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Studies in Cuprate Rearrangement and Stannylcupration: Application to the Stereo- and Enantiospecific Synthesis of a Stannyldiene C10-C15 Fragment of Des-epoxy-rosaramycin

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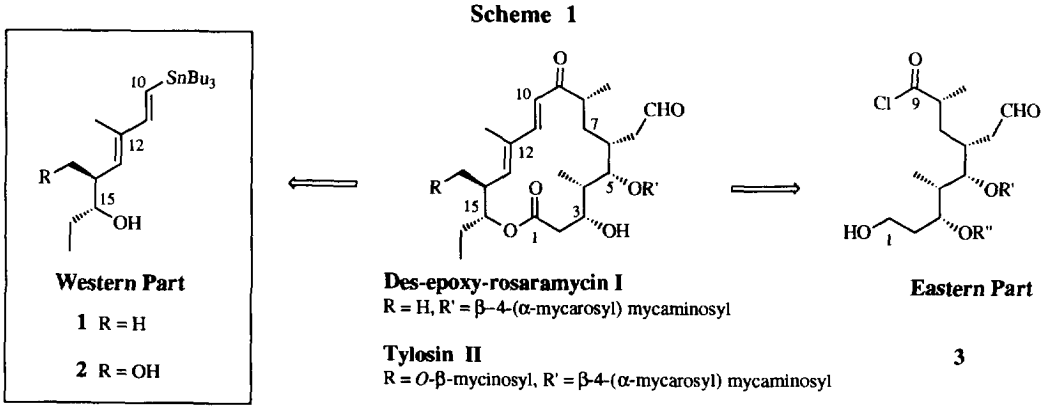
Abstract: *Metallate rearrangements were performed on α-(carbamoyloxy)alkenyl stannanes **4** in high yields to prepare (±)-**8a** and (±)-**8b** via alkyl transfer but failed when stannyl and stannylvinyl transfers were attempted to give **10ab** and **1ab** after quenching with MeI. After we optimized conditions on dihydrofuran **13**, a model study, the dihydrofuran **19** could deliver cuprate rearrangements, leading after methylation to the stannyl derivative **10** and the stannyldiene **1** in good yields. A second approach for the synthesis of stannyldienes was envisaged via a Stille Pd(0) coupling reaction using (E)-1,2-bis(tributylstannyl)ethylene **11**. An efficient method was performed by stannylcupration of the enyne (±)-**24** which gave the expected stannyldiene (±)-**1** in good yield and with high regio-and stereocontrols.*

Due to their wide therapeutic use in human and veterinary medicine, since the 1950's many synthetic efforts are still devoted to macrolide antibiotics.[1] The 14- and 16-membered macrolides such as erythromycin or tylosin are considered the most important but antibiotic resistance appeared, and in spite of various derivatives having been synthesized, a great interest occurred in the synthesis of new compounds.[2]

Scheme 1

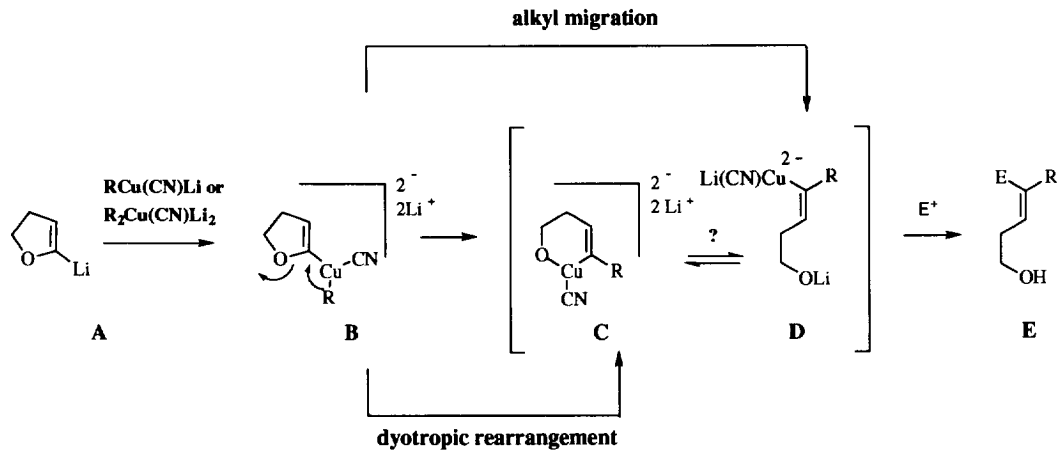


In our synthetic approach to des-epoxy-rosaramycin **I** or tylosin **II** [3] (16 membered macrolides), we look at the preparation of the two respective Western parts C_{10}-C_{15} **1** and **2**, and the Eastern moiety C_1-C_9 **3** as

depicted in Scheme 1.

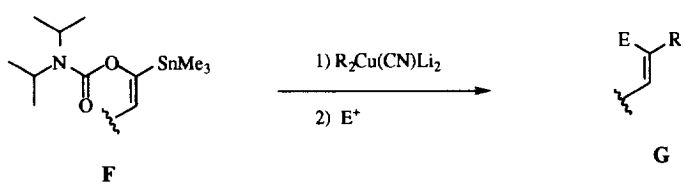
In preliminary work on the synthesis of part **1** or **2**, and for a stereospecific synthesis of trisubstituted alkenes, we turned our attention to Kocienski's procedure,[4] which involves a metallate rearrangement of a cyclic α-alkoxyalkenylcuprate **B**, obtained from the corresponding 5-lithio-2,3-dihydrofuran **A**. In this reaction an alkyl or alkenyl residue R migration occurred on the α vinylic carbon leading to the intermediate vinylcuprates **C** or **D** *via* either a dyotropic rearrangement or an alkyl migration (Scheme 2); subsequent reaction of an electrophilic reagent on **C** or **D** afforded the stereochemically pure substituted alkene **E**.

Scheme 2



Interestingly, a similar reaction was also performed by the Kocienski's group with an α-(carbamoyloxy)alkenyl stannane **F** which led to the corresponding alkene derivative **G** in good yield when the R residue is an alkyl, a vinyl or an aromatic group (Scheme 3).

Scheme 3



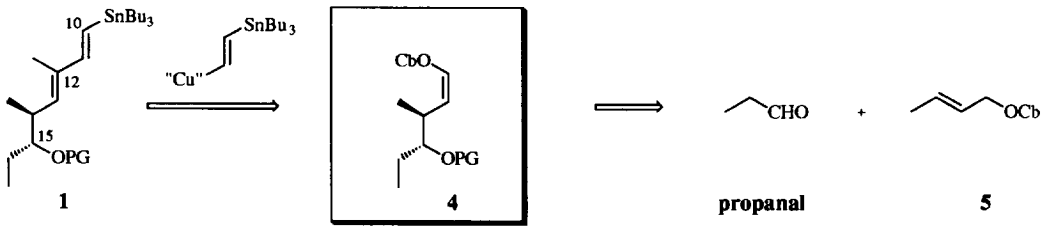
During this work we turned our efforts to the application of this cuprate rearrangement to the stereospecific preparation of the stannyldienes **1** or **2**. For this purpose we also desired a two carbon unit as a potential vinyldianion such as the (*E*)-1,2-bis(tributylstannyl)ethylene, or its lithio or cuprate derivatives to obtain a vinylic stannylated staple via an anionic reaction or a Pd(0) coupling reaction.[5]

I) The metallate rearrangement strategy

As depicted on Scheme 4, our synthetic strategy involved a (stannyl)vinyl transfer starting from the carbamate enol ether **4** in order to obtain the desired stannyldiene **1**. For a stereospecific preparation of the vinylcarbamate precursor **4** we then envisaged an homoaldol reaction between propanal and the allylic carbamate **5** using Hoppe conditions.[6]

We have previously described the preparation of **1** in a racemic form.[7,8] This paper deals with a diastereo- and enantiospecific synthesis of the stannyldiene **1** using the same approach.

Scheme 4

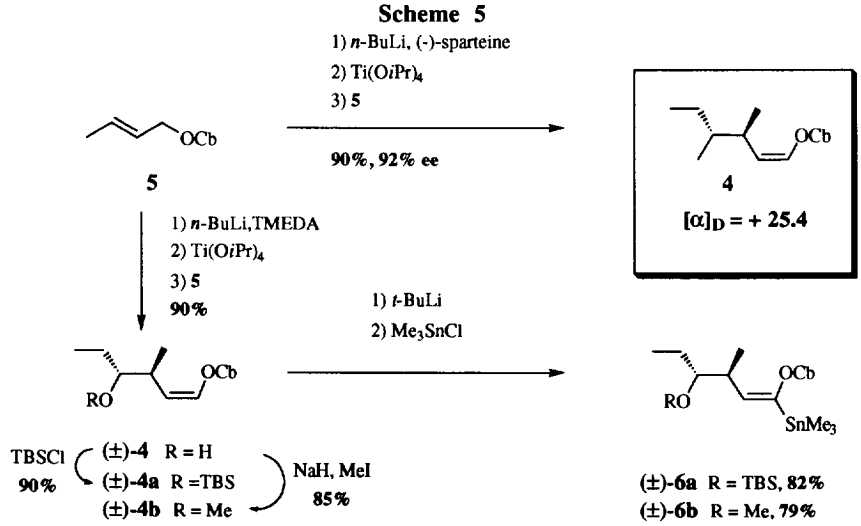


1 **4** **propanal** **5**

The crotyl carbamate **5**,[6] was treated with *n*BuLi in presence of (-)-sparteine, then with titanium tetraisopropoxide [Ti(O*i*Pr)$_4$]. After transmetallation was obtained, reaction with propanal delivered the expected vinylcarbamate **4** in 90% chemical yield and 92% ee (Scheme 5). This reaction occurred with total diastereocontrol. The stereochemistry of **4** was deduced from NMR analysis and NOE experiments performed on the corresponding lactone **17** (see below); absolute configuration of **17** was established by comparison with literature data [**17**: $[\alpha]_D$ = + 66.7 (neat), lit [9] $[\alpha]_D$ = + 67.3 (neat)]. The enantiomeric excess was also deduced after esterification of compound **4** with the (*R*)-acetyl mandelic acid, and NMR analysis of corresponding esters.

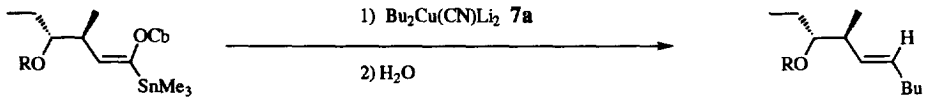
Using the same reaction we also prepared the racemic derivative (±)-**4** in 90% yield from **6** using *n*-BuLi-TMEDA for the preliminary model study. Protection of the secondary alcohol (±)-**4** led to the two derivatives (±)-**4a** and (±)-**4b**; further lithiation [10] and quenching with Me_3SnCl delivered the corresponding vinylstannanes (±)-**6a** and (±)-**6b**. With (±)-**6a** and (±)-**6b** in hand, we tried first to perform an alkyl transfer according to Kocienski's conditions.

Scheme 5



According to this procedure [4] the butyl derivatives (±)-**8a** and (±)-**8b** were obtained in 90% and 80% yields respectively (Scheme 6) when the corresponding vinylstannanes (±)-**6a** and (±)-**6b** were treated with $Bu_2Cu(CN)Li_2$ **7a**.[11] However with tributylstannyl instead of trimethylstannyl derivatives corresponding to (±)-**6a** and (±)-**6b**, the metallate rearrangement reaction did not work.

Scheme 6



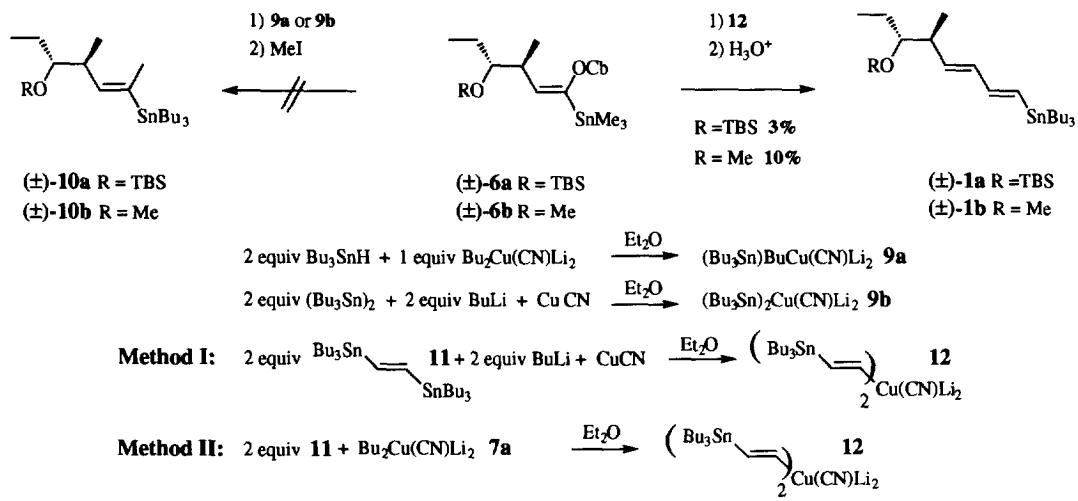
(±)-**6a** R = TBS
(±)-**6b** R = Me

(±)-**8a** R =TBS, **90%**
(±)-**8b** R = Me, **80%**

For our previous purpose we then tried to realize the metallate rearrangement with dilithium bis[(*E*)-2-(tributylstannyl)ethenyl]cyanocuprate **12**, prepared from the (*E*)-1-lithio-2-(tributylstannyl)ethylene (*trans*-LISE) [12] *via* the corresponding (*E*)-1,2-bis(tributylstannyl)ethylene **11** [13] (Method I, Scheme 7). In this reaction the expected stannyldienes (±)-**1a** and (±)-**1b** were produced in poor yields, 3% for (±)-**1a** and 10% for (±)-**1b.**

In order to prepare the vinylstannanes (±)-**10a** or (±)-**10b**, which could be precursors in the preparation of (±)-**1a** and (±)-**1b**, the homo $(Bu_3Sn)_2Cu(CN)Li_2$ **9b** [14] stannylcyanocuprate was employed but stannyl transfer did not occur from (±)-**6a** and (±)-**6b**. (It was checked that stannyl transfer did not occurred even the reaction was quenched with H_3O^+).

Scheme 7



Since the (carbamoyloxy)alkenylcuprate seems to be ineffective in a stannyl or vinyl transfer we then turned our efforts to cyclic α-alkoxyalkenylcuprates, and in a preliminary study we decided to test the reactivity of commercial dihydrofuran **13**. Reaction of one equivalent of the cuprates **7a** and **7b** [11] with the lithiodihydrofuran **13a**, or stannyl derivative **13b** (Scheme 8, Table I), led in good yields [4] to the corresponding alkene **14** [15] after further methylation which was performed efficiently at -30°C–>20°C for 3 h.

