CH$_3$-C$_{ar}$), 0.89 [s, 9 H, (CH$_3$)$_3$CSi], 0.12 [s, 9 H, (CH$_3$)$_3$Si], 0.08 [s, 3 H, (CH$_3$)$_2$Si], 0.04 [s, 3 H, (CH$_3$)$_2$Si] ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz, 3:1 *syn*/*anti* mixture): *syn* isomer: δ = 145.6 (*C*$_{ar}$-CH$_3$), 137.3 (C-2), 135.5, 134.8 (C-1, C$_{ar}$-SO$_2$), 130.0, 129.3 (4×CH$_{ar}$), 102.6 (C-5), 91.8 (C-6), 75.4 (C-3), 65.8 (C-4), 25.8 [(*C*H$_3$)$_3$CSi], 21.6 (*C*H$_3$-C$_{ar}$), 18.2 [(CH$_3$)$_3$*C*Si], –0.3 [(CH$_3$)$_3$Si], –4.5 [(CH$_3$)$_2$Si], –4.8 [(CH$_3$)$_2$Si] ppm; *anti* isomer: δ = 145.0 (*C*$_{ar}$-CH$_3$), 141.3 (C-2), 135.5, 134.8 (C-1, C$_{ar}$-SO$_2$), 130.0, 129.3 (4×CH$_{ar}$), 102.4 (C-5), 92.1 (C-6), 72.8 (C-3), 66.5 (C-4), 25.8 [(*C*H$_3$)$_3$CSi], 21.6 (*C*H$_3$-C$_{ar}$), 18.2 [(CH$_3$)$_3$*C*Si], –0.3 [(CH$_3$)$_3$Si], –4.5 [(CH$_3$)$_2$Si], –4.8 [(CH$_3$)$_2$Si] ppm. MS (CI, NH$_3$): m/z (%) = 504/506 (100) [M$^+$ + 18], 487/489 [M$^+$ + 1], 469/471. IR (neat): $\tilde{\nu}$ = 3492, 2957, 2928, 2857, 1597, 1463, 1334, 1251, 1160, 1087, 842 cm^{-1}.

(*E*)-2-[(*p*-Tolylsulfonyl)vinyl]furan (13): A crystal of *p*-toluenesulfonic acid was added to a solution of vinyl sulfone **10** (600 mg, 1.33 mmol, 2:1 *syn*/*anti* mixture) in 5 mL of ethanol. The reaction mixture was stirred at reflux for 48 h, and then cooled to room temperature. The dark solution was partitioned between 50 mL of diethyl ether and 20 mL of a saturated aqueous NaHCO$_3$ solution. The aqueous phase was extracted three times with 20 mL of diethyl ether and the combined organic phases were washed with brine, dried with anhydrous MgSO$_4$, filtered and concentrated in vacuo. Separation of the residue by silica gel flash chromatography (petroleum ether/diethyl ether, 90:10) gave 165 mg of pure **13** (50% yield). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.81 (d, J = 8.3 Hz, 2 H, 2×H$_{ar}$), 7.47 (d, J = 1.7 Hz, 1 H, H-5), 7.42 (d, J = 15.0 Hz, 1 H, H-1′), 7.34 (d, J = 8.3 Hz, 2 H, 2×H$_{ar}$), 6.74 (d, J = 15.0 Hz, 1 H, H-2′), 6.69 (d, J = 3.0 Hz, 1 H, H-3), 6.48 (dd, J = 3.0, 1.8 Hz, 1 H, H-4) ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ = 148.8 (C-2), 145.5 (C-1′), 143.7 (*C*$_{ar}$-CH$_3$), 138.2 (C$_{ar}$-SO$_2$), 130.0 (2×CH$_{ar}$), 128.5 (C-5 or C-2′), 127.7 (2×CH$_{ar}$), 126.0 (C-5 or C-2′), 116.3, 112.6 (C-4, C-3), 21.6 (*C*H$_3$-C$_{ar}$) ppm. MS (CI, NH$_3$): m/z (%) = 266 (100) [M$^+$ + 18], 249 [M$^+$ + 1]. IR (neat): $\tilde{\nu}$ = 3057, 2985, 2305, 1624, 1316, 1265, 1144, 1086, 1018, 839, 737, 665 cm^{-1}. ^{1}H NMR spectroscopic data for H-1′ and H-2′ are in agreement with those reported by Lee and Oh.[42]

