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Electrophilic *5-Endo-Trig* Cyclisations of 2-Silyl-3-alkenols. A Stereoselective Route to Polysubstituted Tetrahydrofurans.

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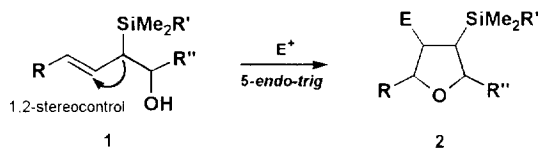
Abstract : Electrophilic *5-endo-trig* cyclisations of allylsilanes have been carried out leading to tri- and tetrasubstituted tetrahydrofurans with reasonable yields and excellent diastereoselectivities. A rationalization of both the regio- and the stereoselectivity has been proposed. A silicon group having a thienyl fragment attached to the silicon has also been devised and was shown to be oxidized under both electrophilic and nucleophilic conditions.

Electrophilic *5-endo-trig* cyclisations are regarded as unfavorable processes according to Baldwin's rules.[1] However, recent reports by Knight, Lipshutz and others have demonstrated that electrophilic *5-endo-trig* cyclisations occur smoothly and are not exceptions to Baldwin's rules since the centre which is attacked is likely to be pyramidalized in the transition state due to the cationic nature of the reaction.[2] This type of electrophilic reaction offers a straightforward entry to polysubstituted tetrahydrofurans, but also to pyrrolidines[3] with excellent yields and diastereoselectivities. In this context, both 1,2- and 1,3-stereocontrol have been used to set up the stereochemistry at the new stereogenic centres.[2]

In the course of our on-going research on the functionalization of new types of allylsilanes,[4] we have investigated the *5-endo-trig*-like cyclisations of 2-silyl-3-alkenols **1** and found that excellent levels of diastereocontrol can be attained with the allylic silicon group ensuring the 1,2-stereocontrol (Scheme 1).[5] The silicon group is particularly convenient for this purpose since it can be further converted into a hydroxy group with retention of configuration.[6] At this point, it is worthy of note that similar *5-endo-trig*-like cyclisation of analogous allylic alcohols proceeds with much lower diastereoselectivity and inversion of topicity leading to the diastereoisomeric tetrahydrofuran of that obtained from an allylsilane.[5,7] We report here the scope and limitations of this electrophilic process as well as the oxidation of a new silicon group which served as a latent hydroxy group. A rationalization of the regio- and the stereoselectivity of the electrophilic attack of PhSeCl on 2-silyl-3-alkenols is proposed.



1 2

Scheme 1

The required homoallylic alcohols **4a-i** have been prepared in 85-95% yield by reduction of the corresponding α-silyl esters **3a-i**[4] using $LiAlH_4$ in ether at 0°C (Scheme 2). It is worthy of note that some recent investigations in our laboratory have shown that such a reduction occurs without racemization at the allylic chiral centre which is particularly relevant in the perspective of an extension of the methodology in homochiral series.[4b] Reduction of the ester **3d** using $LiAlH_4$ produced mainly the desilylated product, so the reaction was best performed using DIBAH in ether at -100°C to finally produce the desired homoallylic alcohol **4d** in 65% yield.

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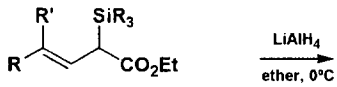
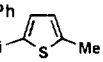
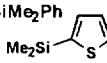
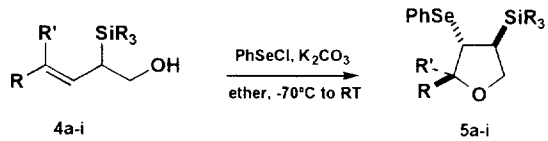


3a, R = Ph, R' = H, SiR_3 = $SiMe_2Ph$
3b, R = Ph, R' = H, SiR_3 = 
3c, R = Ph, R' = H, SiR_3 = $SiMe_2(O\text{-}iPr)$
3d, R = Ph, R' = H, SiR_3 = $Si(i\text{-}Pr)_2F$
3e, R = Ph, R' = Me, SiR_3 = $SiMe_2Ph$
3f, R = Me, R' = H, SiR_3 = $SiMe_2Ph$
3g, R = Et, R' = H, SiR_3 = $SiMe_2Ph$
3h, R = H, R' = Et, SiR_3 = $SiMe_2Ph$
3i, R = t-Bu, R' = H, SiR_3 = $SiMe_2Ph$

4a, R = Ph, R' = H, SiR_3 = $SiMe_2Ph$
4b, R = Ph, R' = H, SiR_3 = 
4c, R = Ph, R' = H, SiR_3 = $SiMe_2(O\text{-}iPr)$
4d, R = Ph, R' = H, SiR_3 = $Si(i\text{-}Pr)_2F$
4e, R = Ph, R' = Me, SiR_3 = $SiMe_2Ph$
4f, R = Me, R' = H, SiR_3 = $SiMe_2Ph$
4g, R = Et, R' = H, SiR_3 = $SiMe_2Ph$
4h, R = H, R' = Et, SiR_3 = $SiMe_2Ph$
4i, R = t-Bu, R' = H, SiR_3 = $SiMe_2Ph$

Scheme 2

The *5-endo-trig* cyclization of the allylsilanes **4a-i** was then performed under kinetic conditions using PhSeCl in ether with K_2CO_3 as a base.[2,3,8] The electrophile was added at -70°C and the reaction mixture was warmed up to room temperature to ensure a complete conversion of the starting material. With substrate **4i** (entry 9), the mixture was refluxed 2 days to afford a low yield of the desired product **5i**, accompanied by unidentified by-products. The resulting tetrahydrofurans are formed in low to good yields depending on the olefinic substitution pattern (*vide supra*). Only one diastereoisomer is formed in each case, having the stereochemistry depicted in Scheme 3. The relative configuration of each centre has easily been obtained through NOE difference experiments (Fig.-1).