Scheme 8

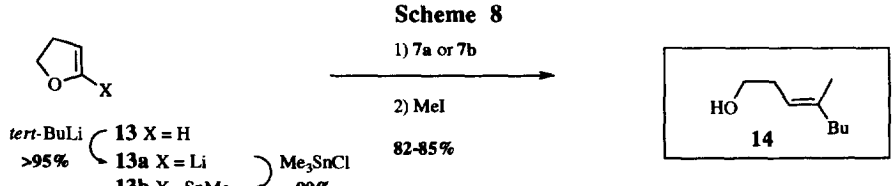


Table I: Butyl transfer from dihydrofuran 13

Entry	X	1) Cuprate (THF/Et_2O 1:1, -5°C->0°C, 30 min) 2) MeI, -30°C->20°C, 3 h	Yield 13 —>14 [a]
1	$SnMe_3$	$Bu_2Cu(CN)Li_2$ **7a** : 1.1 equiv	85%
2	Li	$Bu_2Cu(CN)Li_2$ **7a** : 1.1 equiv	82%
3	Li	BuCu(CN)Li **7b** : 1.1 equiv	83%

[a] Yields are given for isolated products after chromatography.

Reaction of the stannylcuprate $(Bu_3Sn)_2Cu(CN)Li_2$ **9b** with lithiodihydrofuran **13a** gave the cuprate rearrangement and afforded the desired vinylstannane **15** as a single *E* isomer (Scheme 9); yields ranged from 72-77% yields when 1.9 to 3.0 equivalents of Bu_3SnLi were added for the preparation of cuprate **9b**, and increased to 85% when 4 equivalents of Bu_3SnLi were used (Table II, entries 6-8).

Scheme 9

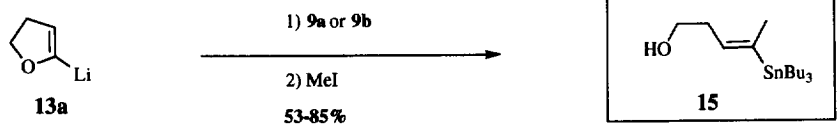


Table II: Stannyl transfer from dihydrofuran 13

Entry	1) Cuprate (THF/Et_2O 1:1, -5°C->0°C, 1.5h) 2) MeI, -30°C->20°C, 3 h	Yield 13 —>15 [a]
4	$(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** : 1 equiv $Bu_2Cu(CN)Li_2$ + 2.0 equiv Bu_3SnH	75%
5	- " + 2.0 equiv Bu_3SnH [b]	53%
6	$(Bu_3Sn)_2Cu(CN)Li_2$ **9b** : 1eq CuCN + 1.9 equiv Bu_3SnLi	72%
7	" **9b** : " + 3.0 equiv Bu_3SnLi	77%
8	" **9b** : " + 4.0 equiv Bu_3SnLi	85%

[a] Yields are given for isolated products after chromatography. [b] For entry 5, pure THF was used.

Stannyl transfer leading to **15** was also performed in the same manner with the mixed cuprate $(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** [16] in 75% yield, (Table II, entries 4, 5).[17]

After we optimized the alkyl and stannyl rearrangement we next turned to the (vinyl)stannyl transfer designed for our synthetic purposes. Therefore we first employed the H.O. cyanocuprate **12** resulting from addition of 1.0 equivalent of CuCN to 1.8 equivalent of (*E*)-1-lithio-2-(tributylstannyl)-ethylene (*trans*-LiSE); metallate rearrangement took place and provided stannyldiene **16** in 66% yield. In this reaction the better yields were obtained when the *trans*-LiSE derivative was prepared by treatment of **11** with 1.2 to 1.4 equivalents of BuLi (Scheme 10, Table III, entries 9, 10).

For an easier and more convenient preparation of the H.O. cuprate **12** we applied a modified Lipshutz exchange method;[18] treatment of 1.8 equivalent of **11** with 1 equivalent of $Bu_2Cu(CN)Li_2$ **7a** gave the expected H.O. homocuprate **12**. Treatment of the 5-lithiodihydrofuran **13a** by this prepared homocuprate afforded, after methylation, the desired stannyldiene **16** in 68% yield. This yield improved to 82% when 4 equivalents of **11** were used for the preparation of **12** (Scheme 10, Table III, entries 11, 12).

Scheme 10

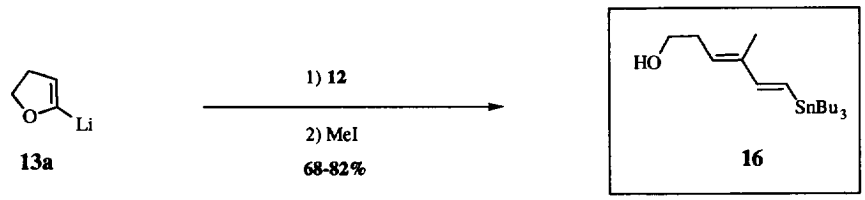


Table III: Vinylstannyl transfer from dihydrofuran 13

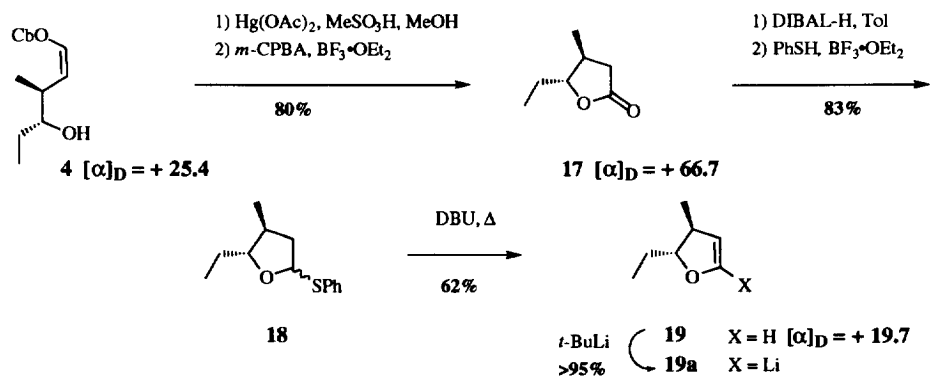
Entry	1) Cuprate (THF/Et_2O 1:1, -5°C, 1.5 h) 2) MeI, -30->20°C, 3 h	Yield 13 ->16 [a]
9	$(Bu_3Sn)_2Cu(CN)Li_2$ 12 1 equiv CuCN + 1.2 equiv Bu_3Sn—Li	40%
10	" 12 " + 1.8 equiv "	66%
11	$(Bu_3Sn)_2Cu(CN)Li_2$ 12 1 equiv $Bu_2CuCNLi_2$ + 1.8 equiv Bu_3Sn—$SnBu_3$	68%
12	" 12 " + 4.0 equiv "	82%

[a] Yields are given for isolated products after chromatography .

For the (vinyl)stannyl transfer we also tried to induced this reaction with CuBr-Me_2S but unfortunately this reagent was less efficient than CuCN. In this case this result was opposite to Kocienski's previous observation,[19] but similarly it seems that four equivalents of the metallate species (with respect to Cu content) were necessary to obtain the better yields.

After this model study was achieved, we turned to the synthesis of the C_{10}-C_{15} fragment **1** of desepoxy-rosaramycin **I**, in which the optically active vinylcarbamate **4** was transformed into the corresponding lithiodihydrofuran **19a** which was then used in the cuprate rearrangement reaction with cyanocuprate **12**.

Scheme 11

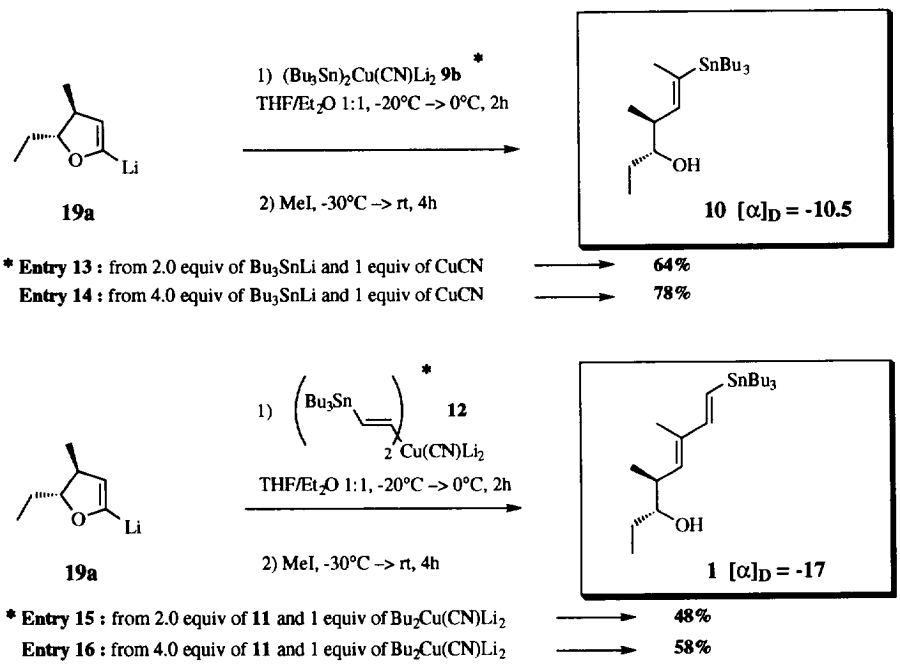


The vinylcarbamate **4** was first oxidized using acidic conditions [20] to give lactone **17** (Scheme 11). This lactone was then reduced into the corresponding lactol which was treated with thiophenol under acidic conditions to furnish the thio derivative **18**. Subsequent pyrolysis of **18** under basic conditions and concomitant distillation gave pure dihydrofuran **19** in 62% yield.[21]

After lithiation of **19** with *t*-BuLi, the lithiodihydrofuran **19a** was treated with both the

stannylcyanocuprate **9b** and (stannyl)vinylcyanocuprate **12**. As expected the stannyl transfer occurred on **19a** leading to the vinylstannyl derivative **10** in 78% yield after methylation (Scheme 12). Reaction of the H.O. cyanocuprate **12** prepared by the Lipshutz exchange method between 2.0 equivalents of (*E*)-1,2-bis(tributylstannyl)ethylene **11** and 1 equivalent of $Bu_2Cu(CN)Li_2$, gave the desired stannyldiene **1** in 48% yield (Scheme 12). The yield of this reaction was enhanced to 58% when 4 equivalents of **11** were employed for the preparation of the cuprate **12**.

Scheme 12



*During this work the synthesis of the western part **1** of des-epoxy-rosaramycin **I** was achieved, and the (E)-vinylstannane **10** and (E,E)-stannyldiene **1** were obtained in a pure form via a cuprate rearrangement. It seems that this reaction could be applied and extended to other total syntheses in regard to the stereoselective preparation of alkenes, vinylstannanes and stannyldienes. Nevertheless in our hope to develop new synthetic strategies in the field of natural compounds, we explored new approaches of the west fragment **1** of des-epoxy-rosaramycin **I**.*

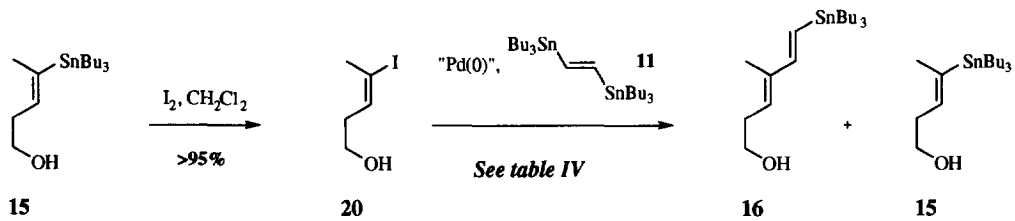
II) The Stille Pd(0) coupling strategy

The cuprate rearrangement strategy developed above shown that a stannyl transfer could be performed with an excellent yield, and the vinylstannane **15** was obtained after methylation in overall 82-85% yield from dihydrofuran **13**. Taking advantage of this reaction we envisaged a direct palladium coupling reaction [22] between (*E*)-1,2-bis(tributylstannyl)ethylene **11** and model iodo compound **20** (Scheme 13), prepared in 90% yield from **15** using Chen exchange method.[23]

Using $PdCl_2(PPh_3)_2$ as catalyst in THF,[24] coupling between the iodo derivative **20** and **11** led to the

stannyldiene **16** in only 10% yield (Scheme 13, Table IV). The second product isolated in this reaction was the unexpected vinylstannane **15** (18%, Table IV, entry 1).When we employed $Pd(CH_3CN)_2Cl_2$ in DMF [25,26] the stannyldiene **16** was obtained in lower yield (6%, Table IV, entry 2). The best results were obtained using $Pd(PPh_3)_4$ in THF; coupling between the iodo compound **20** and distilled **11** furnished the desired stannyldiene **16** in 36% yield whereas the vinylstannane **15** was still obtained in 30% yield (Table IV, entries 3-5).[27]

Scheme 13



15 **20** **16** **15**

Table IV: Stille coupling reaction between 11 and vinyliodide 20

Entry	Conditions					11	16 (yield %) [a]	15 (yield %)
1	5% mol	$PdCl_2(PPh_3)_2$	THF	55°C	1 h	1.3 equiv	10	18
2	"	$Pd(CH_3CN)_2Cl_2$	DMF	20°C	48 h	"	6	19
3	"	$Pd(PPh_3)_4$	THF	70°C	3 h	"	5	18
4	"	$Pd(PPh_3)_4$	THF	40°C	24 h	"	13	20
5	**5% mol**	**$Pd(PPh_3)_4$**	**THF**	**20°C**	**24 h**	**1.3 equiv**	**36**	**30**

[a] Yields are given for isolated products after chromatography.