(1*E*,3*R,4*R**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-chloro-6-(trimethylsilyl)hex-1-en-5-yn-4-ol (*syn* Isomer) (14):** A solution of vinylstannane **9h** (12.66 g, 21.6 mmol, 2:1 *syn*/*anti* mixture) in THF (60 mL) was added at room temperature to a solution of commercial anhydrous copper(II) chloride (7.25 g, 53.9 mmol, 2.5 equiv.) in THF (60 mL). The reaction mixture was stirred at room temperature for 15 h and quenched by addition of 150 mL of diethyl ether and 100 mL of a saturated aqueous NaHCO$_3$ solution. After decantation, the aqueous layer was extracted three times with 150 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 95:5) to give 6.24 g of **14** as a 2:1 mixture of *syn* and *anti* diastereoisomers (87% yield). ^{1}H NMR (CDCl$_3$, 200 MHz, 2:1 *syn*/*anti* mixture): *syn* isomer: δ = 6.26 (d, J = 13.3 Hz, 1 H, H-1), 6.00 (dd, J = 13.3, 6.5 Hz, 1 H, H-2), 4.24 (m, 2 H, H-3, H-4), 2.50 (d, J = 5.9 Hz, 1 H, OH), 0.93 [s, 9 H, (CH$_3$)$_3$CSi], 0.18 [s, 9 H, (CH$_3$)$_3$Si], 0.14 [s, 3 H, (CH$_3$)$_2$Si], 0.10 [s, 3 H, (CH$_3$)$_2$Si] ppm; *anti* isomer: δ = 6.26 (d, J = 13.3 Hz, 1 H, H-1), 6.06 (dd, J = 13.3, 6.0 Hz, 1 H, H-2), 4.24 (m, 2 H, H-3, H-4), 2.34 (d, J = 5.4 Hz, 1 H, OH), 0.93 [s, 9 H, (CH$_3$)$_3$CSi], 0.18 [s, 9 H, (CH$_3$)$_3$Si], 0.12 [s, 3 H, (CH$_3$)$_2$Si], 0.10 [s, 3 H, (CH$_3$)$_2$Si] ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz, 2:1 *syn*/*anti* mixture): *syn* isomer: δ = 132.2 (C-2), 121.7 (C-1), 104.0 (C-5), 91.6 (C-6), 75.4 (C-3), 67.0 (C-4), 26.0 [(*C*H$_3$)$_3$CSi], 18.3 [(CH$_3$)$_3$*C*Si], –0.1 [(CH$_3$)$_3$Si], –4.2 [(CH$_3$)$_2$Si], –4.5 [(CH$_3$)$_2$Si] ppm; *anti* isomer: δ = 132.7 (C-2), 121.7 (C-1), 103.4 (C-5), 92.1 (C-6), 75.0 (C-3), 67.0 (C-4), 26.0 [(*C*H$_3$)$_3$CSi], 18.3 [(CH$_3$)$_3$*C*Si], –0.1 [(CH$_3$)$_3$Si], –4.2 [(CH$_3$)$_2$Si], –4.5 [(CH$_3$)$_2$Si] ppm. MS (CI, NH$_3$): m/z (%) = 350/352 (100) [M$^+$ + 18], 333/335 [M$^+$ + 1], 315, 281, 201, 132, 90. IR (neat): $\tilde{\nu}$ = 3424, 3064, 2957, 2935, 2858, 2176, 1627, 1472, 1362, 1093, 934, 910, 841, 778, 735, 669 cm^{-1}.

(2′*E*,4*R,5*R**)-4-(2-Chlorovinyl)-2,2-dimethyl-5-[(trimethylsilyl)ethynyl][1,3]dioxolane (*syn* Isomer) (15):** A crystal of *p*-toluenesulfonic acid was added to a solution of vinyl chloride **14** (5 g, 15 mmol, 2:1 *syn*/*anti* mixture) in ethanol (100 mL). The reaction mixture was stirred at 55 °C for 15 h, then cooled to room temperature and concentrated in vacuo. The crude product was diluted with 2,2-dimethoxypropane (10 mL) and a crystal of *p*-toluenesulfonic acid. The solution was stirred at room temperature for 3 h then partitioned with 50 mL of diethyl ether and 50 mL of a saturated aqueous NaHCO$_3$ solution. After decantation, the aqueous layer was extracted three times with 100 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 95:5) to give, in order of elution, 1.99 g of acetonide *syn*-**15** (51% yield) and 1.03 g of *anti*-**15** (27% yield). ***syn*-15:** ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 6.42 (d, J = 13.3 Hz, 1 H, H-2′), 5.97 (dd, J = 13.3, 6.9 Hz, 1 H, H-1′), 4.41 (dd, J = 7.8, 6.9 Hz, 1 H, H-4), 4.32 (d, J = 7.8 Hz, 1 H, H-5), 1.50, 1.43 [2 s, 2×3 H, (CH$_3$)$_2$C], 0.19 [s, 9 H, (CH$_3$)$_3$Si] ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ = 129.1 (C-1′), 122.6 (C-2′), 110.5 [(CH$_3$)$_2$*C*], 100.4 (C-1″), 92.5 (C-2″), 80.3 (C-4), 70.8 (C-5), 26.8, 26.4 [(*C*H$_3$)$_2$C], –0.3 [(CH$_3$)$_3$CSi] ppm. MS (CI, NH$_3$): m/z (%) = 276/278 [M$^+$ + 18], 259/261 [M$^+$ + 1], 243/245, 218/220, 201/203, 168, 153, 131, 90 (100). IR (neat): $\tilde{\nu}$ = 2988, 2960, 2937, 2899, 2176, 1634, 1455, 1374, 1251, 1163, 1101, 1055, 932, 843, 761 cm^{-1}. ***anti*-15:** ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 6.36 (d, J = 13.3 Hz, 1 H, H-2′), 6.11 (dd, J = 13.3, 7.8 Hz, 1 H, H-1′), 4.81 (d, J = 6.0 Hz, 1 H, H-5), 4.32 (dd, J = 7.8, 6.0 Hz, 1 H, H-4), 1.57, 1.38 [2 s, 2×3 H, (CH$_3$)$_2$C], 0.20 [s, 9 H, (CH$_3$)$_3$Si] ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ = 129.5 (C-1′), 122.6 (C-2′), 110.6 [(CH$_3$)$_2$*C*], 100.8 (C-1″), 94.1 (C-2″), 76.9 (C-4), 69.5 (C-5), 27.6, 26.0 [(*C*H$_3$)$_2$C], –0.4 [(CH$_3$)$_3$CSi] ppm. MS (CI, NH$_3$): m/z (%) = 276/280 [M$^+$ + 18], 259/261 [M$^+$ + 1], 243/245, 218/220, 201/203, 168, 153, 131, 90 (100). IR (neat): $\tilde{\nu}$ = 3067, 2987, 2959, 2936, 2899, 2176, 1638, 1341, 1251, 1161, 1054, 935, 893, 846, 761 cm^{-1}.

(1*E*,3*R,4*R**)-3,4-Bis[(*tert*-butyldimethylsilyl)oxy]-1-(tributylstannyl)-6-(trimethylsilyl)hex-1-en-5-yne (*syn* Isomer) (16):** Imidazole (2.7 g, 39.7 mmol, 3.0 equiv.) was added to a solution of vinylstannane **9h** (7.76 g, 13.22 mmol, 2:1 *syn*/*anti* mixture) in DMF (10 mL) at room temperature. After complete dissolution, *tert*-butyldimethylsilyl chloride was added (3 g, 19.8 mmol, 1.5 equiv.). The reaction mixture was stirred at room temperature for 15 h, and then added to 100 mL of diethyl ether and 100 mL of water. After decantation, the aqueous layer was extracted three times with 100 mL of diethyl ether. The combined organic layers were washed three times with 100 mL of water, dried with anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 90:10) to give 9.15 g of bis(silyl ether) **16** as a 2:1 mixture of *syn* and *anti* diastereoisomers (99% yield). ^1H NMR ($CDCl_3$, 200 MHz, 2:1 *syn*/*anti* mixture): *syn* isomer: δ = 6.30 (d, J = 19.1 Hz, 1 H, H-1), 6.13 (dd, J = 19.1, 4.8 Hz, 1 H, H-2), 4.18 (d, J = 6.4 Hz, 1 H, H-4), 4.07 (m, 1 H, H-3), 1.51 (m, 6 H, $3\times CH_2C\mathit{H}_2CH_2CH_3$), 1.32 (m, 6 H, $3\times CH_2CH_2C\mathit{H}_2CH_3$), 0.97–0.86 [m, 33 H, $3\times C\mathit{H}_2CH_2CH_2C\mathit{H}_3$, $2\times(CH_3)_3CSi$], 0.16 [s, 9 H, $(CH_3)_3Si$], 0.13 [s, 6 H, $(CH_3)_2Si$], 0.09 [s, 3 H, $(CH_3)_2Si$], 0.06 [s, 3 H, $(CH_3)_2Si$] ppm; *anti* isomer: δ = 6.27 (d, J = 19.0 Hz, 1 H, H-1), 6.03 (dd, J = 19.0, 5.0 Hz, 1 H, H-2), 4.07 (m, 2 H, H-3 + H-4), 1.51 (m, 6 H, $3\times CH_2C\mathit{H}_2CH_2CH_3$), 1.32 (m, 6 H, $3\times CH_2CH_2C\mathit{H}_2CH_3$), 0.97–0.86 [m, 33 H, $3\times C\mathit{H}_2CH_2CH_2C\mathit{H}_3 + 2\times(CH_3)_3CSi$], 0.17 [s, 9 H, $(CH_3)_3Si$], 0.14 [s, 6 H, $(CH_3)_2Si$], 0.10 [s, 3 H, $(CH_3)_2Si$], 0.08 [s, 3 H, $(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 2:1 *syn*/*anti* mixture): *syn* isomer: δ = 141.5 (C-2), 130.3 ($J_{Sn,C}$ = 378 Hz, C-1), 106.0 (C-5), 90.4 (C-6), 79.3 ($J_{Sn,C}$ = 63 Hz, C-3), 68.4 (C-4), 29.5 ($J_{Sn,C}$ = 19 Hz, $3\times