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1,3-Asymmetric Induction in Electrophilic Addition onto Homoallylsilanes. An Approach Towards the Total Synthesis of (+/-)-Kumausyne.

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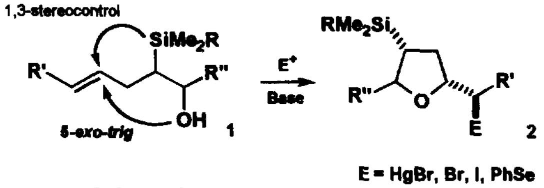
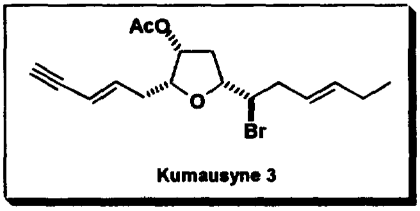
Abstract : Electrophilic *5-exo-trig* cyclizations of homoallylsilanes have been carried out leading to 2,4- and 2,4,5-substituted tetrahydrofurans with good yields and diastereoselectivities. With disubstituted homoallylsilanes, tetrahydrofurans having acyclic chiral centres were also obtained. An application of this methodology to an approach towards the total synthesis of (+/-)-kumausyne is proposed on the basis of these preliminary results. The four chiral centres of this marine natural product have been set up with excellent diastereoselectivities.

Stereocontrol in electrophilic additions to π-systems induced by an already-present chiral centre located in a homoallylic position (1,3-stereocontrol) is a challenging problem which has received only limited attention.[1] The remoteness of the chiral centre would be expected to induce poor diastereofacial selectivity during the electrophilic process. Such a problem is not so acute with *allylic* systems where the proximity of the chiral and the prochiral centres generally allows for a high degree of 1,2-asymmetric induction.[2] Nevertheless, significant 1,3-chiral inductions have been observed during *5-exo-trig* electrophilic cyclizations of alkenols, affording a straightforward and stereocontrolled access to useful heterocycles.[1a-b,3] In the course of our studies directed towards the development of new organosilicon compounds,[4] we have been involved in similar electrophilic cyclofunctionalizations of 2-silyl-4-alkenols, precursors to the ubiquitous polysubstituted tetrahydrofuran skeleton (*i.e.* **2**, Scheme 1).[5] We reasoned that cyclofunctionalization of olefins **1** under kinetic control (E^+ and a base) would lead to tetrahydrofurans such as **2**, having 3 chiral centres formed with concomitant 1,3- and 1,4-stereoinduction. The silicon group on the chiral centre would thus control the stereochemistry at the new chiral centres and could then serve as a latent hydroxy group through oxidation of the C-Si bond with retention of configuration.[6] We report here, in full detail, our investigations on the mercuri-, seleno-, and halogenoetherification of 2-silyl-4-alkenols **1**, and our preliminary studies on the application of this strategy to the total synthesis of (+/-)-kumausyne **3**.

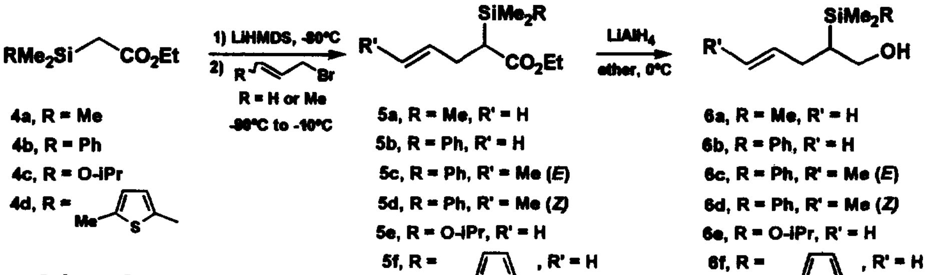


Scheme 1



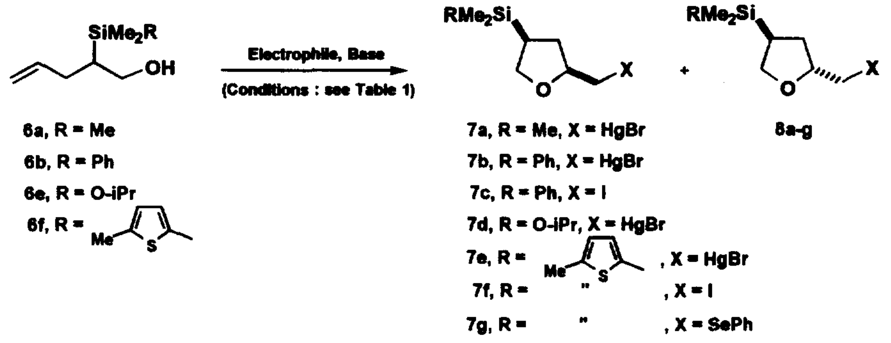
Kumausyne 3

The acyclic precursors were prepared in two steps from the readily available α-silylacetic esters **4a-d**.[4] The alkylation of **4a-d**[7] was carried out through the addition of a suitable allyl or crotyl bromide to a α-silylester enolate (enolization with LiHMDS). Reduction of the α-silyl-α-substituted esters **5a-f** using $LiAlH_4$ in ether at 0°C afforded the requisite homoallylsilanes in good overall yield (65-85%)(Scheme 2).



Scheme 2

We first investigated the kinetically controlled cyclofunctionalization of simple monosubstituted alkenols **6a-b** and **6e-f**. Utilization of the Bartlett kinetic conditions[1c,3c] (I_2 (3 eq.), $NaHCO_3$) was soon deemed unsuitable for our purpose due to extensive decomposition of the cyclized products. The major problem which we feared at that time was the electrophilic desilylation which could compete with the desired electrophilic reaction at the olefinic site. It was finally found that the olefinic moiety is more reactive than the R group (Ph or thienyl) at the silicon centre and that any kind of silicon group could be used in this reaction, providing that the reaction was carried out with a stoichiometric amount of the electrophile relative to the precursor. In this case we were pleased to observe the formation of the *5-exo-trig* product as sole product of the reaction (Scheme 3). Our results (summarized in Table 1) indicate that the cyclization proceeds in good yields with moderate to excellent diastereoselectivities, depending on the nature of the electrophile. The stereochemistry of the substituted tetrahydrofurans was assigned unambiguously using NOESY and NOE difference ^1H NMR experiments (Fig.-1). Reduction of the C-X bond (X = HgBr, SePh, I) using standard methods[8,9] demonstrated that the major diastereoisomer was the 2,4-*cis* **7a-g**, irrespective of the nature of the electrophile.



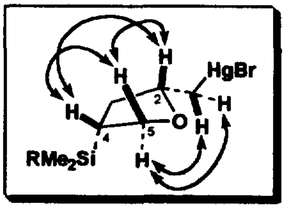
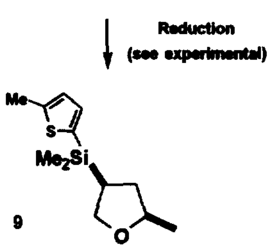


Fig.1. NOE effects in 7e



Scheme 3

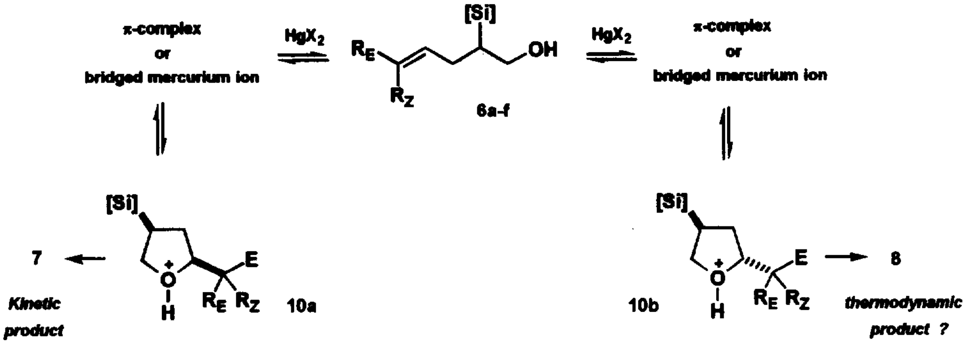
Mercuri-cyclization was found to be by far the most stereoselective: more so than iodoetherification using NIS or selenoetherification with PhSeCl.[2a] From a preparative point of view this is of interest, since mercury derivatives can be functionalized further using radical or organometallic processes.[8] We also noticed that the stereochemical outcome of the mercuri-cyclization was influenced by several factors such as the temperature, the nature of the counter-ion associated with mercury and also the solvent.[10a] Interestingly, the nature of the substituents on the silicon centre has little or no effect on the diastereoselectivity (Entry 4-7). Lowering the temperature has the expected effect of slightly increasing the diastereoselectivity (Compare entry 7 and 8). Changing the nature of the mercury(II) salt also affected the stereoselectivity with $Hg(OAc)_2$ being the best choice (Entry 7, 9 and 10). Finally, the solvent is also critical since we observed a dramatic drop of the selectivity when $Hg(TFA)_2$ and $Hg(NO_3)_2$-mediated cyclizations were carried out in CH_3CN instead of THF (Compare entry 9 and 12, then 10 and 13). It is also worthy of note that such a solvent-dependency is not observed with $Hg(OAc)_2$ (Entry 7 and 11, then 14 and 15). These last points are closely related with the basicity of the counter-ion, since we observed that when the reaction is performed in the absence of a base, the stereoselectivity remained very high only with $Hg(OAc)_2$ (Entry 14-15).[11] This is consistent with AcO^- being more basic than $CF_3CO_2^-$ and NO_3^-.

Table 1. Electrophilic cyclizations of homoallylic silanes 6a-b and 6e-f (Scheme 3).

Entry	Substrate[a]	Electrophiles[b]	Solvent	T (°C)	E	Yield (%)[c]	ratio 7 : 8[d]
1	6f	PhSeCl, K_2CO_3	Et_2O	- 70°	PhSe	70	69 : 31
2	6b	NIS	CH_2Cl_2	+ 20°	I	89	83 : 17
3	6f	NIS	CH_2Cl_2	- 20°	I	89	86 : 14
4	6a	$Hg(OAc)_2$, $CaCO_3$	THF	- 20°	HgBr	88	91 : 9
5	6b	$Hg(OAc)_2$, $CaCO_3$	THF	- 20°	HgBr	82	94 : 6
6	6e	$Hg(OAc)_2$, $CaCO_3$	THF	- 20°	HgBr	71	92 : 8
7	6f	$Hg(OAc)_2$, $CaCO_3$	THF	- 20°	HgBr	81	94 : 6
8	6f	$Hg(OAc)_2$, $CaCO_3$	THF	+ 20°	HgBr	82	88 : 12
9	6f	$Hg(TFA)_2$, $CaCO_3$	THF	- 20°	HgBr	87	80 : 20
10	6f	$Hg(NO_3)_2$, $CaCO_3$	THF	- 20°	HgBr	81	90 : 10
11	6f	$Hg(OAc)_2$, $CaCO_3$	CH_3CN	- 20°	HgBr	78	86 : 14
12	6f	$Hg(TFA)_2$, $CaCO_3$	CH_3CN	- 20°	HgBr	77	57 : 43
13	6f	$Hg(NO_3)_2$, $CaCO_3$	CH_3CN	- 20°	HgBr	82	57 : 43
14	6f	$Hg(OAc)_2$	THF	- 20°	HgBr	88	95 : 5
15	6f	$Hg(OAc)_2$	CH_3CN	- 20°	HgBr	82	90 : 10
16	6f	$Hg(NO_3)_2$	CH_3CN	- 20°	HgBr	78	55 : 45

[a] 0.1M solution (1mmol scale); [b] Electrophile (1.1 eq.), $CaCO_3$ (2.2 eq.), then saturated aqueous KBr; [c] Isolated yields after flash chromatography; [d] Determined by 400 MHz ^1H NMR.

This kinetically controlled mercuri induced cyclization was assumed to involve the formation, in the first step, of diastereoisomeric π-complexes or bridged mercurium ions, which would lead to the formation of protonated tetrahydrofuran intermediates **10a-b**. These latter would then be deprotonated in an irreversible step in the presence of a base to afford mercuri-tetrahydrofurans **7** and **8** (Scheme 4).[2] In the absence of a base, the equilibrium might be shifted, at least to a certain extent, towards the formation of the thermodynamically more stable 2,4-*trans* isomer **8**. When $CaCO_3$ is not in the medium (entry 14-16), then the counter-ion (*i.e.* AcO^-) can act as a base, explaining the high selectivity observed with $Hg(OAc)_2$ even in the absence of a base. Our attempts to modify the course of the reaction to produce mainly diastereoisomer **8**, using acidic conditions or heating the reaction under reflux (thermodynamic conditions), were unsuccessful. Therefore, at this stage, we cannot conclude that 2,4-*trans* **8** is the thermodynamic product, even though this seems reasonable if one considers the steric interactions occuring in the 2,4-*cis* isomer compared to the 2,4-*trans* isomer.

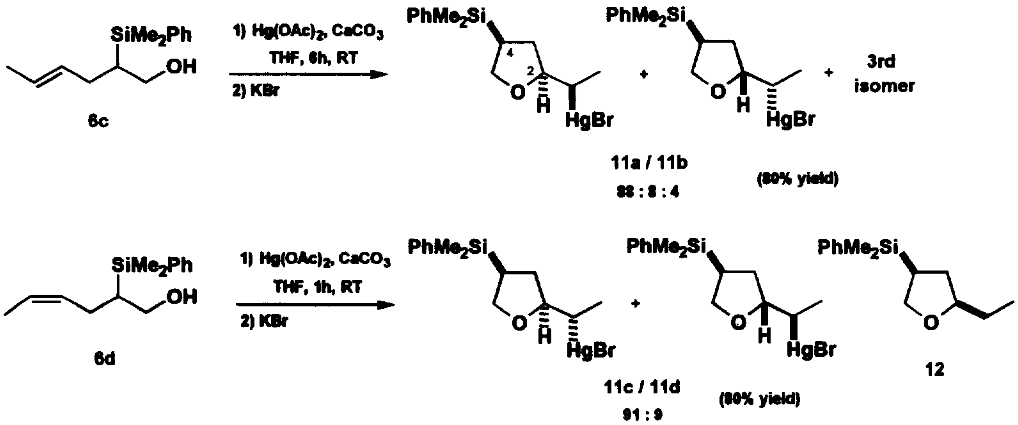


Scheme 4

The solvent effect can be rationalized assuming that the bridged mercurium ion would collapse in polar solvent (CH_3CN, ε=38) to form a stabilized open cation (Scheme 5). Cyclization of this species would then lead to both tetrahydrofurans 7 and 8 with a much lower diastereoselectivity. The fact that such an open cation would exist only with $Hg(TFA)_2$ or $Hg(NO_3)_2$ and not with $Hg(OAc)_2$ is consistent with $CF_3CO_2^-$ and NO_3^- being more electron-withdrawing than AcO^-.

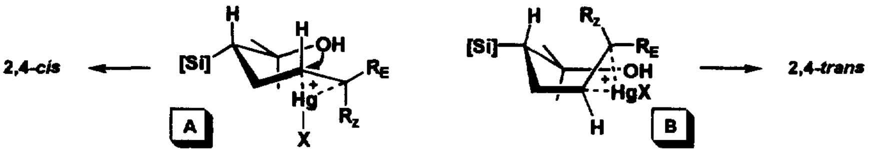
Scheme 5

We then extended our investigations to disubstituted π-systems. The homoallylsilanes (*E*) and (*Z*) **6c-d** were subjected to the same conditions as above (*i.e.* $Hg(OAc)_2$ and $CaCO_3$). Not surprisingly, higher temperatures were required for the cyclization to take place, the disubstituted compounds being unreactive at -20°C.[10b] The cyclizations occurred smoothly (1h) at RT with the (*Z*)-homoallylsilane **6d**, but required 6 hours for the *E*-isomer **6c** (Scheme 6). Cyclization of the *Z*-olefin gave only two diastereoisomers in a 91:9 ratio, with 2,4-cis **11c** as the major isomer. In contrast **6c** afforded the 2,4-*cis* diastereoisomer **11a** as the major product along with two other diastereoisomers in a 88:8:4 ratio (^{1}H NMR).