*The modest yield obtained in this model study led us to prepare the stannyldiene **1** in another way. A direct stannylmetallation of an enyne precursor was then preferred.*

III) The stannylcupration strategy

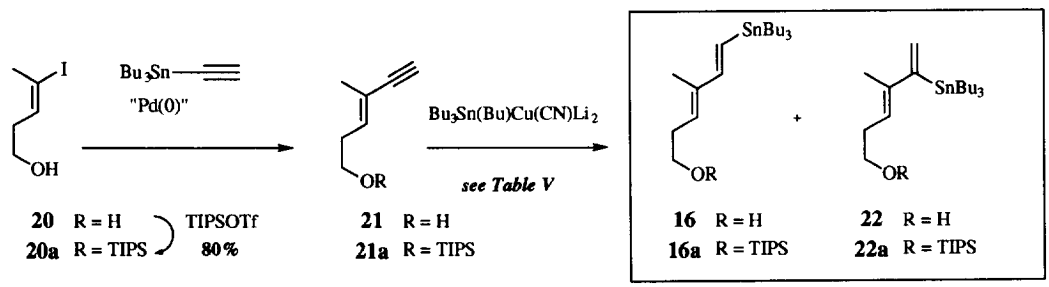
For our model study, enynes **21** and **21a** were prepared through a palladium-catalyzed coupling reaction between tributylstannyl acetylene [28] and vinyliodides **20** and **20a**. Using $Pd(PPh_3)_4$ at 50°C enyne **21** was obtained in 90% yield (Scheme 14), the corresponding silylated enyne **21a** was prepared from **20a** in 97% yield.

Disappointing results obtained for the hydrostannylation of enyne **21a** using Bu_3SnH (Table V, entries 1, 2) led us to turn our efforts to the stannylcupration of enynes. According to the literature,[14a,29,30] stannylcupration of enynes give better regiocontrol and yields when "mixed" H.O. stannylcyanocuprate $(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** are used (Table V, entries 4-16) instead of the corresponding homocuprate $(Bu_3Sn)_2Cu(CN)Li_2$ **9b** (Table V, entry 3). In these stannylcupration reactions, cuprates **9a** and **9b**, used before in a cuprate rearrangement, were prepared in a slighty different procedure in pure THF.

From protected enynol **21a** at -78°C, reaction of $(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** led to a 1:1 mixture of stannyldienes **16a** and **22a** in 50% yield (Table V, entry 4), in contrast with Hamada's and Shioiri's results,[30] which obtained a total regiocontrol and a 95% yield at -78°C. When this stannylcupration was carried out at -40°C

or -25°C on the enyne **21a** yields improved to 90% and the distal stannyldiene **16a** was almost exclusively obtained with no trace of the *Z* isomer being detected (Table V, entries 5, 6, **16a/22a** = 95:5).

Scheme 14



The last step of quenching the stannylcupration reaction, performed at -25°C, was realised by MeOH addition to the reaction mixture; this modification led to a total regio- and stereocontrol (Table V, entry 8), the exclusive stannyldiene **16a** was produced in 85% yield, whereas quenching with NH_4Cl/NH_4OH (4:1) gave a 95:5 mixture of **16a** and **22a** (Table V, entry 7). At -25°C, reaction of two equivalents of the cyanocuprate $(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** on enynol **21** delivered the stannyldiene **16** as the *only isomer* after quenching with MeOH or NH_4Cl/NH_4OH (Table V, entries 11, 12).

Table V: Stannylation of enynes 21 and 21a

Entry	Enyne	Reagent	Conditions	Yield [a]	Stannyl dienes	
1	**21a**	Bu_3SnH, neat / AIBN	100°C, 8h	60%	**16a/22a**	30:70
2	"	"	100°C, 16h	30%	"	90:10
3	"	1 equiv $(Bu_3Sn)_2Cu(CN)Li_2$ **9b** / THF	-40°C, 0.5h	90%	"	50:50
4	"	1 equiv $(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** / THF	-78°C, 1.5h	50% [b]	"	50:50
5	"	"	-40°C, 0.5h	90%	"	95:5
6	"	"	-40°C, 0.5h [c]	90%	"	95:5
7	"	"	-25°C, 0.5h	85%	"	95:5
8	"	"	-25°C, 0.5h [c]	85%	"	100:0
9	**21**	2 equiv $(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** / THF	-40°C, 0.5h	90%	**16/22**	95:5
10	"	"	-40°C, 0.5h [c]	90%	"	95:5
11	"	"	-25°C, 0.5h	85%	"	100:0
12	"	"	-25°C, 0.5h [c]	85%	"	100:0

[a] Yields are given in % for isolated products after chromatography. [b] 38% of starting material were recovered.
[c] In this case, quenching was carried out by MeOH addition to the reaction mixture at -25°C; in other cases the mixture was poured in a saturated aqueous NH_4Cl / concentrated ammonia 9:1 solution at -10°C.

Addition of the "mixed" cuprate $(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** to (±)-**24** at -25°C afforded stannyldienes (±)-**1** and (±)-**25** in 80% yield [(±)-**1**/(±)-**25** = 95:5, Table VI, entry 15,16]; when the reaction was carried out at - 40°C, the yield was improved to 90% and the regiocontrol better than 95:5 (Table VI, entry 13).

From the final preparation of racemic stannyldiene (±)-**1** we then focused on the preparation of the enyne (±)-**24** from the vinylstannane (±)-**10** in the same way we used above (Scheme 15); an iodine exchange performed on (±)-**10** delivered the iodo derivative (±)-**23** which was then coupled with tributylstannyl acetylene to furnish the enyne (±)-**24**.

Scheme 15

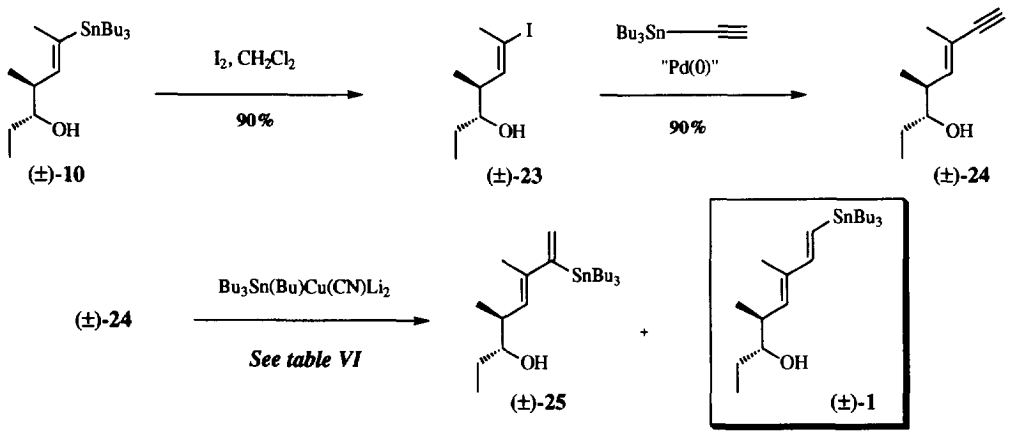


Table VI: Stannylcupration of enyne (±)-24

Entry	Enyne	Reagent	Conditions	Yield[a]	Stannyl dienes	
13	(±)-**24**	2 equiv $(Bu_3Sn)(Bu)Cu(CN)Li_2$ **9a** / THF	-40°C, 0.5h	90%	(±)-**1**/(±)-**25**	>95:5
14	"	"	-40°C, 0.5h[b]	90%	"	95:5
15	"	"	-25°C, 0.5h	80%	"	95:5
16	"	"	-25°C, 0.5h[b]	80%	"	95:5

[a] Yields are given in % for isolated products after chromatography. [b] In this case, quenching was carried out by MeOH addition to the reaction mixture at -25°C; in other cases the mixture was poured in a saturated aqueous NH_4Cl / concentrated ammonia 9:1 solution at -10°C.

IV) Conclusion

In our synthetic approach of the western part 1 of des-epoxy-rosaramycin I, the preparation of the stannyldiene 1 was performed with high yield and in a stereo- and enantioselective pathway. The cuprate rearrangement used in this strategy shown to be an efficient tool in total synthesis of natural products.

Stannylcupration of enynes employed in this work also gave good yields and excellent regio- and stereocontrol. Application of these strategies to the synthesis of the western part 2 of macrocyclic antibiotics such as tylosin II was recently achieved in our Laboratory.[31]

EXPERIMENTAL PART

General methods

Physical data and spectroscopic measurements

Infrared spectra (I.R.) were obtained on a Perkin-Elmer 257 model instrument (wavelength are given in cm^{-1}).

^1H NMR spectra were recorded on a Bruker AM 200 SY instrument at 200 MHz. The chemical shifts are expressed (ppm) referenced to residual chloroform (7.26 ppm). Data are reported as follows: δ, chemical shift; multiplicity (recorded as s, singlet; d, doublet; t, triplet; q, quadruplet and m, multiplet), coupling constants (*J* in Hertz, Hz), integration and assignment (aromatic, Ar). H,H-COSY and H,H-NOESY experiments were routinely carried out to ascertain H-H connectivities and configuration assignments, respectively.

^{13}C NMR spectra were recorded on a Bruker AM 200 SY instrument at 50.3 MHz. The chemical shifts are expressed (ppm), reported from the central peak of deuterochloroform (76.9 ppm). J-modulated spin-echo technique (J-mod) experiments were used for evaluating CH multiplicities. When necessary, ^{13}C spectra were assigned with the aid of HETCOR experiments.

Mass spectra (MS) were obtained on a Nermag/SIDAR V 2.3 spectrometer *via* direct introduction. Ionization was obtained either by electronic impact (EI) or chemical ionization with ammonia (CI, NH_3) . Mass spectral data are reported as m/z.

Optical rotations were determined on a Perkin-Elmer 241 instrument.

Microanalyses were performed on a CHN 240 Perkin Elmer instrument by the Service de Microanalyse, Centre d'Etudes Pharmaceutiques, Châtenay-Malabry, F-92296.

Chromatography

All reactions were monitored by thin-layer chromatography (TLC) carried out on precoated plate of silica gel 60F 254 (Merck, Art. 7735) or aluminum oxide Merck 60F 254 (Art. 5550). Visualization was accomplished with UV light then 7-10% ethanolic phosphomolybdic acid solution, followed by heating was used as developing agents.

Flash chromatography was performed on silica gel Merck 60, 230-400 mesh (Art. 9385) or aluminum oxide Merck 90, 70-230 mesh (Art. 1097).

HPLC chromatography was performed on a Microbondapak C18 Waters (10μ).

Solvents distillation

Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium-benzophenone. Dichloromethane (CH_2Cl_2) from Al_2O_3, triethylamine and pyridine from KOH. Benzene (PhH) and toluene were distilled from sodium-benzophenone. Pentane and hexane were distilled from phosphoric anhydride. Methanol (MeOH) was distilled from the corresponding magnesium derivative.

Usual procedures

All air and/or water sensitive reactions were carried out under a nitrogen or argon atmosphere with dry, freshly distilled solvents using standard syringe-cannula/septa techniques. All corresponding glassware was oven dried (110°C) and/or carefully dried in line with a flameless heat gun.

Bulb-to-bulb distillations were performed on a BUCHI GKR 51 Kugelrohr apparatus.

Yields refer to chromatographically and spectroscopically homogeneous materials, unless otherwise stated.

^1H and ^{13}C NMR of organostannyl compounds

For large Sn-^1H or Sn-^{13}C coupling constants (250-450 Hz), the central signal was associated with two close pairs of satellites corresponding to both ^{117}Sn and ^{119}Sn isotopes; in this case two different coupling constants were reported. For small Sn-^1H and Sn-^{13}C (>100 Hz), the two pairs of satellites collapse and only one coupling constant was observed.

(5*Z*,3*R,4*S**)-6-(Diisopropylcarbamoyloxy)-4-methyl-hex-5-en-3-ol [(±)-4]**

To a solution of N,N,N',N'-tetramethylethylenediamine (TMEDA, 4.4 mL, 29 mmol, 1.15 equiv) in diethyl ether (65 mL) at -78°C, under argon atmosphere, was added a 2 M solution of BuLi in hexane (13.8 mL, 27.6 mmol, 1.1 equiv). After 30 min at -78°C a solution of the allyl carbamate 5 [6] (5.0 g, 25.1 mmol) in diethyl ether (5.0 mL) was slowly added. After stirring for 45 min at -78°C, titanium tetraisopropoxide [$Ti(^iOPr)_4$, 23.0 mL, 75.3 mmol, 3.0 equiv] was slowly added, the mixture became limpid and turned orange. After 30 min at -78°C freshly distilled propionaldehyde (7.2 mL, 100.0 mmol, 4 equiv) was slowly added, and the reaction mixture was stirred for 2 h at -78°C and the temperature was allowed to rise to 0°C before quenching by addition of an aqueous 2 N HCl solution. The mixture was extracted with diethyl ether (x 3) and the organic phases washed with brine. After the organic layer was dried under Na_2SO_4, the solvent was removed under *vacuo* and the residue purified by flash chromatography on silica gel (hexane/ethyl acetate, 8:2) to deliver the title product (±)-**4** as a colorless oil (5.80 g, 90% yield).

IR (CCl_4) ν cm^{-1}: 3500, 1705, 1665.

^1H NMR ($CDCl_3$, 200 MHz) δ 0.96 (t, *J* = 7.5 Hz, 3 H, CH_3, H3-1), 1.04 (d, *J* = 6.4 Hz, 3 H, CH_3, CH_3-4), 1.25 {d, *J* = 6.0 Hz, 12 H, 4 CH_3, N[CH-($C\underline{H}_3$)$_2$]$_2$}, 1.30-1.60 (m, 2 H, H_2-2), 1.74 (s, 1 H, OH), 2.77 (qdd, *J* = 6.4, 10.0, 3.0 Hz, 1 H, H-4), 3.37 (td, *J* = 5.4, 3.0 Hz, 1 H, H-3), 3.80 and 4.10 {2 m, 2 H, N[C$\underline{H}$-(CH$_3$)$_2$]$_2$}, 4.69 (dd, *J* = 10.0, 6.5 Hz, 1 H, H-5), 7.11 (d, *J* = 6.5 Hz, 1 H, H-6).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.7 (CH_3, C-1), 17.2 (CH_3-4), 20.0 and 21.2 {4 CH_3, N[CH-($\underline{C}H_3$)$_2$]$_2$}, 27.1 (C-2), 35.3 (C-4), 45.3 and 46.5 {2 C, N[$\underline{C}$H-(CH$_3$)$_2$]$_2$}, 76.0 (C-3), 111.9 (C-5), 134.7 (C-6), 152.6 (C=O).

MS (C.I., NH_3): *m/z* 258 (MH^+).

Anal calcd for $C_{14}H_{27}O_3N$: C: 65.33; H: 10.57; N: 5.44; Found: C: 65.18; H: 10.62; N: 5.35.