CH_2\mathit{C}H_2CH_2CH_3$), 27.5 ($J_{Sn,C}$ = 63 Hz, $3\times CH_2CH_2\mathit{C}H_2CH_3$), 26.1 [$2\times(\mathit{C}H_3)_3CSi$], 18.5 [$2\times(CH_3)_3\mathit{C}Si$], 13.8 ($3\times CH_2CH_2CH_2\mathit{C}H_3$), 9.7 ($J_{Sn,C}$ = 346 Hz, $3\times \mathit{C}H_2CH_2CH_2CH_3$), –0.3 [$(CH_3)_3Si$], –4.3 [$2\times(CH_3)_2Si$] ppm; *anti* isomer: δ = 148.4 (C-2), 130.3 ($J_{Sn,C}$ = 378 Hz, C-1), 107.2 (C-5), 89.6 (C-6), 79.3 (C-3), 68.4 (C-4), 29.5 ($J_{Sn,C}$ = 19 Hz, $3\times CH_2\mathit{C}H_2CH_2CH_3$), 27.5 ($J_{Sn,C}$ = 63 Hz, $3\times CH_2CH_2\mathit{C}H_2CH_3$), 26.1 [$2\times(\mathit{C}H_3)_3CSi$], 18.5 [$2\times(CH_3)_3\mathit{C}Si$], 13.8 ($3\times CH_2CH_2CH_2\mathit{C}H_3$), 9.7 ($J_{Sn,C}$ = 346 Hz, $3\times \mathit{C}H_2CH_2CH_2CH_3$), –0.3 [$(CH_3)_3Si$], –4.3 [$2\times(CH_3)_2Si$] ppm. MS (CI, NH_3): *m*/*z* (%) = 703 [M^+ + 1], 571, 382, 308 (100), 291, 227, 132. IR (neat): $\tilde{\nu}$ = 2956, 2927, 2868, 2856, 2175, 1601, 1463, 1360, 1250, 1109, 1004, 838, 778, 670 cm^{-1}.

(1*E*,3*R,4*R**)-3,4-Bis[(*tert*-butyldimethylsilyl)oxy]-1-chloro-6-(trimethylsilyl)hex-1-en-5-yne (*syn* Isomer) (17):** A solution of vinylstannane **16** (4.5 g, 6.42 mmol, 1 equiv., 2:1 *syn*/*anti* mixture) in THF (10 mL) was added at room temperature to a solution of anhydrous copper(II) chloride (2.16 g, 16.05 mmol, 2.5 equiv.) in THF (20 mL). The reaction mixture was stirred at room temperature for 15 h and added to 50 mL of diethyl ether and 50 mL of a saturated aqueous $NaHCO_3$ solution. After decantation, the aqueous layer was extracted three times with 50 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 95:5) to give 2.79 g of **17** as a 2:1 mixture of *syn* and *anti* diastereoisomers (97% yield). ^1H NMR ($CDCl_3$, 200 MHz, 2:1 *syn*/*anti* mixture): *syn* isomer: δ = 6.21 (dd, J = 13.5, 0.9 Hz, 1 H, H-1), 6.06 (dd, J = 13.5, 5.6 Hz, 1 H, H-2), 4.26 (d, J = 5.9 Hz, 1 H, H-4), 4.14 (td, J = 5.7, 0.9 Hz, 1 H, H-3), 0.97–0.86 [m, 18 H, $2\times(CH_3)_3CSi$], 0.17 [s, 9 H, $(CH_3)_3Si$], 0.09 [m, 12 H, $2\times(CH_3)_2Si$] ppm; *anti* isomer: δ = 6.19 (dd, J = 13.0, 0.6 Hz, 1 H, H-1), 5.97 (ddd, J = 13.0, 3.5, 2.7 Hz, 1 H, H-2), 4.14 (m, 2 H, H-3, H-4), 0.97–0.86 [m, 18 H, $2\times(CH_3)_3CSi$], 0.16 [s, 9 H, $(CH_3)_3Si$], 0.09 [m, 12 H, $2\times(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 2:1 *syn*/*anti* mixture): *syn* isomer: δ = 133.0 (C-2), 120.6 (C-1), 104.8 (C-5), 91.5 (C-6), 75.0 (C-3), 68.1 (C-4), 26.0 [$2\times(\mathit{C}H_3)_3CSi$], 18.3 [$2\times(CH_3)_3\mathit{C}Si$], –0.1 [$(CH_3)_3Si$], –4.4 [$2\times(CH_3)_2Si$] ppm; *anti* isomer: δ = 134.1 (C-2), 120.6 (C-1), 106.0 (C-5), 90.4 (C-6), 75.4 (C-3), 68.1 (C-4), 26.0 [$2\times(\mathit{C}H_3)_3CSi$], 18.3 [$2\times(CH_3)_3\mathit{C}Si$], –0.1 [$(CH_3)_3Si$], –4.4 [$2\times(CH_3)_2Si$] ppm. MS (CI, NH_3): *m*/*z* (%) = 464/465 [M^+ + 18], 447/449 [M^+ + 1], 389/391, 315/317 (100), 241, 200, 164, 132, 90, 73. IR (neat): $\tilde{\nu}$ = 3312, 3064, 2957, 2928, 2870, 2857, 2711, 2361, 2176, 1630, 1472, 1361, 1251, 1098, 1004, 934, 838, 778 cm^{-1}.