Scheme 6

11a was also reduced using $NaBH_4$-NaOH to afford the corresponding 2-ethyl tetrahydrofuran **12** in good yield. Theoretically, as 3 related chiral centres are present in the product with two generated during the cyclization, we could expect 8 stereoisomers or 4 pairs of enantiomers. The *Z*-olefin produced only 2 pairs of enantiomers with one in great excess. This can be rationalized by considering the conformations in the transition state, illustrated in scheme 7.[12] The 2,4-*cis*-selectivity can be explained by invoking a *chair-like* transition state **A**, with the bulky silicon group occupying the less sterically-demanding pseudo-equatorial position. The nucleophile would then attack "*anti*" relative to the electrophile in a *5-exo-trig* fashion to give a 5-membered ring skeleton possessing substituents with a 2,4-*cis* relationship. A similar transition state has been proposed by Harding and Burks[12] for mercuri-cyclization of olefinic amides and more recently by Labelle and Guindon[1a] for the iodoetherification of homoallylic alcohols. The latter group also performed some calculations and showed that electronegative groups in homoallylic positions preferred the axial position, eventually leading to the 2,4-*trans* diastereoisomer. In our case, we believe that the minor *trans* tetrahydrofuran is formed via a *boat-like* transition state **B** with the large Si group remaining in an equatorial position.[13] Using these models, it emerges that 1,3- and 1,4-chiral inductions occurred concomitantly, the stereochemistry of the acyclic chiral centre only relying on the geometry of the starting double bond. This rationalizes the formation, under kinetically controlled conditions, of only 2 products during the cyclization of **6d**. The generation in small amount of a third diastereoisomer during the cyclization of the olefin *E* **6c** is probably due to a partial isomerization of the double bond during the electrophilic process. The slow reaction observed with *E* olefins would support this hypothesis.

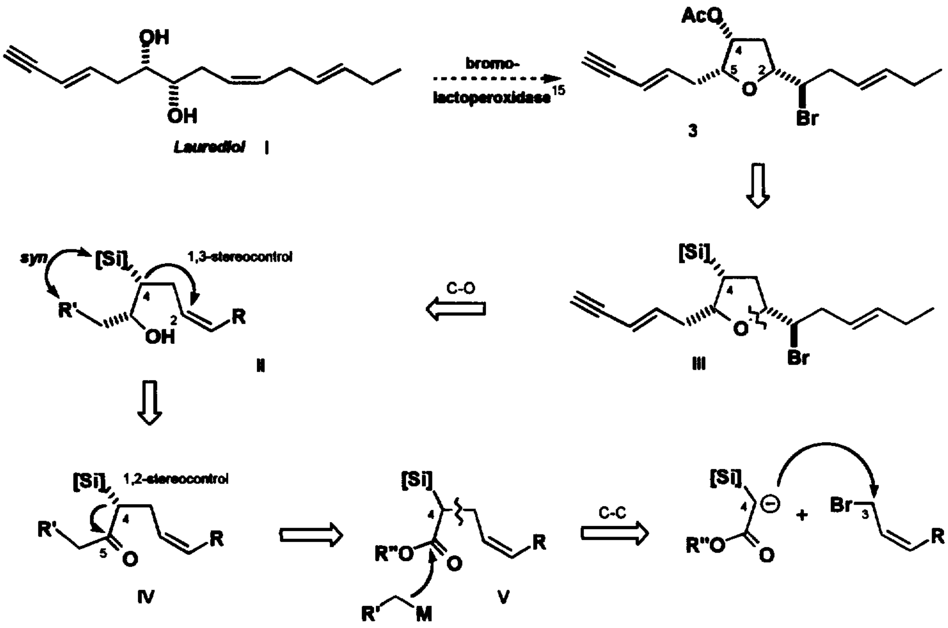


Scheme 7

The 2,4-*cis* relationship of the tetrahydrofurans **11a** and **11c** has been deduced from the NOESY and NOE difference experiments, but we have been unable to prove the stereochemistry of the acyclic chiral centre. However, based on precedents from the literature[1a] and on the formation of only two diastereoisomers (instead of 4), we assume confidently that the two new chiral centres are formed simultaneously and, consequently, the stereochemistry of the tetrahydrofurans **11a-d** is that illustrated in scheme 6.

Approach towards the total synthesis of (+/-)-kumausyne

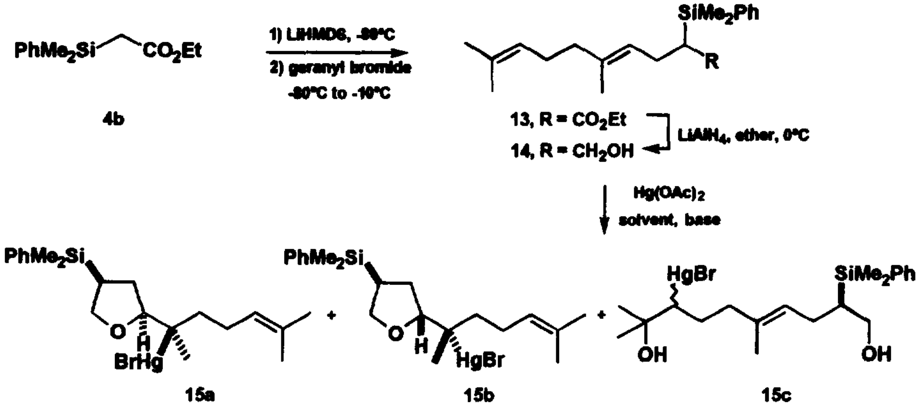
With these preliminary results in hand, we envisaged the application of our methodology to the total synthesis of (+/-)-kumausyne **3**,[14] an halogenated tetrahydrofuran isolated from a red algae of the genus *Laurencia*. It has been suggested that such compounds and congeners were formed by halocyclization of pentadeca-3,9,12-trien-1-yn-6,7-diol intermediates (also called laurediols **I**).[15] Also, an approach to the kumausynes[16] involving a biomimetic cyclization of these laurediols would be straightforward. Such a strategy was indeed examined by Martin et al.[16d] who showed that bromocyclization of a structurally close 1,2-*syn* diol analogue of **I**, afforded a tetrahydrofuran having a 2,4-*trans* instead of the requisite 2,4-*cis* relationship. We thus envisioned another approach, where the OH group in homoallylic position relative to the (*Z*)-double bond would be replaced by a silicon group (*i.e.* **II**). It is now well recognized that silicon groups can be used as masked hydroxy groups.[6] Therefore, combining this unique property of the silicon group with its ability to control the stereochemistry of proximal chiral centres, we devised the disconnection outlined in Scheme 8. The silicon group ([Si]) is expected to control the stereoselectivity at C-2 and C-5, first during the reduction of the α-silylketone **IV** (1,2-stereocontrol)[17] and then during the electrophilic cyclization of **II** into **III** (1,3-stereocontrol). In the latter stage of the synthesis, the silicon group in **III** would then be converted into a OH group with retention of configuration at C-4.[6] The construction of the carbon framework would be carried out starting from α-allyl-α-silylacetic esters of type **V** by alkylation of the parent α-silylacetic esters, then transformation of the ester function into the ketone through condensation of a suitable Grignard reagent. Interestingly, our approach towards (+/-)-kumausyne **3** should also be applicable in homochiral series, starting from optically active α-silylacetic esters **V**, since the chiral centre of **V** (*i.e.* C-4) is expected to control all the other chiral centres through 1,2- and 1,3-stereocontrol.



Scheme 8

Elaboration of the C-2 chain

We have shown previously that 2 chiral centres could be introduced simultaneously during the cyclofunctionalization (Scheme 6). Another point which remained to be addressed was the regioselectivity of the electrophilic addition when one is dealing with a polyenic system.[18] In order to gain some insight into this problem, we carried out preliminary studies using the readily available geranyl system. The dienol **14** was easily prepared by alkylation of **4b**, with the geranyl bromide, followed by a clean reduction of the ester function using $LiAlH_4$ (Scheme 9). Cyclization using $Hg(OAc)_2$ led mainly to two tetrahydrofurans along with an acyclic product whose structure, elucidated using ^{13}C and ^{1}H NMR, was consistent with **15c**, the product of addition of $Hg(OAc)_2$ on the terminal double bond. We observed again that steric hindrance around the double bond slowed down the cyclization. Moreover, increasing the temperature not only raised the diastereoselectivity in the favour of the 2,4-*cis* diastereoisomer but also favoured the reaction at the proximal double bond relative to the distal one, the best result being obtained at 100°C (entry 1,2,6). The absence of a base during the reaction also provoked a decrease in the stereoselectivity with the 2,4-*cis* product still being the major one (entry 3-5).



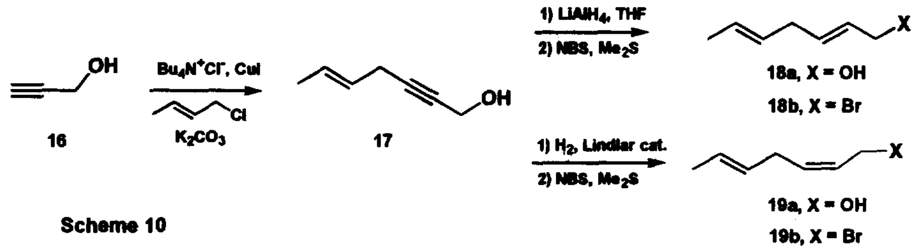
Scheme 9

Table 2. Cyclization of geranyl derivative 14 with $Hg(OAc)_2$ (Scheme 9).

Entry	Solvent	Base	T(°C)	Time	Ratio (15a : 15b : 15c)[b]	Yield (%)[c]
1	THF	$CaCO_3$	20	1h	40 : 6 : 54	95
2	THF	$CaCO_3$	reflux	1h	46 : 10 : 44	92
3	$n\text{-}Bu_2O$	-	100	2 min.[a]	57 : 24 : 19	91
4	$n\text{-}Bu_2O$	-	100	10 min.[a]	51 : 31 : 18	88
5	$n\text{-}Bu_2O$	-	100	1h[a]	52 : 28 : 20	92
6	$n\text{-}Bu_2O$	$CaCO_3$	100	1h[a]	62 : 18 : 20	92

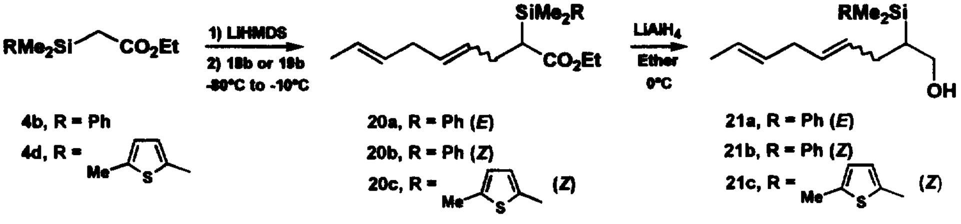
[a] $Hg(OAc)_2$ was added at 100°C. [b] Ratio measured using 400 MHz ^1H NMR. [c] Crude overall yield.

The lack of regioselectivity encountered with the geranyl model was not encouraging. Nevertheless, we decided to turn our attention to a model possessing a C-2 chain structurally close to that of the kumausyne. Therefore, following the strategy described for simpler models, we needed the dienyl bromides **18b** and **19b** to alkylate the α-silylacetic ester **4b** and **4d**. These were prepared in 3 steps starting from commercially available propargylic alcohol **16** (Scheme 10). Jeffery cross-coupling[19] between **16** and *E*-crotylchloride gave the enyne **17**[20a] in 52% yield. Reduction of the triple bond using $LiAlH_4$ or hydrogenation over Lindlar catalyst gave the dienols **18a** and **19a** respectively, which were then brominated with $NBS\text{-}Me_2S$. *E,E* and *Z,E*-dienyl bromides **18b** and **19b** were thus obtained in good overall yield (60-70%) with an excellent stereocontrol (>98%, GC).[20]



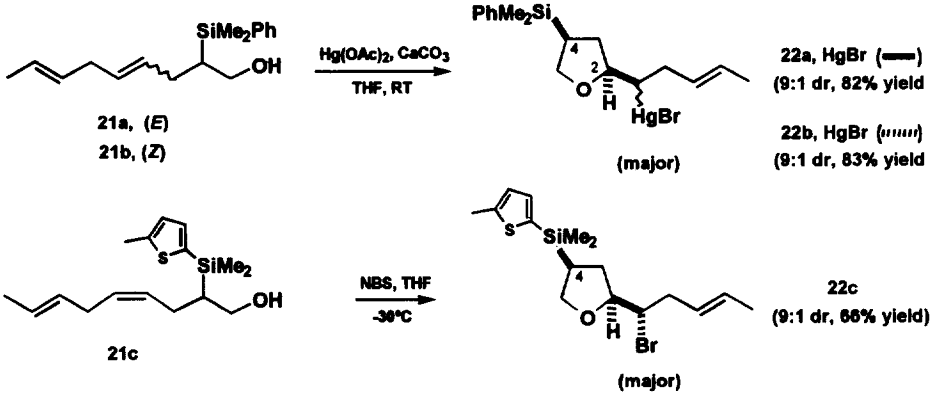
Scheme 10

Alkylation of the α-silylacetic esters **4b** and **4d** with the bromides **18b** and **19b**, followed by reduction of the ester function afforded the required homoallylsilanes **21a-c** with 40-60% overall yield (Scheme 11).



Scheme 11

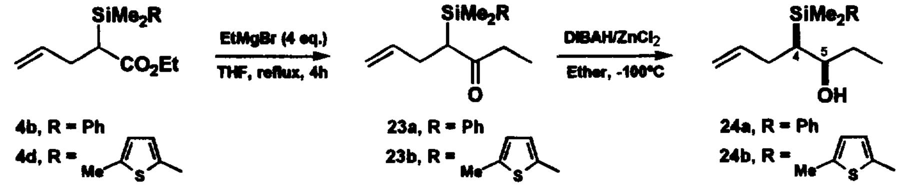
The treatment of **21a** and **21b** with $Hg(OAc)_2$ at room temperature gave the desired tetrahydrofuran **22a** and **22b** respectively, without products of addition onto the terminal double bond (Scheme 12). The diastereoselectivity (dr 9:1) is in the range of that observed with simpler olefins **6c** and **6d**. More relevant, the cyclization of **21c** with NBS in THF afforded the bromo-tetrahydrofuran **22c** in a 9:1 ratio in favour of the 2,4-*cis* diastereoisomer. This tetrahydrofuran possesses both the stereochemistry and the functionality of the kumausyne at C-2. Moreover, the presence of a 5-(methylthienyl)dimethylsilyl group at C-4 should allow for a milder oxidative cleavage of the C-Si bond, than that with $PhMe_2Si$.[21]



Scheme 12

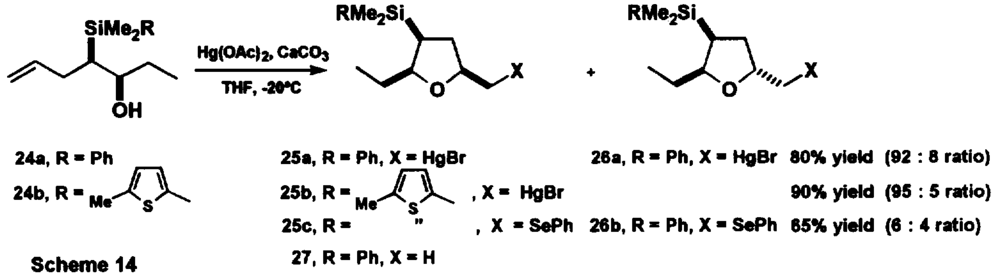
Elaboration of the C-5 chain

Following our retrosynthetic analysis (Scheme 8), the chain at C-5 was to be introduced using the condensation of a Grignard reagent on the ester function of an α-silylacetic ester. This strategy has been initiated by Larson and co-workers[22] and was found particularly efficient for the transformation of α-silylesters into the corresponding α-silylketones. The utilization of an excess of the organometallic reagent allows first the formation of the ketone which on reaction with a second equivalent of the Grignard reagent easily enolizes to avoid further and unwanted addition. Applying this procedure to our case, we were pleased to find that the desired α-silylketones **23a-b** could be obtained in quantitative crude yields, as unstable products which were directly reduced into the *syn* β-hydroxysilane **24a-b** using $DIBAH/ZnCl_2$[17b-c,23] at -100°C in ether (Scheme 13). In these conditions, the *syn*-alcohols **24a-b** were obtained in 50% overall yield (from **4b,d**) with selectivities as high as 95% d.e. $DIBAH/SnCl_4$ or DIBAH alone also afforded the *syn*-alcohol as the major isomer but with lower d.e. Other conditions were also studied showing that reversal of the diastereoselectivity could be obtained for instance with $LiAl(O\text{-}tBu)_3$ or $LiAlH_4$ but generally with poor selectivities (30-40% d.e.).