(5*Z*,3*R*,4*S*)-6-(Diisopropylcarbamoyloxy)-4-methyl-hex-5-en-3-ol (4)

To a rapidly stirred solution of the allyl carbamate 5 [6] (1.84 g, 9.25 mmol) and (-)-sparteine (2.24 g, 9.52 mmol, 1.03 equiv) in pentane (12.3 mL) and cyclohexane (1.8 mL) at -78°C, was added a solution of *n*-BuLi in hexane (1.6 M in hexane, 6.2 mL, 9.90 mmol, 1.07 equiv) and white crystals appeared in 10 min. After 3 h of crystallization at -78°C, a precooled (-50°C, 30 min) solution of titanium tetraisopropoxide ($Ti(^iOPr)_4$, 8.25 mL, 27.7 mmol, 3.0 equiv) in pentane (21.6 mL) was quickly added *via* cannula to the reaction mixture of lithiocarbamate which became limpid and turned orange. After 1 h at -78°C distilled propionaldehyde (2.7 mL, 37.0 mmol, 4.0 equiv) was slowly added to the orange solution. The reaction mixture was stirred for 2 h at -78°C and the temperature was allowed to rise to 0°C before quenching by addition of an aqueous 2 N HCl solution. The mixture was extracted with diethyl ether (3 x) and the organic phases washed with brine. After the organic layer was dried under $MgSO_4$, the solvent was removed under *vacuo* and the residue purified by flash chromatography on silica gel (hexane/ethyl acetate, 8:2) to deliver the title product **4** as a colorless oil (2.14 g, 90% yield, 92% ee).

$[\alpha]_D$ = -10.5 (c = 1.05, MeOH).

(+)-Acetyl mandelate derivative of 4

To a cooled solution (0°C) of carbamate **4** (155 mg, 0.6 mmol), (+)-acetyl mandelic acid (164 mg, 0.84 mmol, 1.4 equiv) and DMAP (11.6 mg, 0.06 mmol, 0.1 equiv), was added dropwise a solution of DCC (162 mg, 7.8 mmol, 1.3 equiv) in dried CH_2Cl_2 (1 mL). After stirring for 12 h at 20°C, the mixture was diluted at 0°C with an aqueous 0.5 N HCl solution. The reaction mixture was extracted with CH_2Cl_2 (x 3) and the organic phases washed successively with aqueous saturated NaCl, $NaHCO_3$ and NaCl solutions. After the solvent was removed under *vacuo*, the crude residue was purified by flash chromatography on silica gel (hexane/ ethyl acetate, 8:2) to deliver the acetyl mandelate derivative (233mg, 90% yield) which was analyzed with the aid of ^1H NMR to determine the enantiomeric excess of **4** (92% ee).

[1*R*(5*Z*,3*R*,4*S*)-[6-(Diisopropylcarbamoyloxy)-4-methyl-hex-5-en-3-yl] acetyl mandelate.
^1H NMR ($CDCl_3$, 200 MHz) δ 0.51 (d, *J* = 6.0 Hz, 3 H, CH_3, CH_3-4), 0.74 (t, *J* = 6.4 Hz, 3 H, CH_3, H_3-1), 1.03 (m, 2 H, H_2-2), 1.25 {d, *J* = 6.0 Hz, 12 H, 4 CH_3, N[CH-(CH_3)$_2$]$_2$}, 2.10 (s, 3 H, CH_3, OAc), 2.75 (m, 1 H, H-4), 3.70 and 4.07 {2 m, 2 H, N[CH-(CH_3)$_2$]$_2$}, 4.30 (dd, *J* = 9.1, 6.0 Hz, 1 H, H-5), 4.73 (m, 1 H, H-3), 5.83 (s, 1 H, Ph-CHOAc-), 6.85 (d, *J* = 6.0 Hz, 1 H, H-6), 7.17 (m, 2 H, Ar-H), 7.48 (m, 3 H, Ar-H). For minor isomer ^1H NMR ($CDCl_3$, 200 MHz) δ 0.96 (d, *J* = 6.0 Hz, 3 H, CH_3, CH_3-4), 0.5 (t, *J* = 6.4 Hz, 3 H, CH_3, H_3-1), 2.85 (m, 1 H, H-4), 4.59 (dd, *J* = 9.1, 6.0 Hz, 1 H, H-5), 7.0 (d, *J* = 6.0 Hz, 1 H, H-6).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.64 (CH_3, C-1), 16.88 (CH_3-4), 20.57 (CH_3, OAc), 21.20 {4 CH_3, N[CH-(CH_3)$_2$]$_2$}, 25.08 (C-2), 33.43 (C-4), 45.74 {2 C, N[CH-(CH_3)$_2$]$_2$}, 74.70 (PhCHOAc), 79.65 (C-3), 110.51 (C-5), 127.53, 128.16, 129.11 (C, Ar), 135.53 (C-6), 152.42 (C=O, OCb), 168.66 (C=O), 170.13 (C=O).

(5*Z*,3*R,4*S**)-3-(*tert*-Butyldimethylsilyloxy)-6-(diisopropylcarbamoyloxy)-4-methyl-hex-5-ene [(±)-4a]**

To a solution of (±)-**4** (2.6 g, 10.0 mmol) in dried CH_2Cl_2 (10 mL), was slowly added a solution of TBSCl (1.7 g, 11.3 mmol, 1.1 equiv) and imidazole (1.0 g, 15 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL). After stirring for 12 h at 20°C the reaction mixture was partitioned between CH_2Cl_2 and an aqueous saturated NH_4Cl solution and extracted by CH_2Cl_2 (x 3). The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 93:7), to give the title compound (±)-**4a** (3.34g, 90% yield).

IR (CCl_4) ν cm^{-1}: 1705, 1665.
^1H NMR ($CDCl_3$, 200 MHz) δ 0.07 [s, 6 H, 2 CH_3, Si(CH_3)$_2$], 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3, H_3-1), 0.93 [s, 9 H, 3 CH_3, SiC(CH_3)$_3$], 1.01 (d, *J* = 7.0 Hz, 3 H, CH_3, CH_3-4), 1.29 {d, *J* = 7.0 Hz, 12 H, 4 CH_3, N[CH-(CH_3)$_2$]$_2$}, 1.37-157 (m, 2 H, H_2-2), 2.86 (m, 1 H, H-4), 3.49 (td, *J* = 6.0, 3.0 Hz, 1 H, H-3), 3.74 and 4.21 {2 m, 2 H, N[CH-(CH_3)$_2$]$_2$}, 4.72 (dd, *J* = 10.0, 7.0 Hz, 1 H, H-5), 7.03 (d, *J* = 7.0 Hz, 1 H, H-6).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ - 4.41, - 4.66 [2 CH_3, Si(CH_3)$_2$], 9.79 (CH_3, C-1), 17.23 (CH_3-4), 17.96 [C, SiC(CH_3)$_3$], 20.42 and 21.03 {4 CH_3, N[CH-(CH_3)$_2$]$_2$}, 25.74 [3 CH_3, SiC(CH_3)$_3$], 27.20 (C-2), 34.30 (C-4), 45.95 {2 C, N[CH-(CH_3)$_2$]$_2$}, 76.68 (C-3), 112.43 (C-5), 134.63 (C-6), 152.86 (C=O).
MS (C.I., NH_3): *m/z* 372 (MH^+).

(5*Z*,3*R,4*S**)-6-(Diisopropylcarbamoyloxy)-3-methoxy-4-methyl-hex-5-ene [(±)-4b]**

In dried THF (5 mL), was added NaH (80% in oil, 173 mg, 5.77 mmol, 1.3 equiv). After stirring for 5 min at -78°C the solvent was removed and the residue washed twice with dried THF. The residue was dissolved in THF (5 mL) at -78°C, a solution of (±)-**4** (1.15 g, 4.45 mmol) in THF (5mL) was added dropwise and stirred for 30 min at -78°C, MeI (1 mL, 16 mmol, 4 equiv) was added to the alcoolate and the reaction mixture was immediately warmed to 55°-60°C for 2 h. The reaction mixture was cooling down to 0°-10°C and partitioned between CH_2Cl_2 and aqueous NH_4Cl solution, and extracted with CH_2Cl_2; the residue obtained after the solvent was removed under reduced pressure was purified by flash chromatography (hexane/ethyl acetate, 93:7), to give the title compound (±)-**4b** (1.32 g, 85% yield).

IR (CCl_4) ν cm^{-1}: 1710, 1660.
^1H NMR ($CDCl_3$, 200 MHz) δ 0.86 (t, *J* = 7.0 Hz, 3 H, CH_3, H_3-1), 0.97 (d, *J* = 7.0 Hz, 3 H, CH_3, CH_3-4), 1.04 (t, *J* = 7.0 Hz,

3 H, CH_3, H3-1), 1.23 {d, J = 7.0 Hz, 12 H, 4 CH_3, N[CH-($C\underline{H}_3$)2]2}, 1.31-1.57 (m, 2 H, H_2-2), 2.94 (m, 2 H, H-3, H-4), 3.37 (s, 3 H, CH_3, OCH_3), 3.69 and 4.17 {2 m, 2 H, N[C$\underline{H}$-(CH_3)2]2}, 4.66 (dd, J = 10.0, 7.0 Hz, 1 H, H-5), 6.99 (d, J = 7.0 Hz, 1 H, H-6).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 10.19 (CH_3, C-1), 16.39 (CH_3-4), 20.26 and 21.34 {4 CH_3, N[CH-($\underline{C}H_3$)2]2}, 23.59 (C-2), 32.46 (C-4), 45.53, 46.58 {2 C, N[$\underline{C}$H-(CH_3)2]2}, 57.73 (CH_3, OCH_3), 86.07 (C-3), 112.56 (C-5), 136.65 (C-6), 152.71 (C=O).

MS (C.I., NH_3): *m/z* 272 (MH^+).

(5*E*,3*R,4*S**)-3-(*tert*-Butyldimethylsilyloxy)-6-(diisopropylcarbamoyloxy)-6-(trimethylstannyl)-4-methyl-hex-5-ene [(±)-6a]**

To a solution of (±)-**4a** (0.98 g, 2.65 mmol) in dried THF (5 mL) at -78°C, was slowly added *tert*-BuLi (1.7N in hexane, 2.3 mL, 4.0 mmol, 1.5 equiv). After stirring for 15 min at -78°C a 1M THF solution of Me_3SnCl (4.5 mL, 4.5mmol, 1.7 equiv) was added and the reaction mixture stirred for 1 h at -78°C, partitioned between CH_2Cl_2 and aqueous NH_4Cl solution, and extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on Al_2O_3 (hexane/NEt_3, 97:3), to give the title compound (±)-**6a** (1.16 g, 82% yield).

IR (CCl_4) ν $^{cm-1}$: 1710, 1660.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.07 [s, 6 H, 2 CH_3, Si(CH_3)2], 0.15 [s, 9 H, 3 CH_3, Sn(CH_3)3, J ^{119}Sn-H ~ J ^{117}Sn-H = 54.0 Hz], 0.82 (t, J = 7.0 Hz, 3 H, CH_3, H3-1), 0.93 [s, 9 H, 3 CH_3, SiC(CH_3)3], 0.99 (d, J = 7.0 Hz, 3 H, CH_3, CH_3-4), 1.26 {d, J = 7.0 Hz, 12 H, 4 CH_3, N[CH-($C\underline{H}_3$)2]2}, 1.40-1.60 (m, 2 H, H_2-2), 2.85-3.09 (m, 1 H, H-4), 3.49 (q, J = 6.0 Hz, 1 H, H-3), 3.72 and 4.17 {2 m, 2 H, N[C$\underline{H}$(CH_3)2]2}, 4.86 (d, J = 9.0 Hz, 1 H, H-5, J ^{119}Sn-H ~ J ^{117}Sn-H = 36.0 Hz).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ -6.23 [3 CH_3, Sn(CH_3)3, J ^{119}Sn-C = 375.0 Hz, J ^{117}Sn-C = 360.0 Hz), -4.15, -4.40 [2 CH_3, Si(CH_3)2], 9.56 (CH_3, C-1), 17.50 (CH_3-4), 18.06 [C, Si$\underline{C}$(CH_3)3], 22.54 {4 CH_3, N[CH-($\underline{C}H_3$)2]2}, 25.84 [3 CH_3, SiC($\underline{C}H_3$)3], 27.26 (C-2), 35.56 (C-4, J ^{119}Sn-C ~ J ^{117}Sn-C = 35.0 Hz), 45.87 {2 C, N[$\underline{C}$H-CH_3)2]2}, 76.80 (C-3), 126.36 (C-5), 154.00 (C-6), 154.85 (C=O).

MS (C.I., NH_3): *m/z* 536 (MH^+) for major ^{120}Sn isotope.

(5*E*,3*R,4*S**)-6-(Diisopropylcarbamoyloxy)-3-methoxy-4-methyl-6-(trimethylstannyl)-hex-5-ene [(±)-6b]**

To a solution of (±)-**4b** (535 mg, 1.97 mmol) in dried THF (5 mL) at -78°C, was slowly added *tert*-BuLi (1.7N in hexane, 1.8 mL, 3.0 mmol, 1.5 equiv). After stirring for 15 min at -78°C a 1M THF solution of Me_3SnCl (3.4 mmol, 1.7 equiv) was added and stirred for 1 h at -78°C. The reaction mixture was partitioned between CH_2Cl_2 and aqueous NH_4Cl solution, and extracted with CH_2Cl_2. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on Al_2O_3 (hexane/NEt_3, 95:5), to give the title compound (±)-**6b** (676 mg, 79% yield).

IR (CCl_4) ν $^{cm-1}$: 1708, 1660.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.10 [s, 9 H, 3 CH_3, Sn(CH_3)3], 0.87 (t, J = 7.0 Hz, 3 H, CH_3, H3-1), 0.97 (d, J = 7.0 Hz, 3 H, CH_3, CH_3-4), 1.24 {d, J = 7.0 Hz, 12 H, 4 CH_3, N[CH-($C\underline{H}_3$)2]2}, 1.40-1.60 (m, 2 H, H_2-2), 2.90 (m, 2 H, H-3, H-4), 3.36 (s, 3 H, CH_3, OCH_3), 3.75 and 4.11 {2 m, 2 H, N[C$\underline{H}$-(CH_3)2]2}, 4.90 (d, J = 9.0 Hz, 1 H, H-5).

MS (C.I., NH_3): *m/z* 436 (MH^+) for major ^{120}Sn isotope.

(5*Z*,3*R,4*S**)-3-(*tert*-Butyldimethylsilyloxy)-4-methyl-dec-5-ene [(±)-8a]**

From trimethylstannane **6a** and cuprate **7a**

-Dilithium dibutylcyanocuprate **7a**: Cuprate **7a** was prepared according to Lipshutz procedure.[11] To a suspension of dried CuCN (59 mg, 0.65 mmol, 1 equiv) in diethyl ether (2 mL) at -40°C, was added a 1.6 N BuLi solution in hexane (0.9 mL, 1.44 mmol, 2.25 equiv). The mixture was stirred at -40°C for 5 min, at 20°C for 10 min. The temperature of the cuprate was then kept at -30°C before use.