(1*Z*,3*R,4*R**)-3,4-Bis[(*tert*-butyldimethylsilyl)oxy]-1-chloro-1-iodo-6-(trimethylsilyl)hex-1-en-5-yne (*syn* Isomer) (18):** A 1.55 M solution of *n*BuLi in pentanes (3 mL, 4.62 mmol, 1.2 equiv.) was added at –100 °C to a stirred solution of **17** (2:1 *syn*/*anti* mixture, 1.72 g, 3.85 mmol) in a THF/Et_2O/pentane mixture (20 mL, 1.3:1:1). The mixture was stirred at –100 °C for 40 min and then treated with a cold (–60 °C) solution of iodine (1.08 g, 4.24 mmol, 1.2 equiv.) in THF (4 mL). The reaction mixture was warmed slowly to –40 °C then added to 10 mL of water and extracted three times with 50 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 98:2) to give 2.02 g of **18** as a 2:1 mixture of *syn* and *anti* diastereoisomers contaminated with around 20% of starting material (ca. 76% yield). ^1H NMR ($CDCl_3$, 200 MHz; 52:28:20 *syn*-**18**/*anti*-**18** mixture and **17**): *syn*-**18**: δ = 6.14 (d, J = 8.7 Hz, 1 H, H-2), 4.34 (d, J = 5.8 Hz, 1 H, H-4), 4.11 (dd, J = 8.7, 5.8 Hz, 1 H, H-3), 0.90 [m, 18 H, $2\times(CH_3)_3CSi$], 0.17 [s, 9 H, $(CH_3)_3Si$], 0.14 [s, 6 H, $(CH_3)_2Si$], 0.13 [s, 6 H, $(CH_3)_2Si$] ppm; *anti*-**18**: δ = 6.03 (d, J = 8.5 Hz, 1 H, H-2), 4.23 (d, J = 6.7 Hz, 1 H, H-4), 4.11 (m, 1 H, H-3), 0.90 [m, 18 H, $2\times(CH_3)_3CSi$], 0.16 [s, 9 H, $(CH_3)_3Si$], 0.14 [s, 6 H, $(CH_3)_2Si$], 0.13 [s, 6 H, $(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, same mixture as above): *syn*-**18**: δ = 140.1 (C-2), 104.6 (C-5), 91.4 (C-6), 79.7 (C-3), 76.1 (C-1), 67.3 (C-4), 26.0 [$2\times(\mathit{C}H_3)_3CSi$], 18.2 [$2\times(CH_3)_3\mathit{C}Si$], –0.1 [$(CH_3)_3Si$], –4.4 [$2\times(CH_3)_2Si$] ppm: *anti*-**18**: δ = 140.8 (C-2), 106.3 (C-5), 90.6 (C-6), 80.1 (C-3), 76.1 (C-1), 68.0 (C-4), 26.0 [$2\times(\mathit{C}H_3)_3CSi$], 18.2 [$2\times(CH_3)_3\mathit{C}Si$], –0.1 [$(CH_3)_3Si$], –4.4 [$2\times(CH_3)_2Si$] ppm. MS (CI, NH_3, same mixture as above): *m*/*z* (%) = 590/592 [M^+ + 18], 573/575 [M^+ + 1], 515/517, 441/443 (100), 326/328, 241, 206, 164, 132, 90. IR (neat, same mixture as above): $\tilde{\nu}$ = 2956, 2929, 2896, 2857, 2176, 1600, 1463, 1361, 1251, 1114, 1005, 842, 778 cm^{-1}.