Scheme 13

Having introduced the secondary centre at C-5, we then treated the β-hydroxysilanes **24a-b** with $Hg(OAc)_2$ in the same conditions as above to form the desired tetrahydrofurans with good yields and excellent diastereoselectivities (Scheme 14). As previously, the 2,4-*cis* diastereoisomer was largely predominant giving access to the 2,4,5-trisubstituted all-*cis* tetrahydrofurans. Reduction of the mercuri-tetrahydrofuran **25a** was easily accomplished to furnish the corresponding 2-methyl analogue **27**.[8] Therefore, we demonstrated using this simple sequence that the 3 chiral centres of the tetrahydrofuran ring of kumausyne **3** can be readily set up with the correct stereochemistry in only 2 steps starting from the suitable α-silylketone. Considering what is described above, the control of the 4 chiral centres of the natural product starting from a disubstituted dienyl system is theoretically possible. We also carried out the selenoetherification of **24b** which gave a diastereoisomeric mixture of **25c** and **26b** in a 60:40 ratio. The all-*cis* stereochemistry was assigned unambiguously from the NOE experiments carried out on diastereoisomers **25a** and **26a** (Fig.-2).



Scheme 14

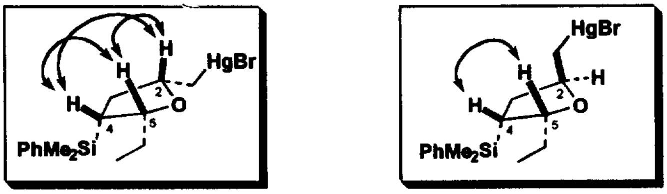


Fig.-2. NOE effects in 25a and 26a

In summary, we have shown that 2,4-*cis* and all-*cis*-2,4,5-substituted tetrahydrofurans can be obtained in good yields with excellent 1,3-stereocontrol using electrophilic *5-exo-trig* cyclizations of 2-silyl-4-alkenols. The utility of this strategy has also been demonstrated with an approach to the total synthesis of kumausyne. We have shown that the strategy is workable since we have been able to introduce the correct chain on the C-2 centre with the correct stereochemistry at each of the stereogenic centres. The Larson strategy[22] allows an easy access to the C-5 chain. Further research is now under way to introduce the enyne system on C-5 and to carry out the C-Si bond oxidation on the fully functionalized kumausyne skeleton. It is noteworthy that the oxidation of a thienylsilyl has already been carried out on tetrahydrofuran model and was found a good alternative to the oxidation of the $PhMe_2Si$ group.[6,21] Finally, an enantioselective approach could also be envisaged by controlling the absolute configuration of the chiral centre on the substituted α-silylacetic esters.[24]

EXPERIMENTAL SECTION

^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER 250FT (250 MHz) and BRUKER WH-360FT (360 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. IR spectra were recorded on a Perkin-Elmer 1710 spectrophotometer. All commercial products were used without further purifications.

CH_2Cl_2, and hexamethyldisilazane were distilled from CaH_2. THF was distilled from sodium and benzophenone. Commercially available allyl and geranyl bromide were purified by distillation before use.

Elemental analyses were performed by the I. Beetz laboratory, W-8640 Kronach (Germany). Mass spectra were recorded on a Nermag R10-10C (Chemical ionization mode, NH_3).

The numbering of the protons and carbons in ^{1}H NMR and ^{13}C NMR spectra of tetrahydrofurans have been made according to the numbering outlined in Figure 1 and 2.

Ethyl[dimethyl-(5-methylthien-2-yl)-silyl]ethanoate 4d.^{7} To a solution of 2-methylthiophene (15 ml, 0.16 mol) in anhydrous THF (350 ml) was added at -80°C a 1.6$\underline{M}$ solution of n-BuLi in hexane (134 ml, 0.187 mol). The mixture was stirred for 2 hours at -20°C then a solution of chloromethyldimethylchlorosilane (27.8 ml, 0.210 mol) in anhydrous THF (350 ml) was added dropwise at -60°C. The mixture was allowed to warm to 0°C, then stirred during 1h at this temperature and hydrolyzed with a saturated solution of $NaHCO_3$. The organic layer was decanted and the aqueous layer was extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo* to give a brown oil which was purified by distillation (75°C, 1 mmHg) to afford the chloromethylsilane intermediate as a colourless oil (29.5 g, 97%). **^{1}H NMR** (δ ppm) : 7.15 (1H, d, J 3.2, H-3 thio), 6.88-6.87 (1H, m, H-4 thio), 2.94 (2H, s, CH_2Cl), 2.55 (3H, d, J 0.6, CH_3), 0.45 (6H, s, $Si(CH_3)_2$). **^{13}C NMR** (δ ppm) : 146.5 (s, C-thio), 135.6 (d, J 165, C thio), 133.0 (s, C thio), 127.0 (d, J 164, C thio), 30.7 (t, J 139, CH_2Cl), 15.0 (q, J 129, CH_3), -3.5 (2C, q, J 121, $Si(CH_3)_2$). **IR** (CH_2Cl_2)(υ_{max}) : 3000 (C-H), 2960 (C-H), 2920 (C-H), 1440, 1390, 1250 (Si-C), 960, 840 cm^{-1}. **MS** (EI): 206 ($M^{+\cdot}$+1, 4), 205 ($M^{+\cdot}$, 2), 204 ($M^{+\cdot}$-1, 14), 157 (14), 155 ($M^{+\cdot}$-CH_2Cl, 100), 111 (11), 77 ($SiCH_2Cl^{+\cdot}$, 11). **Anal.** Calcd for $C_8H_{13}ClSSi$: C, 46.92; H, 6.40; S, 15.66; Si, 13.71. Found : C, 46.75; H, 6.28; S, 15.68; Si, 13.73. To a suspension of magnesium (3.37 g, 0.138 mol) in anhydrous THF (5ml) was added a small amount of the preceding chloromethylsilane to initiate the reaction. The remaining of the solution (27.0 g, 0.132 mol) in dry THF (70 ml) was then added dropwise at such a rate as to maintain a gentle reflux. The mixture was refluxed for 1h, then a solution of freshly distilled ethyl chloroformiate (18.9 ml, 0.198 mol) in anhydrous THF (100 ml) was added at 0°C. The mixture was stirred overnight at room temperature then quenched with a 1$\underline{M}$ solution of HCl. The organic layer was decanted and the aqueous layer was extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo* to give a yellow oil which was purified by distillation (95-100°C, 0.4 mmHg) to afford **4d** (22.7 g, 75%): **^{1}H NMR** (δ ppm) : 7.12 (1H, d, J 3.2, H-3 thio), 6.86-6.84 (1H, m, H-4 thio), 4.08 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.53 (3H, d, J 1.1, CH_3), 2.13 (2H, s, $SiCH_2$), 1.21 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.42 (6H, s, $Si(C\underline{H}_3)_2$). **^{13}C NMR** (δ ppm) : 172.1 (s, CO), 146.2 (s, C thio), 135.3 (d, J 164, C thio), 134.1 (s, C thio), 126.8 (d, J 163, C thio), 59.9 (t, J 151, $CO_2\underline{C}H_2CH_3$), 27.0 (t, J 125, $SiCH_2$), 14.9 (q, J 130, $\underline{C}H_3$ thio), 14.2 (q, J 126, $CO_2CH_2\underline{C}H_3$), -1.7 (2C, q, J 120, $Si(\underline{C}H_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960, (C-H), 1710 (C=O), 1440, 1360, 1250 (Si-C), 1140, 1100, 960 cm^{-1}. **MS** (EI): 243 ($M^{+\cdot}$+1, 10), 242 ($M^{+\cdot}$, 37), 228 ($M^{+\cdot}$+1-CH_3, 20), 227 ($M^{+\cdot}$-CH_3, 100), 197 ($M^{+\cdot}$-OCH_2CH_3, 11), 185 (39), 155 ($M^{+\cdot}$-(, 13), 145 (30), 117 (14), 77 (18), 75($Si(CH_3)_2OH^{+\cdot}$, 36).

General procedure for the alkylation of α-(alkoxysilyl)acetic esters 4. Ethyl-2-[dimethyl-(5-methylthien-2-yl)silyl]pent-4-enoate 5f. To a solution of hexamethyldisilazane (0.20 ml, 0.99 mmol) in dry THF (3 ml) was added at -20°C a 1.6$\underline{M}$ solution of n-BuLi in hexane (0.53 ml, 0.85 mmol). The mixture was stirred at -5°C for 15 minutes then cooled to -60°C and a solution of the ester **4d** (0.172 g, 0.71 mmol) in dry THF (1 ml) was added dropwise. The mixture was stirred at -60°C for 2h, then a solution of allyl bromide (0.3 ml, 3.55 mmol) in dry THF (1 ml) was added dropwise at -80°C. The mixture was allowed to warm to -20°C over 0.5h then treated with a saturated solution of $NaHCO_3$ and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo* to give a yellow oil which was filtered through Florisil® (Petroleum ether/EtOAc 95:5) to afford **5f** as a colourless oil (0.17 g, 85%). **^{1}H NMR** (δ ppm) : 7.10 (1H, d, J 3.3, H-3 thio), 6.86-6.84 (1H, m, H-4 thio), 5.86-5.70 (1H, m, $CH_2C\underline{H}{:}CH_2$), 5.05-4.91 (2H, m, $CH_2CH{:}C\underline{H}_2$), 4.08 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.56-2.47 (1H, m, $C\underline{H}_aH_bCH{:}CH_2$), 2.54 (3H, d, J 0.9, $C\underline{H}_3$ thio), 2.28 (1H, dd, J 3.0, 11.5, SiCH), 2.22-2.12 (1H, m, $CH_a\underline{H}_bCH{:}CH_2$), 1.20 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.39 (6H, s, $Si(CH_3)_2$). **^{13}C NMR** (δ ppm) : 174.2 (s, CO), 146.4 (s, C thio), 137.7 (d, J 165, $CH_2\underline{C}H{:}CH_2$), 135.8 (d, J 165, C thio), 133.1 (s, C thio), 126.9 (d, J 164, C thio), 114.9 (t, J 159, $CH_2CH{:}\underline{C}H_2$), 59.9 (t, J 145, $CO_2\underline{C}H_2CH_3$), 37.5 (d, J 124, SiCH), 30.8 (t, J 125, $\underline{C}H_2CH{:}CH_2$), 15.0 (q, J 128, $\underline{C}H_3$ thio), 14.3 (q, J 127, $CO_2CH_2\underline{C}H_3$), -3.5 (2C, q, J 121, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3040 (C-H), 2980 (C-H), 1705

(C=O), 1440, 1360, 1250 (Si-C), 1210, 1000, 915 cm^{-1}. **MS** (EI): 282 ($M^{+\cdot}$, 8), 281 ($M^{+\cdot}$-1, 7), 267 ($M^{+\cdot}$-CH_3, 11), 237 ($M^{+\cdot}$-OCH_2CH_3, 31), 185 (54), 155 (54), 138 (100), 103 (60), 97 (26), 85 (33), 83 (35), 75 ($Si(CH_3)_2OH^{+\cdot}$, 87). **Anal.** Calcd for $C_{14}H_{22}O_2SSi$: C, 59.53; H, 7.85; S, 11.35; Si, 9.94. Found : C, 59.39; H, 7.86; S, 11.33; Si, 9.93.

Methyl-2-trimethylsilylpent-4-enoate 5a. Purified by flash chromatography (Petroleum ether/EtOAc/NEt_3 97.5:2:0.5) (95%). ^{1}**H NMR** (δ ppm) : 5.86-5.70 (1H, m, $CH_2C\underline{H}{:}CH_2$), 5.06-4.90 (2H, m, $CH_2CH{:}C\underline{H}_2$), 3.62 (3H, s, CO_2CH_3), 2.58-2.44 (1H, m, $C\underline{H}_aH_bCH{:}CH_2$), 2.18-2.08 (1H, m, $CH_a\underline{H}_bCH{:}CH_2$), 2.11-2.06 (1H, m, SiCH), 0.06 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 1705 (C=O), 1430, 1340, 1250 (Si-C), 1160, 915, 840 cm^{-1}. **MS** (CI, NH_3) : 187 ($M^{+\cdot}$+1, 100), 89 (47), 82 (71), 73 ($Si(CH_3)_3^{+\cdot}$, 74). **Anal.** Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74. Found : C, 58.06; H, 9.65.

Ethyl-2-(dimethylphenylsilyl)pent-4-enoate 5b. Purified by flash chromatography (Petroleum ether/EtOAc/NEt_3 98:1:1) (85%). ^{1}**H NMR** (δ ppm) : 7.65-7.35 (5H, m, Aromatic H), 5.83-5.72 (1H, m, $C\underline{H}{:}CH_2$), 4.97 (2H, m, $CH{:}C\underline{H}_2$), 4.31-4.01 (2H, m, $CO_2C\underline{H}_2CH_3$), 2.55 (1H, ddd, J 14.1, 12.1, $C\underline{H}_aH_b$), 2.33 (1H, dd, J 12.1, 2.8, CHSi), 2.12 (1H, ddd, J 14.1, 2.8, $CH_a\underline{H}_b$), 1.14 (3H, t, J 6.6, $CO_2CH_2C\underline{H}_3$), 0.34 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$). **IR** (film, KBr)(υ_{max}) : 3600, 3200, 3095, 1250, 1100, 1000, 900, 820 cm^{-1}. **MS** (CI, NH_3): 262 (M^+, 14), 236 (3), 202 (43), 185 (100), 156 (25), 135 (49), 120 (20), 82 (18). **Anal.** Calcd for $C_{15}H_{22}O_2Si$: C, 68.74; H, 8.47; Si, 10.56. **Found** : C, 68.67; H, 8.46; Si, 10.67.

(*E*)-Ethyl-2-(dimethylphenylsilyl)hex-4-enoate 5c. Purified by flash chromatography (Petroleum ether/EtOAc 95:5) (95%). ^{1}**H NMR** (δ ppm) : 7.56-7.49 (2H, m, Aromatic H), 7.41-7.35 (3H, m, Aromatic H), 5.45-5.34 (2H, m, $C\underline{H}{:}C\underline{H}CH_3$), 4.05 (1H, dq, J 7.2, 10.8, $C\underline{H}_aH_bCH_3$), 3.99 (1H, dq, J 7.2, 10.9, $CH_a\underline{H}_bCH_3$), 2.50-2.40 (1H, m, $SiCHC\underline{H}_aH_b$), 2.26 (1H, dd, J 3.2, 11.3, SiCH), 2.10-2.02 (1H, m, $SiCHCH_a\underline{H}_b$), 1.60-1.58 (3H, m, $CH{:}CHC\underline{H}_3$), 1.14 (3H, t, J 7.1, $CH_2C\underline{H}_3$), 0.40 (3H, s, $SiCH_3$), 0.38 (3H, s, $SiC\underline{H}_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2800 (C-H), 1720 (C=O), 1250 (Si-C), 960, 735 cm^{-1}. **MS** (CI, NH_3) : 276 ($M^{+\cdot}$, 3), 261 ($M^{+\cdot}$-CH_3, 40), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 103 (39). **Anal.** Calcd for $C_{16}H_{24}O_2Si$: C, 69.52; H, 8.75; Si, 10.16. Found : C, 69.45; H, 8.60; Si, 10.13.