To a solution of the dilithium dibutylcyanocuprate **7a** (0.65 mmol, 1 equiv) at -30°C (see below), was added a solution of the carbamate (±)-**5a** (350 mg, 0.65 mmol) in dried diethyl ether (2 mL). The mixture was stirred at -5°C-0°C for 30 min. The reaction was then stopped by addition of a saturated aqueous NH_4Cl solution (2 mL). After stirring for 15 min at 0°C the mixture was poured in a cooled (0°C) solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1), and the reaction mixture was extracted with diethyl ether. Purification by flash chromatography on silica gel led to the title product (±)-**8a** (167 mg, 90% yield).

IR (CCl_4) ν $^{cm-1}$: 2980, 1625, 1450, 1380.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.03 [s, 6 H, 2 CH_3, Si(CH_3)2], 0.85 (t, J = 8.0 Hz, 3 H, CH_3, H3-1), 0.96 [s, 9 H, 3 CH_3, SiC(CH_3)3], 1.03 (d, J = 8.0 Hz, 3 H, CH_3, CH_3-4), 1.33 (m, 9 H), 1.95 (m, 2 H, H_2-7), 2.23 (m, 1 H, H-4), 3.43 (td, J = 4.0, 6.0 Hz, 1 H, H-3), 5.31 (m, 2 H, H-5, H-6).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ -4.30 [2 CH_3, Si(CH_3)2], 10.18 (CH_3, C-1), 13.95 (C-10), 15.95 (CH_3-4), 18.18 [C, Si$\underline{C}$(CH_3)3], 22.19 (C-9), 25.95 [3 CH_3, SiC($\underline{C}H_3$)3], 26.19 (C-2), 31.81 (C-8), 32.42 (C-7), 41.63 (C-4), 77.79 (C-3), 130.17, 132.46 (C-5, C-6).

MS (C.I., NH_3): *m/z* 285 (MH^+).

(5*Z*,3*R,4*S**)-3-Methoxy-4-methyl-dec-5-ene [(±)-8b]**

From trimethylstannane **6b** and cuprate **7a**

To a solution of the dilithium dibutylcyanocuprate **7a** (0.65 mmol, 1 equiv) at -30°C (see above), was added a solution of the carbamate (±)-**6b** (300 mg, 0.65 mmol) in dried diethyl ether (3 mL). The mixture was stirred at -5°C-0°C for 30 min. The reaction was then stopped by addition of an saturated aqueous NH_4Cl solution (2 mL). After stirring for 15 min at 0°C the mixture was poured in a cooled (0°C) solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1), and the reaction mixture was extracted with diethyl ether. Purification by flash chromatography on silica gel led to the title product (±)-**8b** (102 mg, 80% yield).

IR (CCl_4) ν cm^{-1}: 2980, 1625, 1450, 1380.
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.83 (t, *J* = 8.0 Hz, 3 H, CH_3, H_3-1), 1.02 (t, *J* = 8.0 Hz, 3 H, CH_3, CH_3-4), 1.33 (m, 7 H), 1.95 (m, 2 H, H_2-2), 2.23 (m, 1 H, H-4), 3.0 (m, 1 H, H-3), 3.32 (s, 3 H, CH_3, OMe), 5.34 (m, 2 H, H-5, H-6).
MS (C.I., NH_3): *m/z* 185 (MH^+).

(5*E*,7*E*,3*R,4*S**)-3-(*tert*-Butyldimethylsilyloxy)-4-methyl-8-(tributylstannyl)-octa-5,7-diene [(±)-1a]**
From trimethylstannane **6a** and cuprate **12**
-Dilithium bis[(*E*)-2-(tributylstannyl)ethenyl]cyanocuprate (**12**): **Method I:** From BuLi, CuCN and **11** prepared according to Corey procedure.[12] To a solution of **11** (1.57 g, 2.5 mmol, 2.5 equiv) in dried THF (4 mL) at -78°C, was added a 1.6 M solution of *n*-BuLi in pentane (2.3 mL, 3.6 mmol, 3.6 equiv). The temperature was then allowed to warm to -10°C in 30 min before addition *via* cannula to a suspension of CuCN (94 mg, 1.0 mmol, 1 equiv) in dried diethyl ether (5 mL) at -60°C. The temperature was then allowed to rise to -15°C in 1 h.

A THF solution (2 mL) of the carbamate (±)-**6a** (550 mg, 1.0 mmol) was then slowly added to the solution (-15°C) of cuprate **12** (1 equiv). After stirring for 1 h at -15°C the reaction mixture was diluted with an aqueous saturated NH_4Cl solution and the temperature allowed to rise to 20°C in 30 min before to poured the reaction mixture in a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1), stirred for 10 min, and extracted with diethyl ether. Purification of the crude residue by chromatography on Al_2O_3 column led to the title compound (±)-**1a** (18 mg, 3% yield).

IR (CCl_4) ν cm^{-1}: 3500, 1705, 1665.
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.03 [s, 6 H, 2 CH_3, $Si(CH_3)_2$], 0.96 [s, 9 H, 3 CH_3, $SiC(CH_3)_3$], 0.66 -1.8 [m, 35 H, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, H_3-1, CH_3-4, H_2-2], 2.55 (m, 1 H, H-4), 2.92 (q, *J* = 8.0 Hz, 1 H, H-3), 3.40 (s, 3 H, CH_3, OCH_3), 5.66 (dd, *J* = 15.0, 8.0 Hz, 1 H, H-5), 6.07 (dd, *J* = 15.0, 10.0 Hz, 1 H, H-6), 6.12 (d, *J* = 20.0 Hz, 1 H, H-8), 6.37 (dd, *J* = 20.0, 10 Hz, 1 H, H-7).
MS (C.I., NH_3): *m/z* 545 (MH^+) for major ^{120}Sn isotope.

(5*E*,7*E*,3*R,4*S**)-3-Methoxy-4-methyl-8-(tributylstannyl)-octa-5,7-diene [(±)-1b]**
From trimethylstannane **6b** and cuprate **12**
A THF solution (2 mL) of the carbamate (±)-**6b** (450 mg, 1.0 mmol) was slowly added to the solution (-15°C) of the cuprate **12** (1 equiv, see above). After stirring for 1 h at -15°C the reaction mixture was diluted with an aqueous saturated NH_4Cl solution and the temperature allowed to rise to 20°C in 30 min before to poured the reaction mixture in a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1), stirred for 10 min, and extracted with diethyl ether. Purification of the crude residue by chromatography on Al_2O_3 column led to the title compound (±)-**1b** (44 mg, 9% yield).

IR (CCl_4) ν cm^{-1}: 2980, 1625, 1450, 1380.
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.66 -1.8 [m, 35 H, $Sn(CH_2$-CH_2-CH-$CH_3)_3$, H_3-1, CH_3-4, H_2-2], 2.52 (m, 1 H, H-4), 2.97 (q, *J* = 8.0 Hz, 1 H, H-3), 3.42 (s, 3 H, CH_3, OCH_3), 5.64 (dd, *J* = 15.0, 8.0 Hz, 1 H, H-5), 6.04 (dd, *J* = 15.0, 10.0 Hz, 1 H, H-6), 6.10 (d, *J* = 20.0 Hz, 1 H, H-8), 6.39 (dd, *J* = 20.0, 10 Hz, 1 H, H-7).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.45 [3 CH_2, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, *J* ^{119}Sn-C = 342.0 Hz *J* ^{117}Sn-C = 320.0 Hz), 10.19 (CH_3, C-1), 13.63 [3 CH_3, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$], 15.75 (CH_3-4), 23.53 (C-2), 27.25 [3 CH_2, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, *J* ^{119}Sn-C ~ *J* ^{117}Sn-C = 55.0 Hz], 29.08 [3 CH_2, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, *J* ^{119}Sn-C ~ *J* ^{117}Sn-C = 20.0 Hz], 38.97 (C-4), 57.91 (CH_3, OCH_3), 86.78 (C-3), 131.21, 133.69, 135.67, 147.26 (C-5, C-6, C-7, C-8).
MS (C.I., NH_3): *m/z* 445 (MH^+) for major ^{120}Sn isotope.

(3*E*)-4-Methyl-oct-3-en-1-ol (14)[15]
From lithiodihydrofuran **13a** or stannyl dihydrofuran **13b** and cuprates **7a** and **7b**
-5-Lithio-2,3-dihydrofuran (**13a**): A 1.7M solution of *t*-BuLi in hexane (3.5 mL, 6 mmol, 1.2 equiv) was slowly added to a solution of freshly distilled dihydrofuran **13** (DHF, 357 mg, 5 mmol) in THF (5 mL) at -60°C. Stirring was maintained for 10 min at -60°C and the flask was rapidly put in an ice bath for 50 min.

-5-(Trimethylstannyl)-2,3-dihydrofuran (**13b**): To the solution of 5-lithio-2,3-dihydrofuran **13a** prepared before (5 mmol) and cooled at -60°C, was added a 1M THF solution (6.5 mL) of trimethylstannyl chloride (Me_3SnCl, 6.5 mmol, 1.3 equiv). The reaction mixture was stirred for 1.5 h at 0°C and extracted with diethyl ether after dilution with an aqueous saturated NH_4Cl solution. The crude residue obtained after removal of the solvent was purified by distillation under reduced pressure (150°C, 30 mm/Hg), or by flash chromatography on Al_2O_3 (hexane/NEt_3 97:3), to afford the title compound **13b** (1.05 g, 90% yield).

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.20 [s, 9 H, 3 CH_3, $Sn(CH_3)_3$, *J* ^{119}Sn-H ~ *J* ^{117}Sn-H = 57.0 Hz)], 2.54 (td, *J* = 10.0, 3.0 Hz,

2 H, H_2-3), 4.20 (t, J = 10.0 Hz, 2 H, H_2-2), 5.03 [t, J = 3.0 Hz, 1 H, H-4].
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ -10.07 [3 CH_3, $Sn(CH_3)_3$, J ^{119}Sn-C = 369.0 Hz, J ^{117}Sn-C = 353.0 Hz], 29.81 (C-3), 69.91 (C-2, J ^{119}Sn-C ~ J ^{117}Sn-C = 30.0 Hz), 110.95 (C-4, J ^{119}Sn-C ~ J ^{117}Sn-C = 77.0 Hz), 162.37 (C-5).
MS (C.I., NH_3): *m/z* 235 (MH^+) for major ^{120}Sn isotope.

-Lithium butylcyanocuprate **7b**: Cuprate **7b** was prepared according to Lipshutz procedure.[11] To a suspension of dried CuCN (450 mg, 5.0 mmol, 1 equiv) in diethyl ether (16 mL) at -40°C, was added a 1.6 N BuLi solution in hexane (3.5 mL, 5.5 mmol, 1.1 equiv). The mixture was stirred at -40°C for 10 min, at 20°C for 10 min. The cuprate solution was then stored at -30°C before used.

A solution of the 5-lithio-2,3-dihydrofuran derivative **13a** (5mmol) (or 5-(trimethylstannyl)-2,3-dihydrofuran **13b**, 5 mmol in 5 mL of diethyl ether), prepared before, was added, *via* cannula, to a solution of the cuprate **7a** (5 mmol, see preparation of (±)-**8a** or **7b** (5.0 mmol) at -30°C (see above). The mixture was stirred at -5°- 0°C for 30 min. The mixture was then cooled at -30°C and MeI (2.2 mL, 35 mmol, 7 equiv) was added. The temperature was allowed to rise to 20°C for 1 h, stirring was maintained for 3 h at this temperature. The reaction mixture was poured into a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1) at -5°C and stirred for 30 min before extraction with diethyl ether (82 to 85% yields, see Table I).

14:
IR (CCl_4) ν $^{cm-1}$: 3700, 2970, 1705, 1665.
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.87 (t, J = 7.0 Hz, 3 H, CH_3, H_3-8), 1.2-1.5 (m, 4 H, H_2-6, H_2-7), 1.65 (s, 3 H, CH_3, CH_3-4), 1.98 (t, J = 7.0 Hz, 2 H, H_2-5), 2.26 (dt, J = 7.5, 6.5 Hz, 2 H, H_2-2), 3.58 (t, J = 6.5 Hz, 2 H, H_2-1), 5.14 (t, J = 7.5 Hz, 1 H, H-3).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.95 (CH_3, C-8), 17.25 (CH_3, CH_3-4), 22.50 (C-7), 30.33 (C-6), 31.45 (C-5), 39.63 (C-2), 62.48 (C-1), 120.12 (C-3), 139.38 (C-4).
MS (C.I., NH_3): *m/z* 143 (MH^+).

(3*E*)-4-Methyl-4-(tributylstannyl)-but-3-en-1-ol (15)
From lithiodihydrofuran **13a** and cuprates **9a** and **9b**
-Dilithium butyl-(tributylstannyl)cyanocuprate (**9a**): To a suspension of dried CuCN (450 mg, 5 mmol) in a mixture of diethyl ether (10 mL) and THF (6 mL) at -30°C, was slowly added a 2 M pentane solution of *n*-BuLi (5 mL, 10 mmol, 2 equiv). After 5 min at -30°C the cold bath was removed for 15 min. The solution was then cooled at -30°C and Bu_3SnH (2.7 mL, 10 mmol, 2 equiv) was added. The mixture was stirred for 30 min to 1 h at -30°C.

-Dilithium bis(tributylstannyl)cyanocuprate (**9b**): To a solution of hexabutyldistannane [$(Bu_3Sn)_2$, 5 mL, 10 mmol, 1.9 equiv] in THF (6 mL) at -40°C, was slowly added a 2 M pentane solution of *n*-BuLi (5 mL, 10 mmol, 2 equiv). The mixture was stirred for 15 min at -40°C and then added, *via* cannula, to a suspension of CuCN (450 mg, 5 mmol, 1 equiv) in diethyl ether (10 mL) at -40°C, the mixture was stirred for 30 min to 1 h between -20° to -30°C.

-5-Lithio-2,3-dihydrofuran (**13a**): A 1.7M solution of *tert*-BuLi in hexane (3.5 mL, 6 mmol, 1.2 equiv) was slowly added to a solution of freshly distilled dihydrofuran **13** (DHF, 350 mg, 5 mmol) in tetrahydrofuran (THF, 5 mL) at -60°C. Stirring was maintained for 10 min at -60°C and the flask was rapidly put in an ice bath for 50 min.