(1*Z*,3*R,4*R**)-3,4-Bis[(*tert*-butyldimethylsilyl)oxy]-1-chloro-1-iodohex-1-en-5-yne (*syn* Isomer) (20):** K_2CO_3 (140 mg, 1.01 mmol, 1.5 equiv.) was added to a solution of the preceding vinyl compound **18** (386 mg, 52/28/20 *syn*-**18**/*anti*-**18**/**17** mixture) in methanol (5 mL) at room temperature. The reaction mixture was stirred at this temperature for 3 h and then partitioned between 10 mL of a saturated $NaHCO_3$ aqueous solution and 50 mL of diethyl ether. The phases were separated and the aqueous phase was extracted three times with 30 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 95:5) to give 328 mg of **20** as a 2:1 mixture of *syn* and *anti* diastereoisomers contaminated with about 20% of desilylated starting material (ca. 98% yield). ^1H NMR ($CDCl_3$, 200 MHz, 52:28:20 *syn*-**20**/*anti*-**20**/desilylated **17** mixture): *syn*-**20**: δ = 6.21 (d, J = 8.7 Hz, 1 H, H-2), 4.37 (dd, J = 5.3, 2.1 Hz, 1 H, H-4), 4.14 (dd, J = 8.7, 5.3 Hz, 1 H, H-3), 2.42 (d, J = 2.1 Hz, 1 H, H-6), 0.92 [m, 18 H, $2\times(CH_3)_3CSi$], 0.18 [s, 12 H, $2\times(CH_3)_2Si$] ppm; *anti*-**20**: δ = 6.06 (d, J = 8.3 Hz, 1 H, H-2), 4.25 (dd, J = 5.4, 2.0 Hz, 1 H, H-4), 4.16 (dd, J = 8.3, 5.4 Hz, 1 H, H-3), 2.40 (d, J = 2.0 Hz, 1 H, H-6), 0.92 [s, 18 H, $2\times(CH_3)_3CSi$], 0.16 [s, 12 H, $2\times(CH_3)_2Si$] ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, same mixture as above): *syn*-**20**: δ = 139.8 (C-

2), 82.6 (C-5), 79.3 (C-3), 76.3 (C-1), 74.4 (C-6), 66.8 (C-4), 26.0 [2×(*C*H$_3$)$_3$CSi], 18.4 [(CH$_3$)$_3$*C*Si], 18.3 [(CH$_3$)$_3$*C*Si], –3.9 [(CH$_3$)Si], –4.3 [(CH$_3$)Si], –4.5 [(CH$_3$)Si], –4.9 [(CH$_3$)Si] ppm; *anti*-**20**: δ = 140.5 (C-2), 83.3 (C-5), 80.2 (C-3), 76.3 (C-1), 73.7 (C-6), 66.8 (C-4), 26.0 [2×(*C*H$_3$)$_3$CSi], 18.4 [(CH$_3$)$_3$*C*Si], 18.3 [(CH$_3$)$_3$*C*Si], –3.9 [(CH$_3$)Si], –4.3 [(CH$_3$)Si], –4.5 [(CH$_3$)Si], –4.9 [(CH$_3$)Si] ppm. MS (CI, NH$_3$, same mixture as above): *m*/*z* (%) = 518/520 [M$^+$ + 18], 501/503 [M$^+$ + 1], 369/371, 243, 132 (100). IR (neat, same mixture as above): ṽ = 3310, 2955, 2929, 2886, 2857, 2710, 2360, 2186, 2118, 1601, 1472, 1463, 1361, 1254, 1115, 1005, 938, 900, 836, 778 cm^{-1}.

(3E,5Z,1R*,2R*)-1,2-Bis[(tert-butyldimethylsilyl)oxy]-4-chloro-5-(prop-2′-ynylidene)cyclopent-3-ene (trans Isomer) (21): A solution of **20** (400 mg, 0.799 mmol, 1.0 equiv., 52/28/20 *syn*-**20**/*anti*-**20**/desilylated **17** mixture) in THF (3 mL) and tributylstannyl acetylene (755 mg, 2.397 mmol, 3.0 equiv.) were added successively to a suspension of [Pd(PPh$_3$)$_4$] (92 mg, 0.08 mmol, 0.1 equiv.) under argon in THF (2 mL) at room temperature. The reaction mixture was stirred and gently refluxed for 6 h. After cooling, the resulting mixture was poured into 10 mL of a saturated aqueous NaHCO$_3$ solution. The aqueous layer was extracted three times with 20 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 98:2) to give 318 mg of **21** as a 3:1 mixture of *trans* and *cis* diastereoisomers, which