(*Z*)-Ethyl-2-(dimethylphenylsilyl)hex-4-enoate 5d. Purified by flash chromatography (Petroleum ether/EtOAc 95:5) (85%). ^{1}**H NMR** (δ ppm) : 7.55-7.50 (2H, m, Aromatic H), 7.41-7.35 (3H, m, Aromatic H), 5.44-5.28 (2H, m, $C\underline{H}{:}C\underline{H}CH_3$), 4.04 (1H, dq, J 7.2, 11.0, $C\underline{H}_a{:}CH_bCH_3$), 3.99 (1H, dq, J 7.1, 11.0, $CH_a{:}C\underline{H}_bCH_3$), 2.55-2.45 (1H, m, $SiCHC\underline{H}_aH_b$), 2.22 (1H, dd, J 3.4, 11.1, SiCH), 2.15-2.07 (1H, m, $SiCHCH_a\underline{H}_b$), 1.54-1.51 (3H, m, $CH{:}CHC\underline{H}_3$), 1.13 (3H, t, J 7.2, $CH_2C\underline{H}_3$), 0.41 (3H, s, $SiCH_3$), 0.40 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2980 (C-H), 2960 (C-H), 1705 (C=O), 1250 (Si-C), 1110, 910, 840 cm^{-1}. **MS** (CI, NH_3) : 276 ($M^{+\cdot}$, 19), 261 ($M^{+\cdot}$-CH_3, 100), 230 (38), 198 ($M^{+\cdot}$-(Ph+1), 25), 157 (34), 135 ($PhSi(CH_3)_2^{+\cdot}$, 60), 116 (26). **Anal.** Calcd for $C_{16}H_{24}O_2Si$: C, 69.52; H, 8.75; Si, 10.16. Found : C, 69.35; H, 8.70; Si, 10.21.

General procedure for the reduction of 5a-f. 2-[Dimethyl-(5-methylthien-2-yl)silyl]pent-4-enol 6f. To a suspension of $LiAlH_4$ (140 mg, 3.5 mmol) in anhydrous ether (25 ml) was added dropwise at 0°C a solution of ester **5f** (1 g, 3.5 mmol) in dry ether (10 ml). The mixture was stirred at 0°C for 1h, then treated with a 1$\underline{M}$ solution of HCl and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated *in vacuo* to give an oil which was purified by flash chromatography (Petroleum ether/EtOAc/NEt_3 98:1.5:0.5) (0.70 g, 83%), affording the alcohol **6f** as a colourless oil : ^{1}**H NMR** (δ ppm) : 7.08 (1H, d, J 3.2, H-3 thio), 6.86-6.84 (1H, m, H-4 thio), 5.95-5.78 (1H, m, $CH_2C\underline{H}{:}CH_2$), 5.13-4.98 (2H, m, $CH_2CH{:}C\underline{H}_2$), 3.83 (1H, dd, J 4.4, 10.9, $C\underline{H}_aH_bOH$), 3.74 (1H, dd, J 7.0, 10.9, $CH_a\underline{H}_bOH$), 2.53 (3H, d, J 0.9, CH_3), 2.54-2.31 (1H, m, $C\underline{H}_aH_bCH{:}CH_2$), 2.25-2.12 (1H, m, $CH_a\underline{H}_bCH{:}CH_2$), 1.42 (1H, broad s, OH), 1.30-1.16 (1H, m, SiCH), 0.36 (3H, s, $SiCH_3$), 0.35 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3040 (C-H), 2980 (C-H), 1440, 1250 (Si-C), 1210 cm^{-1}. **MS** (EI) : 178 (32), 176 (23), 157 ($ArSiCH_3OH^{+\cdot}$, 95), 155 (46), 124 (20), 115 (19), 97 (21), 85 (30), 75 ($Si(CH_3)_2OH^{+\cdot}$, 100), 71 (47). **Anal.** Calcd for $C_{12}H_{20}OSSi$: C, 59.95; H, 8.38; S, 13.34; Si, 11.68. Found : C, 60.00; H, 8.44; S, 13.24; Si, 11.65.

2-(Trimethylsilyl)pent-4-enol 6a. Purified by flash chromatography (Petroleum ether/EtOAc/NEt_3 97.5:2:0.5) (88%). ^{1}**H NMR** (δ ppm) : 5.96-5.79 (1H, m, $CH_2C\underline{H}{:}CH_2$), 5.12-4.95 (2H, m, $CH_2CH{:}C\underline{H}_2$), 3.79-3.64 (2H, m, $C\underline{H}_2OH$), 2.36-2.10 (2H, m, $C\underline{H}_2CH{:}CH_2$), 1.77 (1H, broad s, OH), 1.03-0.96 (1H, m, SiCH), 0.02 (9H, s, $Si(CH_3)_3$). **IR** ($CHCl_3$) (υ_{max}) : 3000, 2950 (C-H), 1250 (Si-C), 990, 915, 860, 840 cm^{-1}. **Anal.** Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46; Si, 17.74. **Found** : C, 60.75; H, 11.48; Si, 17.68.

2-(Dimethylphenylsilyl)pent-4-enol 6b. Purified by flash chromatography (Petroleum ether/EtOAc/NEt_3 92:7.5:0.5) (94%). ^{1}**H NMR** (δ ppm) : 7.55-7.52 (2H, m, Aromatic H), 7.39-7.56 (3H, m, Aromatic H), 5.9-5.8 (1H, m, $C\underline{H}{:}CH_2$), 5.06 (1H, d, J 17, $CH{:}C\underline{H}_aH_b$), 4.98 (1H, d, J 10, $CH{:}CH_a\underline{H}_b$), 3.79 (1H, dd, J 10.9, 4.1, $C\underline{H}_aH_bOH$), 3.69 (1H, dd, J 10.9, 7.4, $CH_a\underline{H}_bOH$), 3.5 (1H, ddd, J 14.5, 6.1, $C\underline{H}_aH_bCHSi$), 2.2 (1H, ddd, J 7.9, 14.5, $CH_a\underline{H}_bCHSi$), 1.22-1.29 (1H, m, CHSi), 0.35 (6H, s, $Si(CH_3)_2$). **IR** (film, KBr)(υ_{max}) : 3600, 3200, 3095, 1250, 1100, 1000, 900, 820 cm^{-1}. **MS** (CI, NH_3): 220 (M^+, 5), 203 (15), 175 (2), 152 (100), 137 (56), 105 (5), 92 (15). **Anal.** Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15; Si, 12.74. **Found** : C, 70.21; H, 9.06; Si, 12.69.

(*E*)-2-(Dimethylphenylsilyl)hex-4-enol 6c. Purified by flash chromatography (Petroleum ether/EtOAc/NEt_3 96:3:1) (88%). **^1H NMR** (δ ppm) : 7.57-7.51 (2H, m, Aromatic H), 7.40-7.35 (3H, m, Aromatic H), 5.50-5.44 (2H, m, $C\underline{H}:C\underline{H}CH_3$), 3.82-3.65 (2H, m, $C\underline{H}_2OH$), 2.33-2.06 (2H, m, $C\underline{H}_2CH:CH$), 1.66-1.62 (3H, m, $CH:CHC\underline{H}_3$), 1.35-1.18 (1H, m, SiCH), 0.35 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3500 (O-H), 2860, 2800 (C-H), 1720 (C=O), 1250 (Si-C), 965, 810, 735 cm^{-1}. **MS** (CI, NH_3) : 217 (M^+-OH·, 2), 137 ($PhSi(CH_3)OH^{+\cdot}$,100), 135 ($PhSi(CH_3)_2^{+\cdot}$, 57), 118 (59). **Anal.** Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46; Si, 11.98. Found : C, 71.81; H, 9.46; Si, 11.95.

(*Z*)-2-(Dimethylphenylsilyl)hex-4-enol 6d. Purified by flash chromatography (Petroleum ether/EtOAc/NEt_3 98:1.5:0.5) (74%). **^1H NMR** (δ ppm) : 7.56-7.51 (2H, m, Aromatic H), 7.40-7.34 (3H, m, Aromatic H), 5.53-5.41 (2H, m, $C\underline{H}:C\underline{H}CH_3$), 3.83-3.64 (2H, m, $C\underline{H}_2OH$), 2.26-2.21 (2H, m, $C\underline{H}_2CH:CH$), 1.62-1.59 (3H, m, $CH:CHC\underline{H}_3$), 1.28-1.18 (1H, m, SiCH), 0.35 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 1430, 1250 (Si-C), 1110, 840, 810 cm^{-1}. **MS** (CI, NH_3) : 137 ($PhSi(CH_3)OH^{+\cdot}$,100), 135 ($PhSi(CH_3)_2^{+\cdot}$, 43), 118 (21), 82 (37), 75 (20). **Anal.** Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46; Si, 11.98. Found : C, 71.79; H, 9.43; Si, 11.98.

General procedure for the *5-exo-trig* mercuri-cyclization of diols 6. To a mixture of the alcohol 6 (0.46 mmol) and $CaCO_3$ (0.1 g, 1 mmol) in dry THF (5 ml; ≈ 0.1 $\underline{M}$ solution) was added $Hg(OAc)_2$ (0.16 g, 0.5 mmol) at - 40°C. The heterogeneous mixture was then stirred at -20°C for 3h then quenched with a saturated solution of KBr. The resulting solution was stirred for 1h then decanted and the aqueous layer was extracted with ether. The combined extracts were washed with a saturated solution of KBr, then H_2O and dried over $MgSO_4$. Removal of the solvent under vacuum afforded a colourless oil which was purified using flash chromatography (Petroleum ether/EtOAc 97:3) to give the desired tetrahydrofuran as a mixture of two diastereoisomers 7 and 8 (70-90% overall yield).

7a. **^1H NMR** (δ ppm) : 4.30-4.24 (1H, m, H-2), 3.97 (1H, dd, J 8.5, 8.7, H-5a), 3.71 (1H, dd, J 8.3, 10.5, H-5b), 2.38 (1H, dd, J 5.5, 11.7, $C\underline{H}_aH_bHgBr$), 2.23 (1H, dd, J 5.8, 11.7, $CH_a\underline{H}_bHgBr$), 2.21-2.15 (1H, m, H-3a), 1.60-1.49 (1H, m, CHSi), 1.17 (1H, ddd, J 9.4, 12.3, H-3b), 0.24 (9H, s, $Si(CH_3)_3$). **IR** (film, KBr)(υ_{max}) : 2950, 2850, 1280, 1060, 860 cm^{-1}. **MS** (CI, NH_3) : 397 (4), 262 (1.5), 137 (4.4), 114 (25), 90 (19), 73 (100). **Anal.** Calcd for $C_8H_{17}OSiHgBr$: C, 21.95; H, 3.91; Si, 6.42. Found : C, 21.96; H, 3.93; Si, 6.33.

7b. **^1H NMR** (δ ppm) : 7.51-7.48 (2H, m, Aromatic H), 7.47-7.37 (3H, m, Aromatic H), 4.30-4.23 (1H, m, H-2), 3.98 (1H, dd, J 8.6, 10.4, H-5a), 3.77 (1H, dd, J 8.3, 10.4, H-5b), 2.33 (1H, dd, J 5.6, 11.8, $C\underline{H}_aH_bHgBr$), 2.18 (1H, dd, J 5.8, 11.7, $CH_a\underline{H}_bHgBr$), 2.15 (1H, m, H-3a), 1.85-1.74 (1H, m, CHSi), 1.39-1.17 (1H, m, H-3b), 0.32 (3H, s, $SiCH_3$), 0.31 (3H, s, $SiCH_3$). **IR** (film, KBr)(υ_{max}) : 2950, 2800, 1250, 925, 840 cm^{-1}. **MS** (CI, NH_3) : 459 (0.4), 419 (0.5), 300 (1.1), 201 (4.5), 135 (100), 75 (21). **Anal.** Calcd for $C_{13}H_{19}OSiHgBr$: C, 31.24; H, 3.83; Si, 5.62. Found : C, 31.26; H, 3.88; Si, 5.55.

7d. **^1H NMR** (δ ppm) : 4.31-4.24 (1H, m, H-2), 4.02-3.95 (2H, m, H-5a + $(CH_3)_2C\underline{H}O$), 3.79 (1H, dd, J 8.3, 10.3, H-5b), 2.39 (1H, dd, J 5.4, 11.8, $C\underline{H}_aH_bHgBr$), 2.24 (1H, dd, J 5.7, 11.7, $CH_a\underline{H}_bHgBr$), 2.18 (1H, dd, J 4.9, 7.0, H-3a), 1.68-1.57 (1H, m, CHSi), 1.30-1.20 (1H, m, H-3b), 1.17 (3H, s, CH_3), 1.15 (3H, s, CH_3), 0.13 (3H, s, $SiCH_3$), 0.12 (3H, s, $SiCH_3$). **IR** (film, KBr)(υ_{max}) : 2980, 2850, 1380, 1250, 1170, 1130, 1020, 840 cm^{-1}. **MS** (CI, NH_3): 482 (M+, 0.16), 441 (1.3), 413 (3), 262 (1.5), 399 (2), 355 (2), 300 (5), 201 (1.9), 143 (4), 117 (76), 75 (100). **Anal.** Calcd for $C_{10}H_{21}OSiHgBr$: C, 24.93; H, 4.39; Si, 5.83. Found : C, 24.99; H, 4.39; Si, 5.74.

7e. **^1H NMR** (δ ppm) : 7.06 (1H, d, J 3.3, Aromatic H), 6.84 (1H, dt, J 0.9, 3.3, Aromatic H), 4.31 (1H, dddd, J 5.3, 9.2, H-2), 4.0 (1H, dd, J 8.0, 8.3, H-5a), 3.80 (1H, dd, J 8.3, 10.2, H-5b), 2.55 (3H, d, J 0.9, CH_3 thio), 2.36 (1H, dd, J 5.4, 11.8, $C\underline{H}_aH_bHgBr$), 2.22 (1H, dd, J 7.2, 12.1, $CH_a\underline{H}_bHgBr$), 2.19 (1H, ddd, J 6.7, 9.9, 12.0, H-3a), 1.75 (1H, dddd, J 8.0, 9.9, 10.2, 12.4, CHSi), 1.25 (1H, ddd, J 9.2, 11.9, 12.3, H-3b), 0.32 (3H, s, $SiCH_3$), 0.31 (3H, s, $SiCH_3$). **^{13}C NMR** (δ ppm) : 146.2 (s, Aromatic C), 135.3 (d, J 164.6, Aromatic C), 126.9 (d, J 164.6, Aromatic C), 79.1 (d, J 144.7, C-2), 69.7 (t, J 144.5, C-5), 41.1 (t, J 131.6, CH_2), 39.4 (t, J 131.6, CH_2), 28.5 (d, J 121.2, CHSi), 15.33 (q, J 129.3, CH_3 thio), -3.13 (q, J 121.1, $SiCH_3$), -3.18 (q, J 121.1, $SiCH_3$). **IR** (film, KBr)(υ_{max}) : 3050, 2980, 2840, 1250, 1010, 800 cm^{-1}. **MS** (CI, NH_3) : 520 (M^+, 0.64), 298 (1.1), 237 (13.2), 155 (100), 141 (75), 115 (20.4), 75 (49). **Anal.** Calcd for $C_{12}H_{19}OSSiHgBr$: C, 27.72; H, 3.68; S, 6.17; Si, 5.40. Found : C, 27.75; H, 3.68; S, 6.02; Si, 5.32.

8e. **^1H NMR** (δ ppm) : 7.06 (1H, d, J 3.3, Aromatic H), 6.85 (1H, m, Aromatic H), 4.28-4.22 (1H, m, H-2), 4.11 (1H, dd, J 8.2, 8.7, H-5a), 3.51 (1H, dd, J 8.7, 11.1, H-5b), 2.53 (3H, d, J 0.69, CH_3 thio), 2.33 (1H, dd, J 5.1, 11.7, $C\underline{H}_aH_bHgBr$), 2.17 (1H, dd, J 6.4, 11.7, $CH_a\underline{H}_bHgBr$), 2.03 (1H, ddd, J 7.6, 9.7, 12.1, H-3a), 1.73 (1H, dddd, J 8.2, 9.6, 9.6, 11.0, CHSi), 1.59 (1H, ddd, J 5.1, 9.6, 12.2, H-3b), 0.32 (3H, s, $SiCH_3$), 0.31 (3H, s, $SiCH_3$). **^{13}C NMR** (δ ppm) : 146.1 (s, Aromatic C), 135.2 (d, J 164.5, Aromatic C), 126.9 (d, J 169.5, Aromatic C), 77.8 (d, C-2), 70.6 (t, J 147.9, C-5), 42.5 (t, J 136.1, CH_2), 37.1 (t, J 128, CH_2), 26.7 (d, J 120.7, CHSi), 15.04 (q, J 126.7, CH_3 thio), -3.12 (q, J 120, $Si(CH_3)_2$). **IR** (film, KBr)(υ_{max}) : 3053, 2953, 2858, 1474, 1250, 1000, 800 cm^{-1}. **MS** (CI, NH_3) : 336 (18), 277 (3), 198 (11), 135 (100), 77 (12). **Anal.** Calcd for $C_{12}H_{19}OSSiHgBr$: C, 27.72; H, 3.68; S, 6.17; Si, 5.40. Found : C, 27.77; H, 3.70; S, 6.13; Si, 5.39.