The solution of the 5-lithio-2,3-dihydrofuran derivative **13a** (5 mmol) was added, *via* cannula, to the solution of the cuprate **9a** or **9b** at -30°C (see above). The mixture was stirred at -5°- 0°C for 1 h 30 min. The mixture was then cooled at -30°C and MeI (2.2 mL, 35 mmol, 7 equiv) was added. The temperature was allowed to rise to 20°C for 1 h, stirring was maintained for 3 h at this temperature. The reaction mixture was poured into a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1) at -5°C and stirred for 30 min before extraction with diethyl ether (53 to 85% yields, see Table II).

15:
IR (CCl_4) ν^{cm-1}: 3550, 2950, 2850.
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.69 -1.05 [m, 15 H, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$], 1.14 - 1.68 [m, 13 H, OH and $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$], 1.86 (d, J = 17 Hz, 3 H, CH_3, CH_3-4, J ^{119}Sn-H ~ J ^{117}Sn-H = 45.0 Hz), 2.40 (q, J = 7.0 Hz, 2 H, H_2-2), 3.64 (t, J = 7.0 Hz, 2 H, H_2-1), 5.50 (tq, J = 7.0, 1.7 Hz, 1 H, H-3, J ^{119}Sn-H ~ J ^{117}Sn-H = 69.0 Hz).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 8.90 [3 CH_2, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, J ^{119}Sn-C = 330.0 Hz, J ^{117}Sn-C = 315.0 Hz], 13.53 [3 CH_3, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$], 19.11 (CH_3-4, J ^{119}Sn-C ~ J ^{117}Sn-C = 45.0 Hz), 27.21 [3 CH_2, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, J ^{119}Sn-C ~ J ^{117}Sn-C = 55.0 Hz], 29.00 [3 CH_2, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, J ^{119}Sn-C ~ J ^{117}Sn-C = 20.0 Hz], 31.51 (C-2, J ^{119}Sn-C ~ J ^{117}Sn-C = 55.0 Hz), 62.00 (C-1), 135.60 (C-3, J ^{119}Sn-C ~ J ^{117}Sn-C = 30.0 Hz), 141.98 (C-4).
MS (C.I., NH_3): *m/z* 376 (MH^+) for major ^{120}Sn isotope.
Anal calcd for $C_{17}H_{36}OSn$: C: 54.42; H: 9.64; O: 4.25; Found: C: 54.43; H: 9.67; O: 4.27

(3*E*,5*E*)-4-Methyl-6-(tributylstannyl)-hex-3,5-dien-1-ol (16)
From lithiodihydrofuran **13a** and cuprate **12**
-Dilithium bis[(*E*)-2-(tributylstannyl)ethenyl]cyanocuprate (**12**): **Method I:** See above for preparation of (±)-**1a**, from BuLi, CuCN and **11** according to Corey procedure.[12] To a solution of **11** prepared according to Still procedure [13] (3.9 g, 6.25 mmol, 2.5 equiv) in dried THF (10 mL) at -78°C, was added a 1.6 M solution of *n*-BuLi in pentane (5.8 mL, 9 mmol, 3.6 equiv). The

temperature was then allowed to warm to -10°C in 30 min before addition *via* cannula to a suspension of CuCN (225 mg, 2.5 mmol, 1 equiv) in dried diethyl ether (15 mL) at -60°C. The temperature was then allowed to rise to -15°C in 1 h.

Method II: From **11** and $Bu_2Cu(CN)Li_2$ **7a** according to modified Lipshutz exchange procedure.[18] To a suspension of CuCN (225 mg, 2.5 mmol, 1 equiv) in dried THF (6 mL) at -40°C was added n-BuLi (1.6 M in hexane, 3.50 mL, 5.63 mmol, 2.25 equiv). The solution was stirred for 5 min at -40°C and 10 min at 20°C. The temperature of the cuprate was then kept to -20°C before used (yellow gold color). To the solution of the dilithium dibutylcyanocuprate **7a** prepared before, a solution of **11** (6.06 g, 10 mmol, 4 equiv) in dried THF (3 mL) was slowly added. Cuprate **12** was obtained after stirring for 1 h at -20°C and 30 min at -15°C (olive-green color). Then, diethyl ether (12 mL) was added to this cuprate solution cooled to -20°C.

5-Lithio-2,3-dihydrofuran (**13a**): A 1.7M solution of *t*-BuLi in hexane (1.8 mL, 3 mmol, 1.2 equiv) was slowly added to a solution of freshly distilled dihydrofuran **13** (DHF, 2.5 mmol) in tetrahydrofuran (THF, 3 mL) at -60°C. Stirring was maintained for 10 min at -60°C and the flask was rapidly put in an ice bath for 50 min.

The solution of the 5-lithio-2,3-dihydrofuran derivative **13a** was added, *via* cannula, to the solution of the cuprate **12** (2.5 mmol, method I or II, see above) at -20°C. The mixture was stirred at -5°C for 1 h 30 min. The mixture was then cooled at -60°C and MeI (1.1 mL, 18 mmol, 7 equiv) was added. The temperature was allowed to rise to 20°C for 1 h, stirring was maintained for 3 h at this temperature. The reaction mixture was poured into a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1) at -5°C and stirred for 30 min before extraction with diethyl ether (40 to 82% yields, see Table III).

16:

IR (CCl_4) ν cm^{-1}: 3600, 2950, 2850, 1550.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.72 -1.08 [m, 15 H, $Sn(\underline{CH_2}\text{-}CH_2\text{-}CH_2\text{-}\underline{CH_3})_3$], 1.17 -1.68 [m, 13 H, OH, $Sn(CH_2\text{-}\underline{CH_2}\text{-}\underline{CH_2}\text{-}CH_3)_3$], 1.77 (d, J = 1.2 Hz, 3 H, CH_3, CH_3-4), 2.46 (td, J = 7.0, 8.0 Hz, 2 H, H_2-2), 3.69 (t, J = 7.0 Hz, 2 H, H_2-1), 5.49 (tq, J = 8.0, 1.2 Hz, 1 H, H-3), 6.14 (d, J = 19.5 Hz, 1 H, H-6 or H-5), 6.58 (d, J = 19.5 Hz, 1 H, H-6 or H-5).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.17 [3 CH_2, $Sn(\underline{C}H_2\text{-}CH_2\text{-}CH_2\text{-}CH_3)_3$, J ^{119}Sn-C = 344.0 Hz, J ^{117}Sn-C = 326.0 Hz], 11.54 (CH_3, CH_3-4), 13.39 [3 CH_3, $Sn(CH_2\text{-}CH_2\text{-}CH_2\text{-}\underline{C}H_3)_3$], 27.03 [3 CH_2, $Sn(CH_2\text{-}CH_2\text{-}\underline{C}H_2\text{-}CH_2)_2$, J ^{119}Sn-C ~ J ^{117}Sn-C = 57.0 Hz], 28.66 [3 CH_2, $Sn(CH_2\text{-}\underline{C}H_2\text{-}CH_2\text{-}CH_3)_3$, J ^{119}Sn-C ~ J ^{117}Sn-C = 20.0 Hz], 31.64 (C-2), 61.71 (C-1), 125.15 (C-6, J ^{119}Sn-C = 395.0 Hz, J ^{117}Sn-C = 377.0 Hz), 127.66 (C-3), 137.52 (C-4, J ^{119}Sn-C ~ J ^{117}Sn-C = 65.0 Hz), 150.46 (C-5).

MS (C.I., NH_3): m/z 402 (MH^+) for major ^{120}Sn isotope.

Anal calcd for $C_{19}H_{38}OSn$: C: 56.87; H: 9.54; O: 3.98; Found: C: 56.88; H: 9.51; O: 3.95.

(5*R*,4*S*)-5-Ethyl-4-methyl-dihydrofuran-2-one (17)

To a solution of the carbamate **4** (13.5 g, 52 mmol) in methanol (6.5 mL, 156 mmol, 3 equiv) at 5°C was added methanesulfonic acid ($MeSO_3H$, 3.7 mL, 58 mmol, 1.1 equiv) and mercuric acetate [$Hg(OAc)_2$, 140 mg, 0.44 mmol, 8.4 10^{-3} equiv). After 15 min at 20°C, dichloromethane (80 mL), BF_3•OEt_2 (1.2 mL, 10.5 mmol, 0.2 equiv) and mCPBA (32.8 g, 89 mmol, 1.7 equiv) were successively added to the preceding solution. After stirring for 12 h at 20°C the mCPBA excess was destroyed at 0°C by addition of Me_2S (8 mL). The mixture was diluted with an aqueous saturated $NaHCO_3$ solution and extracted (x 3) with CH_2Cl_2. The crude residue obtained after removal of the solvent was distilled under reduced pressure to give lactone **17** (5.36 g, 80% yield).

bp: 79°C/3 mm Hg

$[\alpha]_D$ = + 66.7 (neat)

IR (CCl_4) ν cm^{-1}: 2960, 2920, 2870, 1780, 1505, 1455.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.98 (t, J = 7.0 Hz, 3 H, CH_3, $\underline{CH_3}\text{-}CH_2$), 1.06 (d, J = 5.0 Hz, 3 H, CH_3, CH_3-4), 1.4 - 1.7 (m, 2 H, $CH_3\text{-}\underline{CH_2}$), 2.13 (m, 2 H, Ha-3, H-4), 2.59 (m, 1 H, Hb-3), 3.87 (td, J = 9.0, 5.0 Hz, 1 H, H-5).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.51 (CH_3, $\underline{CH_3}\text{-}CH_2$), 17.07 ($CH_3$, CH_3-4), 26.43 ($CH_3\text{-}\underline{CH_2}$), 35.08 (C-4), 36.67 (C-3), 88.15 (C-5), 176.11 (C-2).

MS (C.I., NH_3): m/z 146 (MH^+ + NH_3), 129 (MH^+).

Anal calcd for $C_7H_{12}O_2$: C: 65.59; H: 9.44; Found: C: 65.62; H: 9.40.

(2*R*,3*S*,5*RS*)-2-Ethyl-3-methyl-5-phenylthiotetrahydrofuran (18)

To a solution of lactone **17** (7.7 g, 60 mmol) in dried toluene (27 mL) at -78°C was added dropwise a solution of DIBAL-H in toluene (1.5 M, 44 mL, 66 mmol, 1.1 equiv). Stirring was maintained for 1 h then BF_3•OEt_2 (14.8 mL, 120 mmol, 2 equiv) and thiophenol (6.8 mL, 69 mmol, 1.15 equiv) were added. After stirring for 1 h the mixture was kept at 0°C and diluted with an aqueous saturated NH_4Cl solution before extraction with diethyl ether/10% HCl (x 3). The organic phases were washed with an aqueous saturated $NaHCO_3$ solution. The solvent was removed under *vacuo*, and the residue was purified by flash chromatography (hexane/ethyl acetate, 8:2) to give the title product **18** as a 1:1 mixture of anomers **18** (11 g, 83% yield).

IR (CCl_4) ν cm^{-1}: 3070, 3050, 2960, 2920, 2870, 1580, 1480, 1460.

^{1}H NMR ($CDCl_3$, 200 MHz) *two anomers* δ 1.04-1.05 (m, 6 H, 2 CH_3), 1.6 (m, 3 H, $C\underline{H_2}\text{-}CH_3$, H-3), 2.12 (m, 1 H, Ha-4), 2.63 (m, 1 H, Hb-4), 3.5 (m, 1 H, H-2), 5.54 (t, J = 7.0 Hz, 1 H, H-5), 7.2 (m, 3 H, Ar-H), 7.47 (m, 2 H, Ar-H).

^{13}C NMR ($CDCl_3$, 50.3 MHz) *two anomers* δ 10.32, 10.44 (CH_3, $\underline{CH_3}\text{-}CH_2$), 16.25, 17.10 ($CH_3$, CH_3-3), 25.71, 27.83 ($CH_3\text{-}\underline{CH_2}$), 37.57, 38.05 (C-3), 41.79, 41.90 (C-4), 85.30, 85.73 (C-2), 86.17, 89.36 (C-5), 126.48, 126.61, 128.54, 130.83, 131.32 (C Ar).

MS (C.I., NH_3): *m/z* 240 ($MH^+ + NH_3$), 223 (MH^+).

(2*R*,3*S*)-2-Ethyl-3-methyl-2,3-dihydrofuran (19)

A solution of the thio derivative **18** (7.3 g, 33 mmol) and DBU (5.5 mL, 36.2 mmol, 1.1 equiv) was rapidly heated at 200°C in a short distillator apparatus. The dihydrofuran **19** was obtained as a colorless oil after another distillation (2.3 g, 62 % yield).

$[\alpha]_D$ = + 19.7 (MeOH, c = 2.5)

IR (CCl_4) ν cm^{-1}: 3090, 2950, 2920, 2870, 1610, 1460, 1450.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.94 (t, *J* = 7.5 Hz, 3 H, CH_3, CH_3-CH_2), 1.05 (d, *J* = 7.0 Hz, 3 H, CH_3, CH_3-3), 1.6 (m, 2 H, CH_3-CH_2), 2.62 (qt, *J* = 7.0, 2.5 Hz, 1 H, H-3), 3.9 (q, *J* = 7.0 Hz, 1 H, H-2), 4.8 (t, *J* = 2.5 Hz, 1 H, H-4), 6.23 (t, *J* = 2.5 Hz, 1 H, H-5).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.35 (CH_3, CH_3-CH_2), 20.93 (CH_3, CH_3-3), 28.03 (CH_3-CH_2), 41.67 (C-3), 90.10 (C-2), 105.45 (C-4), 144.26 (C-5).

MS (C.I., NH_3): *m/z* 113 (MH^+).

(5*E*,3*R*,4*S*)-4,6-Dimethyl-6-(tributylstannyl)-hex-5-en-3-ol (10)

From lithio dihydrofuran **19a** and cuprate **9b**

-(2*R*,3*S*)-2-Ethyl-3-methyl-5-lithio-2,3-dihydrofuran (**19a**): a 1.7M solution of *t*-BuLi in hexane (3.5 mL, 6 mmol, 1.2 equiv) was added to a solution of freshly distilled dihydrofuran **19** (560 mg, 5 mmol) in THF (5 mL) at -60°C. The 5-lithio-2,3-dihydrofuran **19a** was obtained after stirring for 10 min at -60°C and 50 min at -5°C - 0°C.

The solution of the 5-lithio-2,3-dihydrofuran derivative **19a** was added, *via* cannula, to a solution of the cuprate **9b** (5 mmol, see above preparation of **15**) at -30°C. The mixture was stirred at -5°- 0°C for 1 h 30 min. The mixture was then cooled at -30°C and MeI (2.2 mL, 35 mmol, 7 equiv) was added. The temperature was allowed to rise to 20°C for 1 h, stirring was maintained for 3 h at this temperature. The reaction mixture was poured into a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1) at -5°C and stirred for 30 min before extraction with diethyl ether (64 to 78% yields, Scheme 12, entries 13 and 14).