were not separated (68% yield, 85% relative to **20**). ^{1}H NMR (CDCl$_3$, 200 MHz, 3:1 *trans*/*cis* mixture): *trans* isomer: δ = 6.04 (m, 1 H, H-3 or H-1′), 5.50 (m, 1 H, H-1′ or H-3), 4.58 (m, 2 H, H-1, H-2), 3.30 (d, *J* = 2.2 Hz, 1 H, H-3′), 0.93 [m, 18 H, 2×(CH$_3$)$_3$CSi], 0.15 [m, 12 H, 2×(CH$_3$)$_2$Si] ppm; *cis* isomer: δ = 6.19 (m, 1 H, H-3 or H-1′), 5.60 (m, 1 H, H-1′ or H-3), 4.47 (m, 1 H, H-1 or H-2), 4.35 (m, 1 H, H-1 or H-2), 3.30 (d, *J* = 2.2 Hz, 1 H, H-3′), 0.93 [m, 18 H, 2×(CH$_3$)$_3$CSi], 0.15 [m, 12 H, 2×(CH$_3$)$_2$Si] ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz, 3:1 *trans*/*cis* mixture): *trans* isomer: δ = 151.4 (C-5), 137.0 (C-3), 133.3 (C-4), 100.7 (C-1′), 85.7 (C-3′), 83.2, 80.2 (C-1,C-2), 79.6 (C-2′), 26.0 [2×(*C*H$_3$)$_3$CSi], 18.4 [(CH$_3$)$_3$*C*Si], 18.1 [(CH$_3$)$_3$*C*Si], –3.9, –4.1, –4.3, –4.5 [2×(CH$_3$)$_2$Si] ppm; *cis* isomer: δ = 152.0 (C-5), 136.7 (C-3), 134.5 (C-4), 102.2 (C-1′), 85.5 (C-3′), 79.1 (C-2′), 75.0, 72.6 (C-1, C-2), 26.0 [2×(*C*H$_3$)$_3$CSi], 18.4 [(CH$_3$)$_3$*C*Si], 18.1 [(CH$_3$)$_3$*C*Si], –3.9, –4.1, –4.3, –4.5 [2×(CH$_3$)$_2$Si] ppm. MS (CI, NH$_3$): *m*/*z* (%) = 399/401 [M$^+$ + 1], 341/343, 284/286, 267/269 (100). IR (neat): ṽ = 3310, 2955, 2929, 2886, 2857, 2360, 1571, 1472, 1463, 1376, 1361, 1256, 1159, 1086, 888, 838, 778 cm^{-1}.

(3E,5Z,1R*,2R*)-1,2-Bis[(tert-butyldimethylsilyl)oxy]-4-chloro-5-(4,4-diethoxybut-2-ynylidene)cyclopent-3-ene (trans Isomer) (22): A solution of vinyl compound **20** (500 mg, 1.0 mmol, 1.0 equiv., same mixture as above) in THF (4 mL) and 3,3-diethoxy-1-(tributylstannyl)prop-1-yne (917 mg, 2.2 mmol, 2.2 equiv.) were added successively to a suspension of [Pd(PPh$_3$)$_4$] (116 mg, 0.1 mmol, 0.1 equiv.) under argon in THF (4 mL) at room temperature. The reaction mixture was stirred and gently refluxed for 15 h. After cooling, the resulting mixture was poured into 10 mL of a saturated aqueous NaHCO$_3$ solution. The aqueous layer was extracted three times with 20 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 98:2) to give 340 mg of **22** as a 3:1 mixture of *trans* and *cis* diastereoisomers (68% yield, 85% based on **20**). ^{1}H NMR (CDCl$_3$, 400 MHz, 3:1 *trans*/*cis* mixture): *trans* isomer: δ = 6.02 (m, 1 H, H-1′ or H-3), 5.54 (m, 1 H, H-3 or H-1′), 5.43 (d, *J* = 1.6 Hz, 1 H, H-4′), 4.56 (dd, *J* = 2.1, 2.4 Hz, 1 H, H-1 or H-2), 4.54 (dd, *J* = 2.3, 2.7 Hz, 1 H, H-2 or H-1), 3.78 (m, 2 H, CH$_3$C*H*$_2$O), 3.62 (m, 2 H, CH$_3$C*H*$_2$O), 1.24 (t, *J* = 7.3 Hz, 6 H, 2×C*H*$_3$CH$_2$O), 0.93 [s, 9 H, (CH$_3$)$_3$CSi], 0.91 [s, 9 H, (CH$_3$)$_3$CSi], 0.14, 0.12 [2 s, 2×3 H, (CH$_3$)$_2$Si], 0.11 [s, 6 H, (CH$_3$)$_2$Si] ppm; *cis* isomer: δ = 6.17 (dd, *J* = 2.5, 1.3 Hz, 1 H, H-3 or H-1′), 5.65 (q, *J* = 1.6 Hz, 1 H, H-1′ or H-3), 5.44 (d, *J* = 1.7 Hz, 1 H, H-4′), 4.47 (dd, *J* = 5.3, 1.8 Hz, 1 H, H-1 or H-2), 4.44 (dd, *J* = 5.3, 2.8 Hz, 1 H, H-2 or H-1), 3.78 (m, 2 H, CH$_3$C*H*$_2$O), 3.62 (m, 2 H, CH$_3$C*H*$_2$O), 1.24 (t, *J* = 7.3 Hz, 6 H, 