General procedure for the *5-exo-trig* iodo-cyclization of diols 6. To a solution of alcohol **6b** (0.1 g, 0.45 mmol) in anhydrous ether (2.1 ml) was added at 0°C, in one portion, N-iodosuccinimide (100 mg, 0.43 mmol). The reaction mixture was then stirred in the dark for 3h at room temperature, then quenched with a saturated solution of $Na_2S_2O_3$ and extracted with ether. The organic layer was decanted and the aqueous layer extracted with ether. The combined extracts were washed with H_2O and dried over $MgSO_4$. Removal of the solvent under vacuum gave the desired iodotetrahydrofurans as a 83/17 mixture of two diastereoisomers (160 mg) which were separated using flash chromatography on silica gel (Petroleum ether/EtOAc 95/5) to afford the major isomer **7c** : ^{1}**H NMR** (δ ppm) : 7.51-7.48 (2H, m, Aromatic H), 7.41-7.35 (3H, m, Aromatic H), 4.01 (1H, dd, J 8.2, 8.3, H-5a), 3.97-3.90 (1H, m, H-2), 3.75 (1H, dd, J 8.2, 11.7, H-5b), 3.25 (1H, dd, J 4.8, 9.9, $C\underline{H}_aH_bI$), 3.18 (1H, dd, J 6.1, 9.9, $CH_a\underline{H}_bI$), 2.26 (1H, ddd, J 6.1, 6.3, 12.3, H-3a), 1.84-1.73 (1H, m, CHSi), 1.42 (1H, ddd, J 8.9, 12.3, 12.6, H-3b), 0.34 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$). **IR** (film, KBr)(υ_{max}) : 2950, 2850, 1420, 1250, 840, 600 cm^{-1}. **MS** (CI, NH_3): 346 (M+,0.2), 331 (3), 305 (10), 247 (23), 141 (48), 135 (100), 121 (12), 105 (27), 91 (13). **Anal.** Calcd for $C_{12}H_{19}OSiI$: C, 45.09; H, 5.53; I, 36.65; Si, 8.11. Found : C, 44.98; H, 5.41; I, 36.69; Si, 8.10.

7f. ^{1}**H NMR** (δ ppm) : 7.06 (1H, d, J 3.3, Aromatic H), 6.86-6.84 (1H, m, Aromatic H), 4.1 (1H, dd, J 8.0, 8.3, H-5a), 3.99-3.93 (1H, m, H-2), 3.77 (1H, dd, J 8.2, 11.6, H-5a), 3.26 (1H, dd, J 5.0, 9.9, $C\underline{H}_aH_bI$), 3.18 (1H, dd, J 6.64, 9.83, $CH_a\underline{H}_bI$), 2.54 (3H, d, J 0.9, CH_3 thio), 2.32-2.26 (1H, m, H-3a), 1.81-1.71 (1H, m, CHSi), 1.44 (1H, ddd, J 8.9, 12.5, 12.6, H-3b), 0.34 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$). **IR** (film, KBr)(υ_{max}) : 3050, 2960, 2850, 1440, 1250, 1010, 800, 600 cm^{-1}. **MS** (CI, NH_3): 366 (M^+, 6), 325 (1.3), 267 (30), 155 (100), 141 (81), 115 (22), 75 (56). **Anal.** Calcd for $C_{12}H_{19}OSSiI$: C, 39.34; H, 5.23; I, 34.00; S, 8.75; Si, 7.67. Found : C, 39.40 ; H, 5.36; I, 33.99; S, 8.72 ; Si, 7.76.

General procedure for the *5-exo-trig* seleno-etherification of diols 6. To a suspension of alcohol **6f** (0.1 g, 0.41 mmol) and K_2CO_3 (57 mg, 0.410 mmol) in anhydrous ether (2.7 ml) was added at -80°C a solution of PhSeCl (75 mg, 0.39 mmol) in dry ether (1 ml). The resulting solution was stirred for 2.5h between -80°C and -60°C, then quenched with a saturated solution of $NaHCO_3$. The organic layer was decanted and the aqueous layer extracted with ether. The combined extracts were washed with H_2O and dried over $MgSO_4$. Removal of the solvent under vacuum gave the desired tetrahydrofuran as a 69/31 mixture of two diastereoisomers **7g** and **8g** (156 mg) which were separated using flash chromatography on silica gel (Petroleum ether/EtOAc 95/5). **7g** (101 mg, 64%) : ^{1}**H NMR** (δ ppm) : 7.54-7.51 (2H, m, Aromatic H), 7.29-7.24 (3H, m, Aromatic H), 7.05 (1H, d, J 3.3, H-3 thio), 6.86-6.85 (1H, m, H-4 thio), 4.13-4.07 (1H, m, H-2 thio), 4.05 (1H, dd, J 8.4, 8.4, H-5a), 3.75 (1H, dd, J 8.3, 11.2, H-5b), 3.15 (1H, dd, J 5.6, 12.1, $C\underline{H}_aH_bSe$), 2.97 (1H, dd, J 6.9, 12.1, $CH_a\underline{H}_bSe$), 2.55 (3H, d, J 0.5, CH_3 thio), 2.23 (1H, ddd, J 5.5, 6.9, 12.1, H-3a), 1.71 (1H, dddd, J 7.1, 8.5, 11.2, 12.6, H-4), 1.45 (1H, ddd, J 9.1, 12.4, 12.4, H-3b), 0.32 (6H, s, $Si(CH_3)_2$). ^{13}**C NMR** (δ ppm) : 146.0 (s, C thio), 135.2 (d, J 165, C thio), 134.5 (s, C thio), 132.5 (d, J 161, Aromatic C), 130.3 (s, Aromatic C), 129.0 (d, J 128, Aromatic C), 126.9 (d, J 165, Aromatic C), 126.8 (d, J 159, Aromatic C), 79.3 (d, J 149, C-2), 70.4 (t, J 141, C-5), 35.2 (t, J 131, $\underline{C}H_2SePh$), 32.8 (t, J 138, C-3), 28.5 (d, J 120, C-4), 15.0 (q, J 128, CH_3 thio), -3.2 (q, J 120, $SiCH_3$), -3.3 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 2920 (C-H), 2860 (C-H), 1580, 1475, 1440, 1250 (Si-C), 900 cm^{-1}. **MS** (CI, NH_3) : 396 ($M^{+\cdot}+1$, 15), 299 (8), 155 (100), 141 (27), 75 ($Si(CH_3)_2OH^{+\cdot}$, 62). **Anal.** Calcd for $C_{18}H_{24}OSSeSi$: C, 54.67; H, 6.12; S, 8.11; Se, 19.95; Si, 7.10. Found : C, 54.87; H, 6.12; S, 8.21; Se, 19.97; Si, 7.23.

8g : ^{1}**H NMR** (δ ppm) : 7.55-7.52 (2H, m, Aromatic H), 7.29-7.24 (3H, m, Aromatic H), 7.05 (1H, d, J 3.3, H-3 thio), 6.86-6.85 (1H, m, H-4 thio), 4.16-4.10 (1H, m, H-2), 4.14 (1H, dd, J 8.2, 8.2, H-5a), 3.57 (1H, dd, J 8.4, 11.4, H-5b), 3.08 (1H, dd, J 5.6, 12.1, $C\underline{H}_aH_bSe$), 2.93 (1H, dd, J 7.5, 12.1, $CH_a\underline{H}_bSe$), 2.54 (3H, d, J 0.9, CH_3 thio), 1.95-1.91 (2H, m, H-3), 1.73-1.65 (1H, m, H-4), 0.32 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$). ^{13}**C NMR** (δ ppm) : 146.0 (s, C thio), 135.2 (d, J 164, C thio), 134.4 (s, C thio), 132.5 (d, J 161, Aromatic C), 130.2 (s, Aromatic C), 129.0 (d, J 159, Aromatic C), 126.9 (d, J 162, Aromatic C), 126.8 (d, J 159, Aromatic C), 78.2 (d, J 157, C-2), 71.0 (t, J 149, C-5), 33.3 (t, J 130, $\underline{C}H_2SePh$), 33.1 (t, J 142, C-3), 26.2 (d, J 120, C-4), 15.0 (q, J 128, CH_3 thio), -3.0 (q, J 120, $SiCH_3$), -3.2 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 2920 (C-H), 2860 (C-H), 1580, 1470, 1440, 1250 (Si-C), 910 cm^{-1}. **MS** (CI, NH_3) : 396 ($M^{+\cdot}+1$, 3), 239 ($M^{+\cdot}$-SePh, 22), 155 (100), 141 (42), 75 ($Si(C\underline{H}_3)_2OH^{+\cdot}$,50). **Anal.** Calcd for $C_{18}H_{24}OSSeSi$: C, 54.67; H, 6.12; S, 8.11; Se, 19.95; Si, 7.10. Found : C, 54.60; H, 6.03; S, 8.11; Se, 19.59; Si, 6.98.

General procedure for the reduction of organomercuri-tetrahydrofuran. $NaBH_4$ (13 mg, 0.334 mmol) in a 2.5 $\underline{M}$ solution of NaOH (2 ml) was added dropwise at 0°C over a period of 30 minutes to a vigorously stirred solution of the mercurial **7e** (304 mg, 0.58 mmol) in a mixture of 0.5$\underline{M}$ NaOH solution (4 ml) and THF (4 ml). The reaction mixture was stirred at 0°C for 1h then powdered NaCl was added and the aqueous layer was extracted 3 times with ether. The combined extracts were washed with brine, dried over $MgSO_4$ and the solvent was removed under vacuum to give an oil (170 mg) which was purified by flash chromatography (Petroleum ether/EtOAc 94:6) to give **9** (0.12 g, 85%). ^{1}**H NMR** (δ ppm) : 7.07 (1H, d, J 3.2, H-3 thio), 6.86-6.85 (1H, m, H-4 thio), 4.13-4.07 (1H, m, H-2), 4.00 (1H, dd, J 8.5, 8.5, H-5a), 4.01-3.88 (1H, m, H-2), 3.75 (1H, dd, J 8.2, 10.5, H-5b), 2.54 (3H, s, CH_3 thio), 2.12 (1H, ddd, J 5.1, 7.1, 12.1, H-3a), 1.71 (1H, dddd, J 7.2, 8.9, 10.4, 12.5, H-4), 1.29 (1H, ddd, J 9.5, 12.2, 12.2, H-3b), 1.24 (3H, d, J 6.0, CH_3), 0.32 (6H, s,

$Si(CH_3)_2$). ^{13}C **NMR** (δ ppm) : 145.8 (s, C thio), 135.0 (d, J 165, C thio), 134.8 (s, C thio), 126.8 (d, J 164, C thio), 76.3 (d, J 143, C-2), 69.6 (t, J 145, C-5), 36.7 (t, J 130, C-3), 28.2 (d, J 120, C-4), 20.5 (q, J 126, CH_3), 15.0 (q, J 129, CH_3 thio), -3.2 (q, J 120, $SiCH_3$), -3.4 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 2920 (C-H), 1250 (Si-C), 1210, 1000, 910 cm^{-1}. **MS** (CI, NH_3) : 240 ($M^{+\cdot}$, 3), 155 (47), 105 (46), 71 (61), 57 (100). **Anal.** Calcd for $C_{12}H_{20}OSSi$: C, 59.95; H, 8.38; S, 13.33; Si, 11.68. **Found** : C, 59.83; H, 8.48; S, 13.34; Si, 11.72.

General procedure for the reduction of iodotetrahydrofuran. To a solution of iodide **7f** (90 mg, 0.24 mmol) in dry benzene (3 ml) was added Bu_3SnH (86 mg, 0.29 mmol) and AIBN (4 mg, 0.025 mmol). The mixture was refluxed for 2h and the solvent evaporated *in vacuo* to give an oil (155 mg) which was purified by flash chromatography (Petroleum ether/EtOAc 93:7) affording the tetrahydrofuran **9** (27 mg, 60%), identical with that prepared above.

General procedure for the reduction of phenylselenotetrahydrofuran. To a solution of **7g** (20 mg, 0.13 mmol) in dry benzene (2 ml) was added Bu_3SnH (40 mg, 0.138 mmol) and AIBN (2 mg, 0.013 mmol). The mixture was refluxed for 4h and the solvent evaporated *in vacuo* to give an oil which was purified by flash chromatography (Petroleum ether/EtOAc 94:6) affording the tetrahydrofuran **9** (10 mg, 85%), identical with that prepared above.

11a. To a suspension of alcohol **6c** (0.24 g, 1.024 mmol) and $CaCO_3$ (0.225 g, 2.25 mmol) in dry THF (10 ml) was added at room temperature $Hg(OAc)_2$ (0.39 g, 1.23 mmol). The resulting heterogeneous solution was stirred for 10h at room temperature, then quenched with a saturated solution of KBr. The mixture was stirred for 1h then decanted and the aqueous layer was extracted with ether. The combined extracts were washed with a saturated solution of KBr, then H_2O and dried over $MgSO_4$. Removal of the solvent under vacuum afforded a 88:4:8 mixture of the diastereoisomers **11a**, **11b** and a third unidentified one as a colourless oil (525 mg), which was purified using flash chromatography (Petroleum ether/EtOAc 92:8). This gave as major product **11a** (0.378 g, 72%). ^1H **NMR** (δ ppm) : 7.54-7.46 (2H, m, Aromatic H), 7.43-7.33 (3H, m, Aromatic H), 4.19 (1H, ddd, J 5.1, 5.1, 9.8, H-2), 4.04 (1H, dd, J 8.6, 8.6, H-5a), 3.76 (1H, dd, J 8.4, 10.8, H-5b), 3.06 (1H, dq, J 5.5, 7.5, CHHgBr), 2.30 (1H, ddd, J 4.9, 6.8, 11.9, H-3a), 1.77 (1H, dddd, J 6.9, 8.9, 10.7, 12.6, H-4), 1.41 (3H, d, J 7.5, CH_3), 1.28 (1H, ddd, J 9.5, 12.4, 12.4, H-3b), 0.35 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$). ^{13}C **NMR** (δ ppm) : 137.0 (s, Aromatic C), 133.6 (d, J 155, Aromatic C), 129.4 (d, J 161, Aromatic C), 128.0 (d, J 157, Aromatic C), 84.3 (d, J 147, C-2), 70.1 (t, J 147, C-5), 57.7 (d, J 137, CHHgBr), 38.1 (t, J 132, C-3), 27.2 (d, J 121, C-4), 17.1 (q, J 127, CH_3), -4.5 (2C, q, J 120, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2910 (C-H), 2860 (C-H), 1375, 1100, 870 cm^{-1}. MS (EI) : 432 (4), 233 ($M^{+\cdot}$-HgBr, 15), 205 ($M^{+\cdot}$-$CHHgBrCH_3$, 20), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 75 ($Si(CH_3)_2OH^{+\cdot}$, 37).

11c. Following the same procedure than above, **6d** was converted into a 91:9 mixture of two diastereoisomers **11c** and **11d**, which after purification using flash chromatography (Petroleum ether/EtOAc 98:2) gave **11c** as a colourless oil (69%). ^1H **NMR** (δ ppm) : 7.51-7.46 (2H, m, Aromatic H), 7.42-7.36 (3H, m, Aromatic H), 4.07-4.02 (1H, m, H-2), 4.00 (1H, dd, J 8.6, 8.6, H-5a), 3.73 (1H, dd, J 8.4, 10.6, H-5b), 2.68 (1H, dq, J 6.4, 7.4, CHHgBr), 2.20 (1H, ddd, J 5.0, 6.9, 12.0, H-3a), 1.78 (1H, dddd, J 7.2, 8.7, 10.4, 12.4, H-4), 1.46 (3H, d, J 7.5, CH_3), 1.24 (1H, ddd, J 9.3, 12.2, 12.2, H-3b), 0.32 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$). ^{13}C **NMR** (δ ppm) : 137.1 (s, Aromatic C), 133.6 (d, J 161, Aromatic C), 129.3 (d, J 159, Aromatic C), 128.0 (d, J 164, Aromatic C), 85.2 (d, J 146, C-2), 69.6 (t, J 147, C-5), 57.6 (d, J 146, CHHgBr), 36.8 (t, J 130, C-3), 27.7 (d, J 121, C-4), 18.6 (q, J 127, CH_3), -4.5 (q, 2C, J 120, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2920 (C-H), 1430, 1250 (Si-C), 1110, 1080, 1020, 840, 810 cm^{-1}. **MS** (CI, NH_3): 233 ($M^{+\cdot}$-HgBr, 5), 137 ($PhSiCH_3OH^{+\cdot}$, 33), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 75 ($Si(CH_3)_2OH^{+\cdot}$, 26). **Anal.** Calcd for $C_{14}H_{21}BrHgOSi$: C, 32.72; H, 4.12; Si, 5.47. Found : C, 32.91; H, 4.27; Si: 5.47.