10:

$[\alpha]_D$ = - 10.5 (MeOH, c = 1.0)

IR (CCl_4) ν cm^{-1}: 3550, 2950, 2850.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 -1.14 [m, 21 H, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, H3-1, CH_3-4], 1.26 -1.72 [m, 12 H, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$], 1.75 (d, *J* = 2.5 Hz, 1 H, OH), 1.95 (d, *J* = 1.7 Hz, 3 H, CH_3, CH_3-6, J^{119}Sn-H = J^{117}Sn-H = 45.0 Hz), 2.74 (m, 1 H, H-4), 3.30 (m, 1 H, H-3), 5.40 (dq, *J* = 9.0, 1.7 Hz, 1 H, H-5, J^{119}Sn-H ~ J^{117}Sn-H = 70.0 Hz).

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.06 [3 CH_2, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, J^{119}Sn-C = 330.0 Hz, J^{117}Sn-C = 315.0 Hz], 9.88 (C-1), 13.55 [3 CH_3, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$], 16.77 (CH_3, CH_3-4), 19.49 (CH_3, CH_3-6, J^{119}Sn-C ~ J^{117}Sn-C = 45.0 Hz), 26.67 (C-2), 27.19 [3 CH_2, $Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, J^{119}Sn-C ~ J^{117}Sn-C = 52.0 Hz], 29.05 [$Sn(CH_2$-CH_2-CH_2-$CH_3)_3$, J^{119}Sn-C ~ J^{117}Sn-C = 20.0 Hz], 37.96 (C-4, J^{119}Sn-C ~ J^{117}Sn-C = 52.0 Hz), 76.46 (C-3), 140.62 (C-6), 142.71 (C-5, J^{119}Sn-C ~ J^{117}Sn-C = 25.0 Hz).

MS (C.I., NH_3): *m/z* 418 (MH^+) for major ^{120}Sn isotope.

Anal calcd for $C_{20}H_{42}OSn$: C: 57.57; H: 10.14; O: 3.83; Found: C: 57.60; H: 10.20; O: 3.80.

(5*E*,7*E*,3*R*,4*S*)-4,6-Dimethyl-8-(tributylstannyl)-octa-5,7-dien-3-ol (1)

From lithiodihydrofuran **19a** and cuprate **12**

- 5-Lithio-2,3-dihydrofuran (**19a**): A 1.7M solution of *t*-BuLi in hexane (3.5 mL, 6 mmol, 1.2 equiv) was added to a solution of freshly distilled dihydrofuran **19** (560 mg, 5 mmol) in tetrahydrofuran (THF, 5 mL) at -60°C. The 5-lithio-2,3-dihydrofuran **19a** was obtained after stirring for 10 min at -60°C and 50 min at -5°C - 0°C.

-Dilithium bis[(*E*)-2-(tributylstannyl)ethenyl]cyanocuprate (**12**): **Method II:** from **11** and $Bu_2Cu(CN)Li_2$ **7a** according to modified Lipshutz exchange procedure.[18] To a suspension of CuCN (450 mg, 5 mmol, 1 equiv) in dried THF (12 mL) at -40°C was added n-BuLi (1.6 M in hexane, 7 mL, 11.3 mmol, 2.25 equiv). The solution was stirred for 5 min at -40°C and 10 min at 20°C. The temperature of the cuprate was then kept to -20°C before used (yellow gold color).

To this solution of the dilithium dibutylcyanocuprate **7a**, a solution of **11** (12.0 g, 20.0 mmol, 4 equiv) in dried THF (6 mL) was slowly added. Cuprate **12** was obtained after stirring for 1 h at -20°C and 30 min at -15°C (olive-green color). Then, diethyl ether (23 mL) was added to the cuprate solution cooled at -20°C.

The solution of the 5-lithio-2,3-dihydrofuran derivative **19a** (5 mmol) was added, *via* cannula, to the solution of the cuprate **12** at -20°C. The mixture was stirred at -5°C for 1 h 30 min. The mixture was then cooled at -60°C and MeI (2.2 mL, 35 mmol, 7 equiv) was added. The temperature was allowed to rise to 20°C for 1 h, stirring was maintained for 3 h at this temperature. The reaction mixture was poured into a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1) at -5°C and stirred for 30 min before extraction with diethyl ether (48 to 58% yields, Scheme 12, entries 15 and 16).

1:

$[\alpha]_D$ = - 17 (MeOH, c = 3.3)

IR (CCl_4) ν cm^{-1}: 3600, 2950, 2850,1550.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.66 -1.05 [m, 21 H, $Sn(C\underline{H}_2\text{-}CH_2\text{-}CH_2\text{-}C\underline{H}_3)_3$, H3-1, CH_3-4], 1.14 -1.70 [m, 15 H, OH, $Sn(CH_2\text{-}C\underline{H}_2\text{-}C\underline{H}_2\text{-}CH_3)_3$, H2-2], 1.75 (d, J = 1.2 Hz, 3 H, CH_3, CH_3-6), 2.46 - 2.67 (m, 1 H, H-4), 3.27 - 3.40 (m, 1 H, H-3), 5.32 (dq, J = 10.0, 1.2 Hz, 1 H, H-5), 6.10 (d, J = 19.5 Hz, 1 H, H-7 or H-8, $J\,^{119}Sn\text{-}H \sim J\,^{117}Sn\text{-}H$ = 70.0 Hz), 6.55 (d, J = 19.5 Hz, 1 H, H-7 or H-8, $J\,^{119}Sn\text{-}H \sim J\,^{117}Sn\text{-}H$ = 65.0 Hz).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.36 [3 CH_2, $Sn(\underline{C}H_2\text{-}CH_2\text{-}CH_2\text{-}CH_3)_3$, $J\,^{119}Sn\text{-}C$ = 342.0 Hz, $J\,^{117}Sn\text{-}C$ = 330.0 Hz], 9.88 (C-1), 12.13 (CH_3-6), 13.54 [3 CH_3, $Sn(CH_2\text{-}CH_2\text{-}CH_2\text{-}\underline{C}H_3)_3$], 17.09 ($CH_3$-4), 27.03 (C-2), 27.18 [3 CH_2, $Sn(CH_2\text{-}CH_2\text{-}\underline{C}H_2\text{-}CH_3)_3$, $J\,^{119}Sn\text{-}C \sim J\,^{117}Sn\text{-}C$ = 57.0 Hz], 29.00 [3 CH_2, $Sn(CH_2\text{-}\underline{C}H_2\text{-}CH_2\text{-}CH_3)_3$, $J\,^{119}Sn\text{-}C \sim J\,^{117}Sn\text{-}C$ = 27.0 Hz], 38.51 (C-4), 76.99 (C-3), 125.83 (C-8, $J\,^{119}Sn\text{-}C$ = 394.0 Hz, $J\,^{117}Sn\text{-}C$ = 377.0 Hz), 133.91 (C-5), 136.91 (C-6, $J\,^{119}Sn\text{-}C \sim J\,^{117}Sn\text{-}C$ = 65.0 Hz), 150.23 (C-7).
MS (C.I., NH_3): *m/z* 445 (MH^+) for major ^{120}Sn isotope.
Anal calcd for $C_{22}H_{44}OSn$: C: 59.60; H: 10.00; O: 3.61; Found: C: 59.56; H: 9.97; O: 3.65.

(3*E*)-4-Iodo-4-methyl-but-3-en-1-ol (20)

To a solution of the vinylstannyl derivative **15** (1.3 g, 3.45 mmol) in CH_2Cl_2 (5 mL) was slowly added a solution of iodine (0.93 g, 3.6 mmol, 1.05 equiv) in CH_2Cl_2 (50 mL) at 0°C. Addition of iodine was stopped when a red color was persistent after 20 min. The solvent was then removed under reduced pressure and the residue was taken in 5 mL of diethyl ether and an aqueous 1M KF solution (7 mL, 7 mmol, 2 equiv). After stirring 3 h at ambient temperature, the solution was filtered of a pad of celite. The organic phase was then decanted and the solvent removed under reduced pressure. Flash chromatography of the residue gave vinyliodide **20** (698 mg, 95% yield, elution CH_2Cl_2/ diethyl ether, 98:2) as a pale yellow oil which was distilled.

bp: 145°C/2 mm Hg
IR (CCl_4) ν cm^{-1}: 3600, 2950, 2850, 1630.
^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.8 (s, 1 H, OH), 2.28 (td, J = 7.5, 7.0 Hz, 2 H, H_2-2), 2.4 (d, J = 1.6 Hz, 3 H, CH_3, CH_3-4), 3.65 (t, J = 7.0 Hz, 2 H, H_2-1), 6.15 (tq, J = 7.5, 1.6 Hz, 1 H, H-3).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 27.58 (CH_3, CH_3-4), 33.76 (C-2), 61.20 (C-1), 96.07 (C-4), 137.25 (C-3).
MS (C.I., NH_3): *m/z* 213 (MH^+).

(3*E*,5*E*)-4-Methyl-6-(tributylstannyl)-hex-3,5-dien-1-ol (16)

General procedure (See Table IV): To a solution of [Pd] (5% mol) in degased THF or DMF (2 mL) an argon atmosphere, were successively added a solution of the vinyliodide **20** (106 mg, 0.5 mmol) in THF or DMF (2 mL) and a solution of the (*E*)-1,2-*bis*-(tributylstannyl)ethylene (393 mg, 0.65 mmol, 1.3 equiv) in THF or DMF (2 mL). The mixture was then stirred for 1 h to 48 h at 20°C to 70°C (see table). After dilution with an aqueous saturated NH_4Cl solution, and extraction with diethyl ether, the crude residue was partitioned between diethyl ether (5 mL) and an aqueous KF solution (1 mL, 1 mmol, 2 equiv). After stirring for 3 h the organic phase was decanted and the solvent removed under reduced pressure. Purification of the residue by flash chromatography on Al_2O_3 (hexane/ethyl acetate, 90:10) led to the stannyldiene **16** and vinylstannane **15** as depicted in Table IV.

(3*E*)-4-Iodo-4-methyl-1-(triisopropylsilyloxy)-but-3-ene (20a)

To a solution of vinyliodide **20** (1.86 g, 8.8 mmol) in CH_2Cl_2 (2 mL) at 0°C were added 2,6-lutidine (3.1 mL, 26.4 mmol, 3 equiv), and TIPSOTf (2.6 mL, 9.7 mmol, 1.1 equiv). After stirring for 30 min the reaction mixture was partitioned between diethyl ether and an aqueous saturated NH_4Cl solution and extracted with diethyl ether. The title compound **20a** was obtained in 80% yield (2.6 g) after chromatography on silica gel.

IR (CCl_4) ν cm^{-1}: 2950, 2850, 1630.
^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.14 {s wide, 21 H, 6 CH_3 + 3 CH, $Si[C\underline{H}(C\underline{H}_3)_2]_3$}, 2.34 (td, J = 7.0, 7.5 Hz, 2 H, H_2-2), 2.46 (d, J = 1.6 Hz, 3 H, CH_3, CH_3-4), 3.75 (t, J = 7.0 Hz, 2 H, H_2-1), 6.22 (td, J = 7.5 Hz, 1.6 Hz, 1 H, H-3).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 11.86 {3 CH, $Si[\underline{C}H(CH_3)_2]_3$}, 17.86 {6 CH_3, $Si[CH(\underline{C}H_3)_2]_3$}, 27.56 ($CH_3$, CH_3-4), 34.21 (C-2), 61.93 (C-1), 95.41 (C-4), 137.72 (C-3).
MS (C.I., NH_3): *m/z* 369 (MH^+).

(3*E*)-4-Methyl-hex-3-en-5-yn-1-ol (21)

To a solution of $Pd(PPh_3)_4$ (73 mg, 5% mol) in THF (3 mL) were successively added a solution of the vinyliodide **20** (267 mg, 1.26 mmol) in THF (3 mL) and a solution of tributyl stannyl acetylene (516 mg, 1.64 mmol, 1.3 equiv) in THF (2 mL). After stirring for 40 min at 50°C the mixture was poured into an aqueous saturated NH_4Cl at -5°C and extracted with diethyl ether. The solvent was then removed under reduced pressure. Bu_3SnI was precipitate as Bu_3SnF upon treatment with a KF solution. After stirring for 3 h at 20°C, the organic phase was filtered in a pad of celite and diethyl ether was removed under reduced pressure. The crude residue was purified by flash chromatrography on silica gel (CH_2Cl_2/diethyl ether, 96:4) to give the title product (125 mg, 90% yield). Purification of **21** was achieved by distillation (60°C, 3 mmHg).

IR (CCl_4) ν cm^{-1}: 3620, 3300, 2950, 2850, 2100.
^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.65 (s, 1 H, OH), 1.86 (d, J = 2.0 Hz, 3 H, CH_3, CH_3-4), 2.41 (td, J = 7.0, 8.0 Hz, 2 H, H_2-2), 2.83 (s, 1 H, H-6), 3.70 (t, J = 7.0 Hz, 2 H, H_2-1), 5.95 (tq, J = 8.0, 2.0 Hz, 1 H, H-3).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 16.97 (CH_3, CH_3-4), 31.92 (C-2), 61.17 (C-1), 73.97 (C-6), 86.25 (C-5), 118.99 (C-4), 135.10 (C-3).

MS (C.I., NH_3): *m/z* 111 (MH^+).

(3*E*)-4-Methyl-1-(triisopropylsilyloxy)-hex-3-en-5-yne (21a)

The procedure was the same as described for the preparation of **21**. In this case, vinyliodide **20a** (465 mg, 1.26 mmol) and tributylstannyl acetylene were stirred for 75 min at 50°C. Purification of the crude residue by flash chromatography (CH_2Cl_2/diethyl ether, 99:1) led to enyne **21a** in 80% yield (268 mg).

IR (CCl_4) ν cm^{-1}: 3300, 2950, 2850, 2100.
^1H NMR ($CDCl_3$, 200 MHz) δ 0.99 {s, 21 H, 6 CH_3 + 3 CH, Si[CH(CH_3)2]3}, 1.77 (d, *J* = 2.0 Hz, 3 H, CH_3, CH_3-4), 2.37 (td, *J* = 7.0, 8.0 Hz, 2 H, H_2-2), 2.77 (s, 1 H, H-6), 3.70 (t, *J* = 7.0 Hz, 2 H, H_2-1), 5.97 (tq, *J* = 8.0, 2.0 Hz, 1 H, H-3).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 11.87 {3 CH, Si[CH(CH_3)2]3}, 17.05 (CH_3, CH_3-4), 17.87 {6 CH_3, Si[CH(CH_3)2]3}, 32.29 (C-2), 62.17 (C-1), 73.54 (C-6), 86.64 (C-5), 118.22 (C-4), 135.88 (C-3).
MS (C.I., NH_3): *m/z* 267 (MH^+).