2×C*H*$_3$CH$_2$O), 0.93 [s, 9 H, (CH$_3$)$_3$CSi], 0.91 [s, 9 H, (CH$_3$)$_3$CSi], 0.14, 0.12 [2 s, 2×3 H, (CH$_3$)$_2$Si], 0.11 [s, 6 H, (CH$_3$)$_2$Si] ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz, 3:1 *trans*/*cis* mixture): *trans* isomer: δ = 151.0 (C-5), 135.5 (C-4), 136.9 (C-3), 101.4 (C-1′), 93.3 (C-2′), 81.4 (C-3′), 92.4 (C-4′), 83.4, 80.6 (C-1, C-2), 61.3 (2×CH$_3$*C*H$_2$O), 26.1 [2×(*C*H$_3$)$_3$CSi], 18.4 [2×(CH$_3$)$_3$*C*Si], 15.2 (2×*C*H$_3$CH$_2$O), –3.9, –4.0, –4.2, –4.4 [2×(CH$_3$)$_2$Si] ppm; *cis* isomer: δ = 151.3 (C-5), 135.5 (C-4), 136.7 (C-3), 102.3 (C-1′), 93.1 (C-2′), 75.3 (C-3′), 92.4 (C-4′), 81.4, 72.9 (C-1, C-2), 61.3 (2×CH$_3$*C*H$_2$O), 26.1 [2×(*C*H$_3$)$_3$CSi], 18.4 [2×(CH$_3$)$_3$*C*Si], 15.2 (2×*C*H$_3$CH$_2$O), –3.9, –4.0, –4.2, –4.4 [2×(CH$_3$)$_2$Si] ppm. MS (CI, NH$_3$): *m*/*z* (%) = 501/503 [M$^+$ + 1], 455/457 (100). IR (neat): ṽ = 2955, 2929, 2886, 2857, 2215, 1571, 1472, 1463, 1376, 1352, 1326, 1255, 1158, 1086, 1006, 893, 836, 778 cm^{-1}.

(3E,5E,1R*,2R*)-1,2-Bis[(tert-butyldimethylsilyl)oxy]-5-(prop-2-ynylidene)-4-(trimethylsilylethynyl)cyclopent-3-ene (23): A solution of dienyne **21** (100 mg, 0.25 mmol, 1.0 equiv., 3:1 *trans*/*cis* mixture) in piperidine (2 mL), CuI (14 mg, 0.075 mmol, 0.3 equiv.) and (trimethylsilyl)acetylene (360 µL, 2.5 mmol, 10 equiv.) were added successively to a suspension of [PdCl$_2$(CH$_3$CN)$_2$] (7 mg, 0.025 mmol, 0.1 equiv.) in piperidine (2 mL) at room temperature under argon. After stirring at 50 °C for 5 h, the mixture was quenched with 10 mL of a saturated aqueous NH$_4$Cl solution, and the aqueous layer was extracted three times with 20 mL of diethyl ether. The combined organic layers were washed with brine, dried with anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (petroleum ether/diethyl ether, 98:2) to give 65 mg of **23** as a single isomer (56% yield). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 6.09 (m, 1 H, H-3 or H-1′), 5.82 (m, 1 H, H-1′ or H-3), 4.69 (m, 1 H, H-1 or H-2), 4.56 (d, *J* = 2.6 Hz, 1 H, H-2 or H-1), 3.30 (d, *J* = 2.6 Hz, 1 H, H-3′), 0.92 [m, 18 H, 2×(CH$_3$)$_3$CSi], 0.15 [m, 21 H, 2×(CH$_3$)$_2$Si + (CH$_3$)$_3$Si] ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ = 154.6 (C-5), 136.3 (C-4), 134.5 (C-3), 104.1 (C-1′), 111.6 (C-1"), 100.7 (C-2′′), 85.7 (C-3′), 81.7, 81.1 (C-1, C-2), 78.9 (C-2′), 26.1 [2×(*C*H$_3$)$_3$CSi], 18.4 [(CH$_3$)$_3$*C*Si], 18.1 [(CH$_3$)$_3$*C*Si], 0.1 [(CH$_3$)$_3$Si], –3.6, –3.8, –4.1, –4.3 [2×(CH$_3$)$_2$Si] ppm. MS (EI): *m*/*z* (%) = 460 [M$^+$], 147, 73 (100), 45. IR (neat): ṽ = 3312, 2956, 2929, 2895, 2857, 2359, 2340, 2141, 1579, 1472, 1463, 1361, 1252, 1079, 886, 840, 777 cm^{-1}.

Acknowledgments

Dr. A. Pancrazi is particularly acknowledged for helpful discussions. Thanks are also due to the CNRS, UMR 7652 and the Ecole Polytechnique for financial support, as well as to La Ligue Nationale Contre le Cancer for a fellowship to D. M.

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Received: May 18, 2005