12. Following the general procedure, **12** was obtained from **11a** as a colourless oil (80%) after purification using flash chromatography (Petroleum ether/EtOAc 95:5). ^1H **NMR** (δ ppm) : 7.53-7.48 (2H, m, Aromatic H), 7.41-7.35 (3H, m, Aromatic H), 3.99 (1H, dd, J 8.4, 8.4, H-5a), 3.73 (1H, dddd, J 5.2, 6.3, 6.3, 9.4, H-2), 3.68 (1H, dd, J 8.2, 10.9, H-5b), 2.08 (1H, ddd, J 5.2, 6.9, 12.0, H-3a), 1.71 (1H, dddd, J 7.0, 8.8, 10.8, 12.5, H-4), 1.70-1.36 (2H, m, $C\underline{H}_2CH_3$), 1.27 (1H, ddd, J 9.4, 12.3, 12.3, H-3b), 0.92 (3H, d, J 7.4, CH_3), 0.31 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$). **IR** (film)(υ_{max}) : 2980 (C-H), 2930 (C-H), 2870 (C-H), 1420, 1250 (Si-C), 1110, 900, 810 cm^{-1}. **MS** (EI) : 235 ($M^{+\cdot}$+1, 10), 169 (29), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 75 ($Si(CH_3)_2OH^{+\cdot}$, 49).

(*E*)-Ethyl-5,9-Dimethyl-2-(dimethylphenylsilyl)deca-4,8-dienoate 13. Following the general procedure, 13 was obtained from **4b** and geranyl bromide as a colourless oil (95%) after purification using flash chromatography (Petroleum ether/EtOAc 95:5). ^1H **NMR** (δ ppm) : 7.56-7.51 (2H, m, Aromatic H), 7.41-7.35 (3H, m, Aromatic H), 5.10-5.03 (2H, m, 2 x vinylic H), 4.05 (1H, dq, J 7.1, 10.9, $C\underline{H}_aH_bCH_3$), 3.99 (1H, dq, J 7.2, 10.9, $CH_a\underline{H}_bCH_3$), 2.54-2.41 (1H, m, $SiCHC\underline{H}_aH_b$), 2.21 (1H, dd, J 3.7, 10.7, SiCH), 2.15-1.90 (5H, m, Aliphatic H), 1.68 (3H, d, J 1.0, CH_3), 1.59 (3H, d, J 0.7, CH_3), 1.52 (3H, d, J 1.1, CH_3), 1.14 (3H, t, J 7.1, $CH_2C\underline{H}_3$), 0.41 (3H, s, $SiCH_3$), 0.39 (3H, s, $SiCH_3$). **IR** ($CHCl_3$) (υ_{max}) : 2880 (C-H), 2780 (C-H), 1720(C=O), 1250 (Si-C), 810, 735 cm^{-1}. **MS** (CI, NH_3) : 359 ($M^{+\cdot}$, 3), 358 ($M^{+\cdot}$-1, 5), 261 (50), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 103 (50), 81 (84). **Anal.** Calcd for $C_{22}H_{34}O_2Si$: C, 73.69; H, 9.56; Si, 7.83. Found : C, 73.51; H, 9.44; Si, 7.79.

(*E*)-5,9-Dimethyl-2-(dimethylphenylsilyl)dec-4,8-dienol 14. Following the general procedure, **14** was obtained from **13** as a colourless oil (87%) after purification using flash chromatography (Petroleum ether/EtOAc/NEt_3, 94.5:5:0.5). **^{1}H NMR** (δ ppm) : 7.57-7.51 (2H, m, Aromatic H), 7.40-7.35 (3H, m, Aromatic H), 5.24-5.06 (2H, m, 2 x vinylic H), 3.82-3.65 (2H, m, $C\underline{H}_2OH$), 2.23-2.17 (2H, m, $SiCHC\underline{H}_2$), 2.10-1.95 (4H, m, Aliphatic H), 1.70 (3H, d, J 1.0, CH_3) 1.62 (3H, d, J 0.5, CH_3), 1.60 (3H, d, J 0.6, CH_3), 1.52 (3H, d, J 1.1, CH_3), 1.14 (3H, t, J 7.1, $CH_2C\underline{H}_3$), 1.31-1.19 (1H, m, SiCH) 0.35 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3500 (O-H),2820 (C-H), 1350, 1250 (Si-C), 1070, 930, 840, 700 cm^{-1}. **MS** (CI, NH_3) : 298 (3), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 95 (37), 75 ($PhSi(CH_3)_2OH^{+\cdot}$). **Anal.** Calcd for $C_{20}H_{32}OSi$: C, 75.88; H, 10.19; Si, 8.87. Found : C, 75.82; H, 10.29; Si, 8.95.

15a. Following the general procedure, **14** was converted into a mixture of the tetrahydrofurans **15a** and **15b** and the addition product **15c** (Table 2). **15a** and **15c** were obtained in pure form after chromatography (Petroleum ether/EtOAc 98:2). **15a** : **^{1}H NMR** (δ ppm) : 7.52-7.48 (2H, m, Aromatic H), 7.42-7.37 (3H, m, Aromatic H), 5.13-5.07 (1H, m, vinylic H), 4.03 (1H, dd, J 8.5, 8.5, H-5a), 3.82 (1H, dd, J 5.0, 9.6, H-2), 3.74 (1H, dd, J 8.4, 10.9, H-5b), 2.24-2.13 (3H, m, H-3a + Allylic H), 1.95-1.67 (3H, m, H-4 + Aliphatic H), 1.84 (3H, s, CH_3), 1.64 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.38 (1H, ddd, J 9.6, 12.3, 12.3, H-3b), 0.33 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2920 (C-H), 2860 (C-H), 1380, 1100, 870 cm^{-1}. **MS** (EI) : 596 ($M^{+\cdot}$,4), 315 ($M^{+\cdot}$-HgBr, 22), 245 (17), 210 (21), 169 (24), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 82 (33). **Anal.** Calcd for $C_{20}H_{31}BrHgOSi$: C, 40.30; H, 5.24; Si, 4.71. Found : C, 40.40; H, 5.32; Si, 4.81. **15c** : **^{1}H NMR** (δ ppm) : 7.50-7.46 (2H, m, Aromatic H), 7.41-7.37 (3H, m, Aromatic H), 5.12-5.06 (1H, m, vinylic H), 3.67 (2H, d, J 9.1, $C\underline{H}_2OH$), 2.86 (1H, dd, J 4.2, 12.9, CHHgBr), 2.20-1.94 (4H, m, Aliphatic H), 1.69 (3H, s, CH_3), 1.62 (3H, s, CH_3), 1.58-1.52 (2H, m, Allylic H), 1.40-1.30 (1H, m, SiCH), 1.32 (3H, s, CH_3), 0.31 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$). **^{13}C NMR** (δ ppm) : 136.5 (s, Aromatic C), 133.7 (d, J 157, Aromatic C), 132.1 (s, $CH{:}\underline{C}$), 129.3 (d, J 160, Aromatic C), 127.9 (d, J 159, Aromatic C), 124.4 (d, J 155, $\underline{C}H{:}C$), 75.8 (s, $\underline{C}(CH_3)_2OH$), 66.9 (d, J 133, CHHgBr), 62.9 (t, J 142, CH_2OH), 47.0 (t, J 130, Allylic CH_2), 30.5 (d, J 120, SiCH), 28.6 (t, J 127, Allylic CH_2), 25.7 (q, J 122, CH_3), 23.2 (q, J 125, CH_3), 21.5 (t, J 124, $\underline{C}H_2CHHgBr$), 17.8 (q, J 122, CH_3), -4.9 (q, J 119, $SiCH_3$), -5.1 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3600 (O-H), 2960 (C-H), 2920 (C-H), 2880 (C-H), 1440, 1380, 1250 (Si-C), 1110, 840 cm^{-1}. **MS** (EI): 613 ($M^{+\cdot}$-1, 1), 596 ($M^{+\cdot}$-OH, 2), 512 (4), 403 (5), 316 (20), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 75 (77).

(*E*)-Hept-5-en-2-yn-1-ol 17.[20a] To a suspension of K_2CO_3 (17.4 g, 0.126 mol), propargyl alcohol **16** (5.5 ml, 92 mmol), n-Bu_4NCl (2.33 g, 8.4 mmol) and Cu(I)I (0.8 g, 4.19 mmol) in dry THF (140 ml) was added dropwise at room temperature, (*E*)-crotyl chloride (8.17 ml, 83 mmol). The deep yellow mixture was stirred at room temperature for 20h then diluted with ether (100 ml) and filtered through celite. The filtrate was washed with brine, dried over $MgSO_4$ and the solvents were carefully evaporated under vacuum to give a residue which was purified through distillation (60°C, 60 mmHg) affording **17**[20a] as a colourless liquid (4.8 g, 52%).

(*E,E*)-1-Bromohepta-2,5-diene 18b.[20b-c] To a suspension of $LiAlH_4$ (0.734 g, 19.33 mmol) in anhydrous THF (15 ml) was added at 0°C, a solution of **17** (1.42 g, 12.9 mmol) in dry THF (20 ml). The mixture was heated under reflux for 5h then quenched at 0°C with a 1$\underline{M}$ HCl solution. The organic layer was decanted and the aqueous layer extracted 3 times with ether. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and the solvent was evaporated under vacuum. The residue was purified by distillation (100°C, 18 mmHg) affording **18a** (1.32 g, 91%), used in the next step without further purification. To a solution of NBS (3.14 g, 17.65 mmol) in dry CH_2Cl_2 (50 ml) was added very slowly at 0°C, dimethylsulfide (1.6 ml, 21.2 mmol). Then, a solution of the alcohol **18a** (1.32 g, 11.77 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise at -20°C. The mixture was stirred at 0°C for 2.5h then hydrolyzed with a saturated solution of $NaHCO_3$. The organic layer was decanted and the aqueous layer was extracted 3 times with CH_2Cl_2. The combined extracts were washed with a 1$\underline{M}$ HCl solution, brine, dried over $MgSO_4$, filtered then the solvent was evaporated under vacuum. The residue was purified through distillation (90°C, 12 mmHg) affording **18b**[20b-c] (1.6 g, 78%).

(*Z,E*)-1-Bromohepta-2,5-diene 19b.[20a] In a two-necked round bottom flask equipped with an inlet for vacuum and an inlet for hydrogen, was placed Lindlar catalyst (480 mg). The air was removed under vacuum and the apparatus was flushed 3 times with hydrogen, then THF (30 ml) was added. The suspension was flushed again 3 times and a solution of the alkyne **17** (4.8 g, 43.6 mmol) in THF (5 ml) was added. The mixture was stirred under an atmosphere of hydrogen for 20h at room temperature and the solvent was evaporated. The residue was distilled (100°C, 12 mmHg) to afford the alcohol **19a** (3.8 g, 78%) as a colourless oil, used in the next step without further purification. **19a** was converted into the bromide **19b**[20a] (80%) following the procedure described above for **18b**.

(*E,E*)-Ethyl-2-(dimethylphenylsilyl)nona-4,7-dienoate 20a. Following the general procedure, **20a** was obtained from **4b** and the bromide **18b** as a colourless oil (85%) after purification using flash chromatography (Petroleum ether/EtOAc 95:5). **^{1}H NMR** (δ ppm) : 7.54-7.47 (2H, m, Aromatic H), 7.42-7.34 (3H, m, Aromatic H), 5.39-5.33 (4H, m, 4 x vinylic H), 4.05 (1H, dq, J 7.1, 10.8, $C\underline{H}_aH_bCH_3$), 3.99 (1H, dq, J 7.1, 10.7, $CH_a\underline{H}_bCH_3$), 2.63-2.58 (2H, m, Allylic H) 2.50-2.41 (1H, m, $SiCHC\underline{H}_aH_b$), 2.26 (1H, dd, J 3.1, 11.4, SiCH), 2.13-2.02 (1H, m, $SiCHCH_a\underline{H}_b$), 1.65-1.62 (3H, m, $CH{:}CHC\underline{H}_3$), 1.14 (3H, t, J 7.1, $CH_2C\underline{H}_3$), 0.39 (3H, s, $SiCH_3$), 0.38 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2880 (C-H), 1700 (C=O), 1390, 1250 (Si-C), 1150, 1110, 965, 870 cm^{-1}. **MS** (CI, NH_3) : 317 ($M^{+\cdot}$, 6), 256 (17), 239 (100), 135 ($PhSi(CH_3)_2^{+\cdot}$, 36), 94 (60). **Anal.** Calcd for $C_{19}H_{28}O_2Si$: C, 72.10; H, 8.92; Si, 8.87. Found : C, 72.14; H, 9.09; Si, 8.83.

(*Z,E*)-Ethyl-2-(dimethylphenylsilyl)nona-4,7-dienoate 20b. Following the general procedure, **20a** was obtained from **4b** and the bromide **19b** as a colourless oil (86%) after purification using flash chromatography (Petroleum ether/EtOAc 95:5). **^{1}H NMR** (δ ppm) : 7.54-7.49 (2H, m, Aromatic H), 7.41-7.35 (3H, m, Aromatic H), 5.40-5.35 (4H, m, 4 x Vinylic H), 4.04 (1H, dq, J 7.1, 10.7, $C\underline{H}_aH_bCH_3$), 3.99 (1H, dq, J 7.1, 10.7, $CH_a\underline{H}_bCH_3$), 2.65-2.60 (2H, m, Allylic H), 2.57-2.44 (1H, m, $SiCHC\underline{H}_aH_b$), 2.20 (1H, dd, J 3.3, 11.0, SiCH), 2.20-2.07 (1H, m, $SiCHCH_a\underline{H}_b$), 1.64-1.62 (3H, m, $CH{:}CHC\underline{H}_3$), 1.13 (3H, t, J 7.1, $CH_2C\underline{H}_3$), 0.40 (3H, s, $SiCH_3$), 0.39 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2880 (C-H), 1705 (C=O), 1430, 1365, 1330, 1250 (Si-C), 1150, 1110, 970, 840 cm^{-1}. **MS** (CI, NH_3) : 315 ($M^{+\cdot}$-2, 3), 288 (6), 212 (13), 135 ($PhSi(CH_3)_2^{+\cdot}$, 27), 107 (25), 94 (100). **Anal.** Calcd for $C_{19}H_{28}O_2Si$: C, 72.10; H, 8.92; Si, 8.87. Found : C, 72.07; H, 8.84; Si, 8.91.

(*Z,E*)-Ethyl-2-[dimethyl-(5-methylthien-2-yl)silyl]nona-4,7-dienoate 20c. Following the general procedure, **20a** was obtained from **4d** and the bromide **19b** as a colourless oil (50%) after purification using flash chromatography (Petroleum ether/EtOAc 95:5). **^{1}H NMR** (δ ppm) : 7.10 (1H, d, J 3.2, H-3 thio), 6.86-6.84 (1H, m, H-4 thio), 5.41-5.32 (4H, m, vinylic H), 4.07 (2H, q, J 7.1, $CO_2C\underline{H}_2CH_3$), 2.70-2.65 (2H, m, Allylic H), 2.59-2.46 (1H, m, $C\underline{H}_aH_bCH{:}CH_2$), 2.54 (3H, d, J 0.8, CH_3 thio), 2.22-2.14 (1H, m, $CH_a\underline{H}_bCH{:}CH_2$), 2.18 (1H, dd, J 3.3, 11.9, SiCH), 1.65-1.63 (3H, m, $CH{:}CHC\underline{H}_3$), 1.20 (3H, t, J 7.1, $CO_2CH_2C\underline{H}_3$), 0.40 (3H, s, $SiCH_3$), 0.39 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2920 (C-H), 1705 (C=O), 1440, 1370, 1330, 1250 (Si-C), 1150, 1000, 910, 810 cm^{-1}. **MS** (CI, NH_3) : 337 ($M^{+\cdot}$+1, 3), 235 ($M^{+\cdot}$- (35), 199 (19), 183 (27), 155 (100), 137 (24), 103 (42), 94 (70), 79 (68), 75 ($Si(CH_3)_2OH^{+\cdot}$, 79). **Anal.** Calcd for $C_{18}H_{28}O_2SSi$: C, 64.24; H, 8.39. Found : C, 64.49; H, 8.22.