(5*E*,3*R,4*S**)-4,6-Dimethyl-6-iodo-hex-5-en-3-ol [(±)-23]**

The procedure used for the preparation of **20** was employed here.

Starting from (±)-**10** (1.46 g, 3.5 mmol) vinyliodide (±)-**23** was obtained after flash chromatography on silica gel (CH_2Cl_2/diethyl ether, 97:3, 800 mg, 90% yield) and then distilled.

bp: 90°C/2 mmHg.
IR (CCl_4) ν cm^{-1}: 3600, 2950, 2850, 1630.
^1H NMR ($CDCl_3$, 200 MHz) δ 0.99 (t, *J* = 7.0 Hz, 3 H, CH_3, H_3-1), 1.11 (d, *J* = 7.0 Hz, 3 H, CH_3, CH_3-4), 1.35 -1.59 (m, 2 H, H_2-2), 1.68 (s, 1 H, OH), 2.41 -2.65 (m, 1 H, H-4), 2.46 (d, *J* = 2.0 Hz, 3 H, CH_3, CH_3-6), 3.3 -3.45 (m, 1 H, H-3), 6.12 (dq, *J* = 11.0, 2.0 Hz, 1 H, H-5).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.88 (C-1), 16.5 (CH_3, CH_3-4), 27.05 (C-2), 27.85 (CH_3, CH_3-6), 40.93 (C-4), 76.12 (C-3), 94.62 (C-6), 142.72 (C-5).
MS (C.I., NH_3): *m/z* 255 (MH^+).

(5*E*,3*R,4*S**)-4,6-Dimethyl-oct-5-en-7-yn-3-ol [(±)-24]**

The procedure used for the preparation of **21** was employed here.

From vinyliodide (±)-**23** (320 mg, 1.26 mmol) and tributylstannylacetylene for 1 h at 50°C, enyne (±)-**24** was obtained in 90% yield (173 mg).

IR (CCl_4) ν cm^{-1}: 3620, 3300, 2950, 2850, 2100.
^1H NMR ($CDCl_3$, 200 MHz) δ 0.98 (t, *J* = 7.0 Hz, 3 H, CH_3, H_3-1), 1.10 (d, *J* = 7.0 Hz, 3 H, CH_3, CH_3-4), 1.30 -1.59 (m, 2 H, H_2-2), 1.67 (s, 1 H, OH), 1.87 (d, *J* = 1.6 Hz, 3 H, CH_3, CH_3-6), 2.41 -2.65 (m, 1 H, H-4), 2.82 (s, 1 H, H-8), 3.40 (m, 1 H, H-3), 5.86 (dq, *J* = 10.5, 1.6 Hz, 1 H, H-5).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.84 (C-1), 16.34 (CH_3, CH_3-4), 17.13 (CH_3, CH_3-6), 27.07 (C-2), 38.47 (C-4), 73.08 (C-8), 76.46 (C-3), 86.43 (C-7), 117.76 (C-6), 140.96 (C-5).
MS (C.I., NH_3): *m/z* 153 (MH^+).

(3*E*,5*E*)-4-Methyl-1-(triisopropylsilyloxy)-6-(tributylstannyl)-hex-3,5-diene (16a)
(3*E*)-4-Methyl-1-(triisopropylsilyloxy)-5-(tributylstannyl)-hex-3,5-diene (22a)

A-hydrostannation (See table V)

-Table V entry 1: To the enyne **21a** (180 mg, 0.67 mmol) was added Bu_3SnH (400 µL, 1.48 mmol, 2.2 equiv) and azobisisobutyronitrile (AIBN, 5 mg, 5% mol). After stirring for 8 h at 100°C the mixture was diluted with diethyl ether and an aqueous saturated NH_4Cl solution and extracted with diethyl ether. After the solvent was removed under reduced pressure, the crude residue was purified by flash chromatography on Al_2O_3 (hexane) to give a mixture of **16a** and **22a** (225 mg, 60% yield, **16a/22a** = 30:70).

-Table V entry 2: When this reaction was performed at 100°C for 16 h on enyne **21a** (0.67 mmol) purification of the crude residue led to a mixture of **16a** and **22a** (112 mg, 30% yield, **16a/22a** = 90:10).

16a:

IR (CCl_4) ν cm^{-1}: 2950, 2850, 1630, 1555.
^1H NMR ($CDCl_3$, 200 MHz) δ 0.75 -1.05 [m, 15 H, Sn(CH_2-CH_2-CH_2-CH_3)3], 1.11 {s, 21 H, 6 CH_3 + 3 CH, Si[CH(CH_3)2]3}, 1.23 -1.65 [m, 12 H, Sn(CH_2-CH_2-CH_2-CH_3)3], 1.82 (d, *J* = 1.2 Hz, 3 H, CH_3, CH_3-4), 2.49 (td, *J* = 7.0, 8.0 Hz, 2 H, H_2-2), 3.75 (t, *J* = 7.0 Hz, 2 H, H_2-1), 5.52 (tq, *J* = 8.0, 1.2 Hz, 1 H, H-3), 6.03 (d, *J* = 19.5 Hz, 1 H, H-6 or H-5, $J^{119}Sn$-H = $J^{117}Sn$-H = 68.0 Hz), 6.59 (d, *J* = 19.5 Hz, 1 H, H-6 or H-5, $J^{119}Sn$-H = $J^{117}Sn$-H = 63.0 Hz)
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 9.40 [3 CH_2, Sn(CH_2-CH_2-CH_2-CH_3)3, $J^{119}Sn$-C = 344.0 Hz, $J^{117}Sn$-C = 326.0 Hz], 11.73 (CH_3, CH_3-4), 11.95 {3 CH, Si[CH(CH_3)2]3}, 13.59 [3 CH_3, Sn(CH_2-CH_2-CH_2-CH_3)3], 17.91 {6 CH_3, Si[CH(CH_3)2]3}, 27.21 [3 CH_2, Sn(CH_2-CH_2-CH_2-CH_3)3, $J^{119}Sn$-C = $J^{117}Sn$-C = 57.0 Hz), 29.03 [3 CH_2, Sn(CH_2-CH_2-CH_2-CH_2)3, $J^{119}Sn$-C = $J^{117}Sn$-C = 20.0 Hz], 32.32 (C-2), 62.92 (C-1), 124.92 (C-6, $J^{119}Sn$-C = 395.0 Hz, $J^{117}Sn$-C = 377.0 Hz), 128.41 (C-3), 136.95

(C-6, J^{119}Sn-C = J^{117}Sn-C = 65.0 Hz), 150.86 (C-5).
MS (C.I., NH_3): *m/z* 558 (MH^+).
Anal calcd for $C_{28}H_{58}OSiSn$: C: 60.32; H: 10.48; O: 2.86; Found: C: 60.34; H: 10.38; O: 2.79.

22a:
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.75 -1.05 [m, 15 H, Sn(CH_2-CH_2-CH_2-CH_3)3], 1.11 {s, 21 H, 6 CH_3 + 3 CH, Si[CH(CH_3)2]3}, 1.23 -1.65 [m, 12 H, Sn(CH_2-CH_2-CH_2-CH_3)3], 1.83 (d, *J* = 1.2 Hz, 3 H, CH_3, CH_3-4), 2.49 (td, *J* = 7.0, 8.0 Hz, 2 H, H_2-2), 3.75 (t, *J* = 7.0 Hz, 2 H, H_2-1), 5.16 (d, *J* = 2.0 Hz, 1 H, Ha-6), 5.32 (tq, *J* = 8.0, 1.2 Hz, 1 H, H-3), 5.85 (d, *J* = 2.0 Hz, 1 H, Hb-6).

B-Stannylcupration (See Table V)
-Table V entry 3: From cuprate **9b**. To a solution of $(Bu_3Sn)_2$ (1 mL, 2.0 mmol, 2.2 equiv) in THF (5 mL) at - 40°C was slowly added BuLi (1.6 M solution in hexane, 1.3 mL, 2.0 mmol, 2.2 equiv). After stirring for 15 min at -40°C, this solution was slowly added *via* cannula to a suspension of CuCN (95 mg, 1.05 mmol, 1.1 equiv) in THF (5 mL) at -40°C and stirred for 30 min at -40°C. A solution of the enyne **21a** (250 mg, 0.94 mmol) in THF (2 mL) was then slowly added to the cuprate solution. After 2 h at -40°C the solution was poured in a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1). After extraction with diethyl ether the organic phase was washed with an aqueous saturated NaCl solution. The crude residue obtained was purified by flash chromatography on Al_2O_3 (hexane).

-Table V entry 4: From cuprate **9a**. To a suspension of CuCN (95 mg, 1.05 mmol, 1.1 equiv) in THF (5 mL) at -30°C was slowly added n-BuLi (1.6 M solution in hexane, 1.3 mL, 2.1 mmol, 2.2 equiv). After 5 min at -30°C the cold bath was removed during 15 min and then the temperature was kept at -30°C to slowly introduce Bu_3SnH (556 µL, 2.1 mmol, 2.2 equiv) The solution was stirred for 30 min at -30°C. After that a solution of the enyne **21a** (250 mg, 0.94 mmol) in THF (2 mL) was slowly added to the preceding solution at -78°C. The solution was stirred for another 30 min at -78°C, poured in a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1), and extracted as described for entry 1 with diethyl ether.

(3*E*,5*E*)-4-Methyl-6-(tributylstannyl)-hex-3,5-dien-1-ol (16)
(3*E*)-4-Methyl-5-(tributylstannyl)-hex-3.5-dien-1-ol (22)
Stannylcupration (See Table V)
Table V, entry 9: To a suspension of CuCN (189 mg, 2.1 mmol, 2.2 equiv) in THF (10 mL) at -30°C was added n-BuLi (1.6 M solution in hexane, 2.6 mL, 4.15 mmol, 4.4 equiv). After stirring for 5 min at -30°C the cold bath was removed during 15 min. The mixture was in turned cold to -30°C and Bu_3SnH (1.1 mL, 4.1 mmol, 4.4 equiv) was added. After stirring for 30 min at -30°C, the mixture was cooled to -40°C and a solution of enyne **21** (103 mg, 0.94 mmol) in THF (2 mL) was slowly added, the reaction mixture was stirred for 30 min and poured in a solution of saturated aqueous NH_4Cl/concentrated ammonia (4:1). After extraction with diethyl ether the crude residue was purified by flash chromatography on Al_2O_3 (hexane) to give a mixture of stannyldienes **16** and **22** (340 mg, 90%, **16 / 22** = 95:5).

22:
^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.89 (d, *J* = 1.2 Hz, 3 H, CH_3, CH_3-4), 5.22 (d, *J* = 2.0 Hz, 1 H, Ha-6), 5.29 (tq, *J* = 7.0, 1.2 Hz, 1 H, H-3), 5.85 (d, *J* = 2.0 Hz, 1 H, Hb-6) .

(5*E*,7*E*,3*R,4*S**)-4,6-Dimethyl-8-(tributylstannyl)-octa-5,7-dien-3-ol [(±)-1]**
(5*E*,3*R,4*S**)-4,6-Dimethyl-7-(tributylstannyl)-octa-5,7-dien-3-ol [(±)-25]**
Stannylcuprations (See Table VI)
Table VI entry 13: As described for entry 5, the enyne (±)-**24** (143 mg, 0.94 mmol) led to formation of stannyldienes (±)-**1** and (±)-**25** (375 mg, 90%, (±)-**1**/(±)-**25** = 95:5) (See Table VI).

(±)-25:
^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.86 (d, *J* = 1.2 Hz, 3 H, CH_3, CH_3-6), 5.22 (d, *J* = 2.0 Hz, 1 H, Ha-8), 5.37 (dq, *J* = 7.0, 1.2 Hz, 1 H, H-5), 5.85 (d, *J* = 2.0 Hz, 1 H, Hb-8).

Note: During purification by chromatography on Al_2O_3, partial protonolysis of vinyltin derivatives was observed leading to corresponding dienes.

(3*E*)-4-Methyl-1-(triisopropylsilyloxy)-hex-3,5-diene
^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.14 {s wide, 21 H, 6 CH_3 + 3 CH,Si[CH(CH_3)2]3}, 1.83 (d, *J* = 1.2 Hz, 3 H, CH_3, CH_3-4), 2.48 (q, *J* = 7.0, 7.0 Hz, 2 H, H_2-2), 3.75 (t, *J* = 7.0 Hz, 2 H, H_2-1), 4.98 (d, *J* = 11.0 Hz, 1 H, H-6*Z*), 5.13 (d, *J* = 18.0 Hz, 1 H, H-6*E*), 5.55 (tq, *J* = 7.0, 1.2 Hz, 1 H, H-3), 6.39 (dd, *J* = 18.0, 11.0 Hz, 1 H, H-5).
^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 11.66 (CH_3, CH_3-4), 11.93 {3 CH, Si[CH(CH_3)2]3}, 17.88 {6 CH_3, Si[CH(CH_3)2]3}, 32.16 (C-2), 62.79 (C-1), 110.62 (C-6), 129.00 (C-3), 135.22 (C-4), 141.40 (C-5).
MS (C.I., NH_3): *m/z* 269 (MH^+).

(5*E*,3*R,4*S**)-4,6-Dimethyl-octa-5,7-dien-3-ol**
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.99 (t, *J* = 7.0 Hz, 3 H, CH_3, H_3-1), 1.11 (d, *J* = 7.0 Hz, 3 H, CH_3, CH_3-4), 1.32 -1.65 (m, 2 H, H_2-2), 1.66 (d, *J* = 3.0 Hz, 1 H, OH), 1.83 (d, *J* = 1.2 Hz, 3 H, CH_3, CH_3-6), 2.52 -2.73 (m, 1 H, H-4), 3.3 -3.46 (m, 1 H, H-

3), 5.01 (d, J = 11.0 Hz, 1 H, H-8*Z*), 5.14 (d, J = 18.0 Hz, 1 H, H-8*E*), 5.4 (dq, J = 7.0, 1.2 Hz, 1 H, H-5), 6.39 (dd, J = 18.0, 11.0 Hz, 1 H, H-7).
MS (C.I., NH_3): *m/z* 155 (MH^+).

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When stannylcuprate **9b** was prepared using 2 equiv Bu_3SnH + 2 equiv LDA + 1 equiv CuCN as described by Gilbertson, S. R.; Challener, C. A.; Bos, M. E.; Wulff, W. D. *Tetrahedron Lett.*,**1988**, *29*, 4795, yields in stannyl transfer leading to **15** were observed to be lower than in other cases (60-67%).
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