(*E,E*)-2-(dimethylphenylsilyl)nona-4,7-dienol 21a. Following the general procedure, **21a** was obtained as a colourless oil (75%) after purification using flash chromatography on silica gel (Petroleum ether/EtOAc/NEt_3 98.5:1:0.5). **^{1}H NMR** (δ ppm) : 7.55-7.50 (2H, m, Aromatic H), 7.39-7.35 (3H, m, Aromatic H), 5.47-5.38 (4H, m, 4 x Vinylic H), 3.79 (1H, dd, J 4.2, 10.9, $C\underline{H}_aCH_bOH$), 3.68 (1H, dd, J 7.5, 10.9, $CH_aC\underline{H}_bOH$), 2.66-2.64 (2H, m, Allylic H), 2.33-2.06 (2H, m, $SiCHC\underline{H}_2$), 1.66 (3H, d, J 4.6, $CH{:}CHC\underline{H}_3$), 1.30-1.18 (1H, m, SiCH), 0.33 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2880 (C-H), 1380, 1250 (Si-C), 1110, 960, 810 cm^{-1}. **MS** (EI) : 274 ($M^{+\cdot}$, 8), 257 ($M^{+\cdot}$-OH, 30), 152 (34), 137 ($PhSiCH_3OH^{+\cdot}$, 48), 135 ($PhSi(CH_3)_2^{+\cdot}$, 95), 81 (100). **Anal.** Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55; Si, 10.23. Found : C, 74.42; H, 9.09; Si, 10.26.

(*Z,E*)-2-(dimethylphenylsilyl)nona-4,7-dienol 21b. As above, **21b** was obtained as a colourless oil (76%). **^{1}H NMR** (δ ppm) : 7.55-7.51 (2H, m, Aromatic H), 7.39-7.35 (3H, m, Aromatic H), 5.48-5.39 (4H, m, 4 x Vinylic H), 3.83-3.64 (2H, m, $C\underline{H}_2OH$), 2.74-2.69 (2H, m, Allylic H), 2.25-2.20 (2H, m, $SiCHC\underline{H}_2$), 1.66-1.64 (3H, m, $CH{:}CHC\underline{H}_3$), 1.22-1.18 (1H, m, SiCH), 0.33 (6H, s, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 1250 (Si-C), 1110, 970, 810 cm^{-1}. **MS** (CI, NH_3) : 158 (38), 137 ($PhSiCH_3OH^{+\cdot}$, 83), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 93 (60), 81 (86), 80 (72), 79 (45). **Anal.** Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55; Si, 10.23. Found : C, 74.27; H, 9.69; Si, 10.23.

(*Z,E*)-2-[dimethyl-(5-methylthien-2-yl)silyl]nona-4,7-dienol 21c. As above, **21c** was obtained as a colourless oil (74%). **^{1}H NMR** (δ ppm) : 7.09 (1H, d, J 3.3, H-3 thio), 6.86-6.84 (1H, m, H-4 thio), 5.54-5.37 (4H, m, Vinylic H), 3.83-3.67 (2H, m, $C\underline{H}_2OH$), 2.77-2.72 (2H, m, Allylic H), 2.54 (3H, d, J 0.8, CH_3 thio), 2.29-2.24 (2H, m, Allylic H), 1.68-1.65 (3H, m, $CH{:}CHC\underline{H}_3$), 1.48 (1H, broad s, OH), 1.22-1.12 (1H, m, SiCH), 0.36 (3H, s, $SiCH_3$), 0.36 (3H, s, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 2860 (C-H), 1440, 1250 (Si-C), 1060, 960, 810 cm^{-1}. **MS** (CI, NH_3): 294 ($M^{+\cdot}$,1), 277 ($M^{+\cdot}$-OH, 1), 221 (2), 178 (8), 163 (13), 157 (42), 155 (31), 112 (6), 98 (10), 75 ($Si(CH_3)_2OH^{+\cdot}$, 100). **Anal.** Calcd for $C_{16}H_{26}OSSi$: C, 65.25; H, 8.90; Si, 9.54. Found : C, 65.14; H, 8.88; Si, 9.68.

22a. Following the general procedure, **21a** was converted into a 9:1 mixture of two tetrahydrofurans (82%). The major isomer **22a** was obtained pure after flash chromatography (Petroleum ether/EtOAc 95:5). **^{1}H NMR** (δ ppm) : 7.52-7.46 (2H, m, Aromatic H), 7.42-7.37 (3H, m, Aromatic H), 5.64-5.46 (2H, m, Vinylic H) 4.23 (1H, ddd, J 5.4, 5.4, 10.7, H-2), 4.02 (1H, dd, J 8.6, 8.6, H-5a), 3.74 (1H, dd, J 8.4, 10.7, H-5b), 3.10 (1H, ddd, J 5.5, 5.5, 11.0, CHHgBr), 2.63-2.52 (1H, m, Allylic H), 2.37-2.23 (2H, m, H-3a + Allylic H), 1.77 (1H, dddd, J 7.0, 8.9, 10.6, 12.7, H-4), 1.67 (3H, d, J 5.3, CH_3), 1.25 (1H, ddd, J 9.6, 12.3, 12.3, H-3b), 0.33 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$). **^{13}C NMR** (δ ppm) : 137.1 (s, Aromatic C), 133.6 (d, J 154, Aromatic C), 131.2 (d, J 159, Aromatic C), 129.9 (d, J 162, $\underline{C}H{:}CH$), 128.1 (d, J 154, Aromatic C), 127.6 (d, J 153, $CH{:}\underline{C}H$), 82.4 (d, J 147, C-2), 70.1 (t, J 146, C-5), 66.6 (d, J 138, CHHgBr), 38.4 (t, J 131, C-3), 34.7 (t, J 125, Allylic CH_2), 29.0 (d, J 121, C-4), 17.9 (q, J 127, Allylic CH_3), -4.5 (q, 2C, J 120, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 2920 (C-H), 2860 (C-H), 1430, 1250 (Si-C), 1110, 1000, 970, 840, 810 cm^{-1}. **MS** (CI, NH_3) : 273 ($M^{+\cdot}$-HgBr, 6), 205 (27), 135 ($PhSi(CH_3)_2^{+\cdot}$,100), 75 ($Si(CH_3)_2OH^{+\cdot}$, 25). **Anal.** Calcd for $C_{17}H_{25}BrHgOSi$: C, 36.86; H, 4.55; Si, 5.07. Found : C, 36.99; H, 4.56; Si, 5.22.

22b. Following the general procedure, **21b** was converted into a 9:1 mixture of two tetrahydrofurans (83%). The major isomer **22b** was obtained pure after chromatography (Petroleum ether/EtOAc 95:5). **^{1}H NMR** (δ ppm) : 7.51-7.45 (2H, m, Aromatic H), 7.43-7.34 (3H, m, Aromatic H), 5.63-5.47 (2H, m, Vinylic H), 4.13 (1H, ddd, J 5.3, 5.3, 9.3, H-2), 3.99 (1H, dd, J 8.6, 8.6, H-5a), 3.73 (1H, dd, J 8.4, 10.6, H-5b), 2.82 (1H, ddd, J 5.7, 5.7, 9.9, CHHgBr), 2.53-2.44 (2H, m, Allylic H), 2.18 (1H, ddd, J 5.1, 7.0, 12.1, H-3a), 1.77 (1H, dddd, J 7.0, 8.9, 10.5, 12.5, H-4), 1.67 (3H, d, J 5.0, CH_3), 1.24 (1H, ddd, J 9.4, 12.3, 12.3, H-3b), 0.32 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$). **^{13}C NMR** (δ ppm) : 137.2 (s, Aromatic C), 133.6 (d, J 159, Aromatic C), 131.4 (d, J 160, Aromatic C), 129.4 (d, J 161, $\underline{C}H{:}CH$), 128.1 (d, J 153, Aromatic C), 127.6 (d, J 153, $CH{:}\underline{C}H$), 83.1 (d, J 144, C-2), 69.6 (t, J 146, C-5), 66.7 (d, J 138, CHHgBr), 37.1 (t, J 130, C-3), 36.2 (t, J 124, Allylic CH_2), 27.7 (d, J 121, C-4), 17.9 (q, J 124, Allylic CH_3), -4.4 (2C, q, J 120, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2940 (C-H), 2860 (C-H), 1430, 1250 (Si-C), 1220, 1110, 970, 820 cm^{-1}. **MS** (CI, NH_3): 273 ($M^{+\cdot}$-HgBr, 16), 205 (64), 135 ($PhSi(CH_3)_2^{+\cdot}$,100), 75 ($Si(CH_3)_2OH^{+\cdot}$, 44). **Anal.** Calcd for $C_{17}H_{25}BrHgOSi$: C, 36.86; H, 4.55; Si, 5.07. Found : C, 36.99; H, 4.46; Si, 4.98.

22c. To a solution of alcohol **21c** (0.237 g, 0.80 mmol) in anhydrous THF (8 ml) was added at - 40°C, powdered NBS (0.172 g, 0.97 mmol). The mixture was stirred 3.5h at -30°C then quenched with a saturated solution of $Na_2S_2O_3$. The organic layer was decanted and the aqueous layer extracted 3 times with ether. The combined extracts were washed with brine, H_2O, then dried over $MgSO_4$, filtered and the solvents were evaporated *in vacuo* to afford the desired tetrahydrofuran as a 9:1 mixture (0.31 g, 100%). The major isomer **22c** was obtained as a colourless oil (0.198 g, 66%) after flash chromatography on Florisil® (Petroleum ether/EtOAc 95:5). **^{1}H NMR** (δ ppm) : 7.07 (1H, d, J 3.2, H thio), 6.87-6.84 (1H, m, H thio), 5.63-5.42 (2H, m, Vinylic H), 4.11-3.91 (3H, m, H-2 + CHBr + H-5a), 3.75 (1H, dd, J 8.2, 11.2, H-5b), 2.67-2.45 (2H, m, Allylic CH_2), 2.54 (3H, d, J 0.8, CH_3 thio), 2.13 (1H, ddd, J 6.2, 6.2, 11.5, H-3a), 1.82-1.59 (2H, m, H-4 + H-3b), 1.69 (3H, d, J 4.7, Allylic CH_3), 0.34 (3H, s, CH_3), 0.33 (3H, s, CH_3). **^{13}C NMR** (δ ppm) : 146.0 (s, C thio), 135.1 (d, J 165, C thio), 134.3 (s, C thio), 128.4 (d, J 153, $\underline{C}H{:}CH$), 127.4 (d, J 153, $CH{:}\underline{C}H$), 126.9 (d, J 164, C thio), 81.9 (d, J 148, C-2), 71.1 (t, J 147, C-5), 58.9 (d, J 151, CHBr), 38.5 (t, J 128, C-3), 32.8 (t, J 132, Allylic CH_2), 28.4 (d, J 123, C-4), 17.9 (q, J 124, Allylic CH_3), 15.1 (q, J 130, CH_3 thio), -3.2 (2C, q, J 120, $Si(CH_3)_2$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 2860 (C-H), 1440, 1250 (Si-C), 1070, 1000, 840, 810 cm^{-1}. **MS** (CI, NH_3) : 292 ($M^{+\cdot}$-Br, 1), 221 (14), 155 (100), 98 (34), 75 ($Si(CH_3)_2OH^{+\cdot}$, 68). **Anal.** Calcd for $C_{16}H_{25}BrOSSi$: C, 51.46; H, 6.75; Si, 7.52. Found : C, 51.47; H, 6.86; Si, 7.62.

4-[Dimethyl-(5-methylthien-2-yl)silyl]hept-6-en-3-one 23b. To a 1$\underline{M}$ solution of ethylmagnesium bromide in THF (14 ml, 14 mmol) was added dropwise at 0°C a solution of the ester **4d** (1 g, 3.5 mmol) in anhydrous THF (8 ml). The mixture was refluxed for 3h then hydrolyzed using wet ether. The resulting white precipitate was removed by filtration and the filtrate dried over $MgSO_4$. The solvent was evaporated under vacuum to give a yellow oil (0.97 g, 100%). Due to its relative unstability, the α-silylketone **23b** was used in the next step without further purification.

4-(Dimethylphenylsilyl)-hept-6-en-3-one 23a. As above **23a** was obtained as a yellow oil (100%) used in next step without further purification.

(*R,*S**)-4-[Dimethyl-(5-methylthien-2-yl)silyl]hept-6-en-3-ol 24b**. To a solution of $ZnCl_2$ (0.312 g, 2.25 mmol) in anhydrous THF (5 ml) was added at -70°C a solution of the ketone **23b** (0.6 g, 2.25 mmol) in dry THF (5 ml). A 1$\underline{M}$ solution of DIBAH in hexane (4.5 ml, 4.5 mmol) was then added very slowly at -100°C. The resulting mixture was stirred at -100°C for 1h then quenched with a saturated solution of NH_4Cl. The organic layer was decanted and the aqueous layer extracted with ether. The combined extracts were washed successively with brine, H_2O then dried over $MgSO_4$ and the solvents were evaporated *in vacuo* to give a colourless oil (532 mg). Purification using flash chromatography (Petroleum ether/EtOAc/NEt_3 96.5:3:0.5) afforded the alcohol **24b** as an oil (273 mg, 50% overall yield from **4d**). **^{1}H NMR** (δ ppm) : 7.08 (1H, d, J 3.3, H-3 thio), 6.84-6.82 (1H, m, H-4 thio), 5.88-5.72 (1H, m, $CH_2C\underline{H}{:}CH_2$), 5.07-4.96 (2H, m, $CH_2CH{:}C\underline{H}_2$), 3.71-3.68 (1H, m, $C\underline{H}OH$), 2.53 (3H, s, CH_3 thio), 2.32-2.25 (2H, m, $C\underline{H}_2CH{:}CH_2$), 1.63 (1H, broad s, OH), 1.56-1.42 (2H, m, $C\underline{H}_2CH_3$), 1.27 (1H, ddd, J 4.2, 7.2, 10.3, SiCH), 0.95 (3H, t, J 7.4, $CH_2C\underline{H}_3$), 0.41 (6H, s, $Si(CH_3)_2$). **^{13}C NMR** (δ ppm) : 145.6 (s, C thio), 139.5 (d, J 151, $CH_2\underline{C}H{:}CH_2$), 136.8 (s, C thio), 135.1 (d, J 164, C thio), 126.8 (d, J 163, C thio), 115.4 (t, J 156, $CH_2CH{:}\underline{C}H_2$), 75.3 (d, J 138, CHOH), 34.7 (d, J 116, SiCH), 32.2 (t, J 124, $\underline{C}H_2CH{:}CH_2$), 29.6 (t, J 124, $\underline{C}H_2CH_3$), 15.1 (q, J 128, CH_3 thio), 10.8 (q, J 124, $CH_2\underline{C}H_3$), -0.8 (q, J 120, $SiCH_3$), -1.2 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2920 (C-H), 2860 (C-H), 1705, 1440, 1250 (Si-C), 1000, 960, 915, 840 cm^{-1}. **MS** (CI, NH_3) : 268 ($M^{+\cdot}$, 6), 251 ($M^{+\cdot}$-OH, 46), 172 (80), 157 (98), 155 (57), 124 (39), 92 (58), 75 ($Si(CH_3)_2OH^{+\cdot}$, 100). **Anal.** Calcd for $C_{14}H_{24}OSSi$: C, 62.63; H, 9.01; S, 11.94; Si, 10.46. Found : C, 62.69; H, 9.19; S, 11.77; Si, 10.55.

(*R,*S**)-4-(Dimethylphenylsilyl)hept-6-en-3-ol 24a**. As above, **24a** was obtained as a colourless oil (50%, 2 steps from **4b**). **^{1}H NMR** (δ ppm) : 7.58-7.53 (3H, m, Aromatic H), 7.38-7.34 (2H, m, Aromatic H), 5.84-5.73 (1H, m, $CH_2C\underline{H}{:}CH_2$), 5.05-4.94 (2H, m, $CH_2CH{:}C\underline{H}_2$), 3.68-3.65 (1H, m, $C\underline{H}OH$), 2.28-2.21 (2H, m, $C\underline{H}_2CH{:}CH_2$), 1.51-1.38 (2H, m, $C\underline{H}_2CH_3$), 1.29 (1H, ddd, J 4.1, 6.7, 6.7, SiCH), 0.90 (3H, t, J 7.4, $CH_2C\underline{H}_3$), 0.38 (3H, s, $SiCH_3$), 0.38 (3H, s,

$SiCH_3$). ^{13}C **NMR** (δ ppm) : 139.6 (d, J 146, $CH_2\underline{C}H{:}CH_2$), 139.3 (s, Aromatic C), 134.0 (s, Aromatic C), 128.8 (d, J 161, Aromatic C), 127.8 (d, J 160, Aromatic C), 115.3 (t, J 154, $CH_2CH{:}\underline{C}H_2$), 75.5 (d, J 122, CHOH), 34.1 (d, J 117, SiCH), 32.0 (t, J 133, $\underline{C}H_2CH{:}CH_2$), 29.6 (t, J 124, $\underline{C}H_2CH_3$), 10.8 (q, J 128, $CH_2\underline{C}H_3$), -2.2 (q, J 120, $SiCH_3$), -2.5 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2920 (C-H), 2880 (C-H), 1250 (Si-C), 1110, 830, 810 cm^{-1}. **MS** (CI, NH_3) : 231 ($M^{+\cdot}$-OH, 18), 137 ($PhSi(CH_3)OH^{+\cdot}$, 100), 135 ($PhSi(CH_3)_2^{+\cdot}$, 59), 96 (57), 81 (70). **Anal.** Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74; Si, 11.30. Found : C, 72.23; H, 9.56; Si, 11.35.

25a and **26a**. As above **24a** was converted into a 92:8 mixture of tetrahydrofurans **25a** and **26a** (Flash chromatography, petroleum ether/EtOAc 9:1)(80%). Major **25a** : ^1H **NMR** (δ ppm) : 7.53-7.48 (2H, m, Aromatic H), 7.41-7.34 (3H, m, Aromatic H), 4.29 (1H, dddd, J 5.1, 5.1, 5.1, 15.1, H-2), 4.03 (1H, ddd, J 2.8, 8.2, 11.0, H-5), 2.45 (1H, dd, J 5.7, 11.6, $C\underline{H}_aH_bHgBr$), 2.26 (1H, dd, J 5.2, 11.6, $CH_a\underline{H}_bHgBr$), 2.10 (1H, ddd, J 4.9, 6.3, 11.9, H-3a), 1.91 (1H, ddd, J 6.3, 8.2, 13.4, H-4), 1.46-1.24 (3H, m, H-3b + $C\underline{H}_2CH_3$), 0.94 (3H, t, J 7.3, $CH_2C\underline{H}_3$), 0.37 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$). ^{13}C **NMR** (δ ppm) : 138.3 (s, Aromatic C), 133.6 (d, J 155, Aromatic C), 129.1 (d, J 160, Aromatic C), 127.9 (d, J 163, Aromatic C), 83.7 (d, J 146, C-2), 78.8 (d, J 145, C-5), 42.4 (t, J 137, $\underline{C}H_2HgBr$), 38.4 (t, J 130, C-3), 33.3 (d, J 115, C-4), 29.7 (t, J 125, $\underline{C}H_2CH_3$), 11.5 (q, J 127, $CH_2\underline{C}H_3$), -2.4 (q, J 120, $SiCH_3$), -3.0 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3000 (C-H), 2960 (C-H), 2920 (C-H), 1250 (Si-C), 880 cm^{-1}. **MS** (CI, NH_3) : 528 ($M^{+\cdot}$, 1), 499 (8), 201 (10), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 69 (44). **Anal.** Calcd for $C_{15}H_{23}BrHgOSi$: C, 34.13; H, 4.39; Br, 15.14; Si, 5.32. Found : C, 34.15; H, 4.49; Br, 15.13; Si, 5.48. Minor **26a** : ^1H **NMR** (δ ppm) : 7.53-7.49 (2H, m, Aromatic H), 7.40-7.36 (3H, m, Aromatic H), 4.48 (1H, dddd, J 3.6, 5.5, 5.5, 7.9, H-2), 4.13 (1H, ddd, J 3.7, 6.8, 10.5, H-5), 2.33 (1H, dd, J 5.2, 11.6, $C\underline{H}_aH_bHgBr$), 2.20 (1H, ddd, J 8.0, 12.2, 12.2, H-3a), 2.15 (1H, dd, J 6.0, 11.6, $CH_a\underline{H}_bHgBr$), 1.88 (1H, ddd, J 6.9, 8.5, 11.9, H-4), 1.53 (1H, ddd, J 3.7, 8.5, 12.4, H-3b), 1.33-1.22 (2H, m, $C\underline{H}_2CH_3$), 0.88 (3H, t, J 7.2, $CH_2C\underline{H}_3$), 0.36 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$). ^{13}C **NMR** (δ ppm) : 138.2 (s, Aromatic C), 133.6 (d, J 155, Aromatic C), 129.1 (d, J 159, Aromatic C), 127.9 (d, J 158, Aromatic C), 84.2 (d, J 146, C-2), 75.2 (d, J 149, C-5), 43.8 (t, J 137, CH_2HgBr), 36.3 (t, J 131, C-3), 31.2 (d, J 116, C-4), 26.3 (t, J 123, $\underline{C}H_2CH_3$), 11.1 (q, J 125, $CH_2\underline{C}H_3$), -2.8 (q, J 120, $SiCH_3$), -3.0 (q, J 120, $SiCH_3$). **MS** (CI, NH_3) : 499 (4), 498 (5), 169 (13), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 75 ($PhSi(CH_3)_2OH^{+\cdot}$, 65). **Anal.** Calcd for $C_{15}H_{23}BrHgOSi$: C, 34.13; H, 4.39; Br, 15.14; Si, 5.32. Found : C, 34.15; H, 4.49; Br, 15.13; Si, 5.48.

25b. Following the general procedure, **24b** was converted into a 95:5 mixture of two diastereoisomers (0.52 g, 91%). Flash chromatography (Petroleum ether/EtOAc 85:15) gave the major tetrahydrofuran **25b** as an oil : ^1H **NMR** (δ ppm) : 7.05 (1H, d, J 3.3, H-3 thio), 6.85-6.84 (1H, m, H-4 thio), 4.31 (1H, dddd, J 5.1, 5.1, 5.1, 15.1, H-2), 4.05 (1H, ddd, J 2.6, 8.3, 11.0, H-5), 2.54 (3H, s, CH_3 thio), 2.46 (1H, dd, J 5.7, 11.8, $C\underline{H}_aH_bHgBr$), 2.27 (1H, dd, J 5.1, 11.8, $CH_a\underline{H}_bHgBr$), 2.15 (1H, ddd, J 4.9, 6.4, 11.8, H-3a), 1.87 (1H, ddd, J 6.4, 8.2, 13.3, H-4), 1.50-1.22 (3H, m, H-3b + $C\underline{H}_2CH_3$), 0.97 (3H, t, J 7.3, $CH_2C\underline{H}_3$), 0.36 (3H, s, $SiCH_3$), 0.35 (3H, s, $SiCH_3$). ^{13}C **NMR** (δ ppm) : 145.9 (s, C thio), 135.6 (s, C thio), 135.0 (d, J 165, C thio), 126.9 (d, J 164, C thio), 83.7 (d, J 146, C-2), 78.8 (d, J 146, C-5), 42.3 (t, J 138, CH_2HgBr), 38.5 (t, J 135, C-3), 34.0 (d, J 116, C-4), 29.7 (t, J 126, $\underline{C}H_2CH_3$), 15.1 (q, J 128, CH_3 thio), 11.5 (q, J 123, $CH_2\underline{C}H_3$), -1.4 (q, J 120, $SiCH_3$), -1.5 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2920 (C-H), 2850 (C-H), 1440, 1250 (Si-C), 1080, 830 cm^{-1}. **MS** (CI, NH_3) : 548 ($M^{+\cdot}$, 1), 268 ($M^{+\cdot}$+1-HgBr, 9), 239 (16), 155 (100), 75 ($Si(CH_3)_2OH^{+\cdot}$,71), 74 (68). **Anal.** Calcd for $C_{14}H_{23}BrHgOSSi$: C, 30.69; H, 4.23; Br, 14.58; Si, 5.13. Found : C, 30.80; H, 4.34; Br, 14.64; Si, 5.28.

25c and **26b**. Following the general procedure, **24b** was converted into a 6:4 mixture of the two diastereoisomers **25c** and **26b** separated using flash chromatography (Petroleum ether/EtOAc 95:5)(0.155 g, 65%). Major **25c** : ^1H **NMR** (δ ppm) : 7.56-7.50 (2H, m, Aromatic H), 7.30-7.22 (3H, m, Aromatic H), 7.05 (1H, d, J 3.2, H-3 thio), 6.85-6.84 (1H, m, H-4 thio), 4.16-4.06 (2H, m, H-2, H-5), 3.24 (1H, dd, J 5.2, 12.1, $C\underline{H}_aH_bSePh$), 2.98 (1H, dd, J 7.4, 12.1, $CH_a\underline{H}_bSePh$), 2.54 (3H, s, CH_3 thio), 2.18 (1H, ddd, J 5.8, 5.8, 11.6, H-3a), 1.82 (1H, ddd, J 6.2, 7.6, 13.5, H-4), 1.60 (1H, ddd, J 9.5, 11.8, 13.5, H-3b), 1.47-1.24 (2H, m, $C\underline{H}_2CH_3$), 0.95 (3H, t, J 7.2, $CH_2C\underline{H}_3$), 0.35 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$). ^{13}C **NMR** (δ ppm) : 145.8 (s, C thio), 135.7 (s, C thio), 134.9 (d, J 164, C thio), 132.4 (d, J 162, Aromatic C), 130.6 (s, Aromatic C), 129.0 (d, J 128, Aromatic C), 126.9 (d, J 169, Aromatic C), 126.7 (d, J 161, Aromatic C), 83.8 (d, J 147, C-2), 79.3 (d, J 156, C-5), 34.2 (t, J 115, CH_2SePh), 33.9 (t, J 148, C-3), 33.6 (d, J 115, C-4), 29.0 (t, J 125, $\underline{C}H_2CH_3$), 15.1 (q, J 129, CH_3 thio), 11.2 (q, J 126, $CH_2\underline{C}H_3$), -1.5 (q, J 120, $SiCH_3$), -1.7 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 3040 (C-H), 2960 (C-H), 2920 (C-H), 1580, 1250 (Si-C), 1210, 960 cm^{-1}. **MS** (CI, NH_3) : 424 ($M^{+\cdot}$, 22), 179 (14), 155 (71), 91 (34), 75 ($Si(CH_3)_2OH^{+\cdot}$, 100). **Anal.** Calcd for $C_{20}H_{28}OSSeSi$: C, 56.72; H, 6.66; S, 7.57; Si, 6.63. Found : C, 56.80; H, 6.77; S, 7.59; Si, 6.72. Minor **26b** : ^1H **NMR** (δ ppm) : 7.57-7.51 (2H, m, Aromatic H), 7.29-7.23 (3H, m, Aromatic H), 7.07 (1H, d, J 3.2, H-3 thio), 6.86-6.85 (1H, m, H-4 thio), 4.31-4.16 (2H, m, H-2 + H-5), 3.13 (1H, dd, J 4.9, 12.1, $C\underline{H}_aH_bSePh$), 2.93 (1H, dd, J 8.2, 12.1, $CH_a\underline{H}_bSePh$), 2.56 (3H, s, CH_3 thio), 2.12 (1H, ddd, J 8.0, 12.4, 12.4, H-3a), 1.94 (1H, ddd, J 3.1, 7.8, 12.4, H-3b), 1.79 (1H, ddd, J 7.6, 7.6, 12.2, H-4), 1.39-1.28 (2H, m, $C\underline{H}_2CH_3$), 0.94 (3H, t, J 7.2, $CH_2C\underline{H}_3$), 0.36 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$). ^{13}C **NMR** (δ ppm) : 145.8 (s, C thio), 135.7 (s, C thio), 134.9 (d, J 169, C thio), 132.5 (d, J 161, Aromatic C), 130.2 (s, Aromatic C), 129.0 (d, J 157, Aromatic C), 126.8 (d, J 167, Aromatic C), 126.8 (d, J 161, Aromatic C), 84.2 (d, J 146, C-2), 76.3 (d, J 146, C-5), 33.5 (t, J 141, CH_2SePh), 32.4 (t, J 128, C-3), 31.1 (d, J 115, C-4), 26.7 (t, J 122, $\underline{C}H_2CH_3$), 15.1 (q, J 128, CH_3 thio), 11.2 (q, J 125, $CH_2\underline{C}H_3$), -1.6 (q, J 120, $SiCH_3$), -1.6 (q, J 120, $SiCH_3$). **MS** (CI, NH_3) : 267 ($M^{+\cdot}$-SePh, 8), 169 (31), 155 (96), 75 ($Si(CH_3)_2OH^{+\cdot}$, 100). **Anal.** Calcd for $C_{20}H_{28}OSSeSi$: C, 56.72; H, 6.66; S, 7.57; Si, 6.63. Found : C, 56.80; H, 6.77; S, 7.59; Si, 6.72.

27. A suspension of $NaBH_4$ (21 mg, 0.547 mmol) in a 2.5$\underline{M}$ solution of NaOH (3.6 ml) was added at 0°C over a period of 15 minutes to a vigorously stirred solution of organomercurial **25a** (0.5 g, 0.98 mmol) in 0.5$\underline{M}$ NaOH (7.2 ml) and THF (7.2 ml). The mixture was stirred 1h at 0°C then powdered NaCl was added. The organic layer was decanted and the aqueous layer extracted 3 times with ether. The combined extracts were washed with brine, H_2O then dried over $MgSO_4$ and the solvents were removed under vacuum to give a colourless oil (280 mg) which was purified by flash chromatography (Petroleum ether/EtOAc 95:5)(0.205 g, 85%). ^{1}**H NMR** (δ ppm) : 7.56-7.49 (2H, m, Aromatic H), 7.39-7.34 (3H, m, Aromatic H), 4.01 (1H, ddd, J 3.4, 7.8, 10.8, H-5), 3.94 (1H, m, H-2), 2.01 (1H, ddd, J 5.3, 6.6, 11.8, H-3a), 1.84 (1H, ddd, J 6.6, 7.8, 12.5, H-4), 1.41 (1H, ddd, J 9.3, 11.8, 12.5, H-3b), 1.37-1.20 (2H, m, $C\underline{H}_2CH_3$), 1.26 (3H, d, J 6.0, CH_3), 0.91 (3H, t, J 7.3, $CH_2C\underline{H}_3$), 0.36 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$). ^{13}**C NMR** (δ ppm) : 138.8 (s, Aromatic C), 133.6 (d, J 155, Aromatic C), 128.9 (d, J 159, Aromatic C), 127.8 (d, J 158, Aromatic C), 83.1 (d, J 145, C-2), 75.9 (d, J 140, C-5), 35.9 (t, J 130, C-3), 32.8 (d, J 115, C-4), 29.1 (t, J 124, $\underline{C}H_2CH_3$), 21.9 (q, J 124, CH_3), 11.3 (q, J 124, $CH_2\underline{C}H_3$), -2.5 (q, J 120, $SiCH_3$), -3.0 (q, J 120, $SiCH_3$). **IR** ($CHCl_3$)(υ_{max}) : 2960 (C-H), 2920 (C-H), 2820 (C-H), 1250 (Si-C), 965, 910 cm^{-1}. **MS** (CI, NH_3) : 219 (24), 179 (5), 135 ($PhSi(CH_3)_2^{+\cdot}$, 100), 75 ($Si(CH_3)_2OH^{+\cdot}$, 45). **Anal.** Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74; Si, 11.30. Found : C, 72.63; H, 9.60; Si, 11.47.

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