4a-i 5a-i

Scheme 3

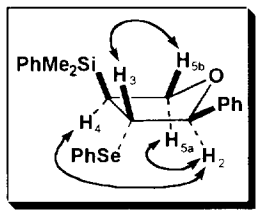


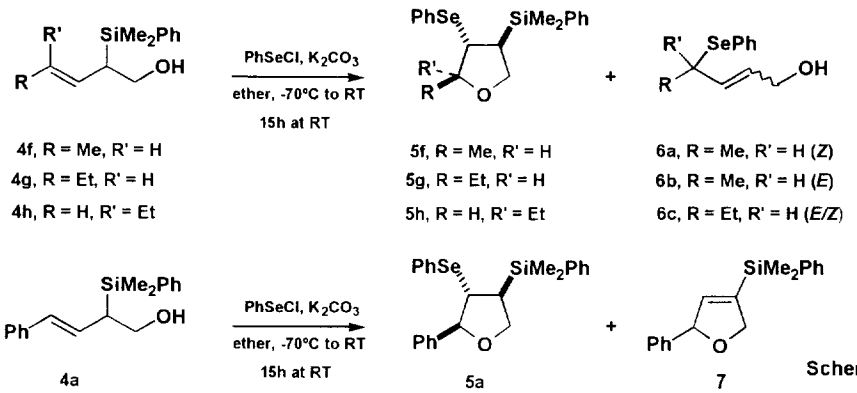
Fig.-1. NOE effects in 5a

Table 1. *5-Endo-trig* electrophilic cyclisations of homoallylic alcohols 4a-i (Scheme 3).

Entry	Allylsilanes[a]	Product	Yield (%)[b]
1	**4a**	**5a**	71
2	**4b**	**5b**	72
3	**4c**	**5c**	74
4	**4d**	**5d**	30
5	**4e**	**5e**	60
6	**4f**	**5f**	44
7	**4g**	**5g**	17
8	**4h**	**5h**	0
9	**4i**	**5i**	17

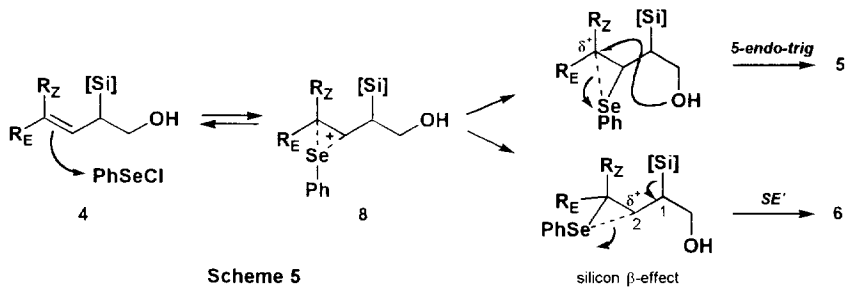
[a] 0.1M solution in ether (2 mmol scale), PhSeCl (1.5 eq.), K_2CO_3 (1.5 eq.).
[b] Isolated yields after flash chromatography.

The reaction mixture was generally free of by-products, with the exception of the SE' products **6**, obtained from precursors **4f-h** (entry 6-8).[9] SE' products and recovered starting material are the only products resulting from the reaction of *Z*-olefin **4h** and PhSeCl (entry 8). This type of substrate probably experience a relatively strong allylic strain[10] in the transition state which disfavours the *5-endo-trig* process relative to the SE' process. We have observed in one case the formation of a deselenylated dihydrotetrahydrofuran **7**, along with the desired **5a**, when the reaction mixture was left for longer period of time (Scheme 4). A relatively slow selenophilic reaction occuring on **5a** in the presence of the excess of PhSeCl might generate a carbocation (stabilized by the silicon group in β position) which would then lead to **7** after elimination.[11]



Scheme 4

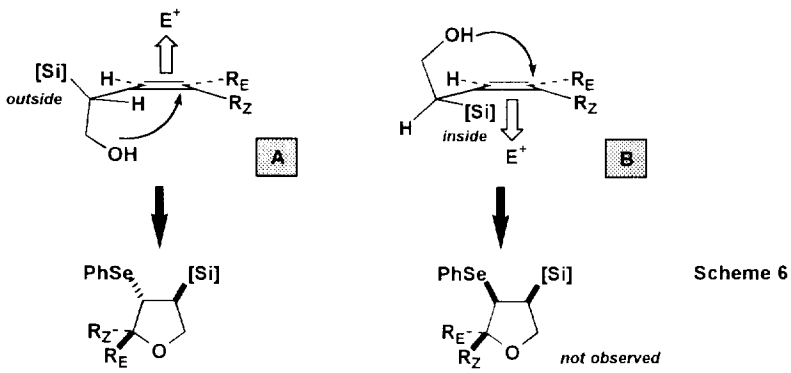
The regioselectivity of the electrophilic attack is principally determined by the electronic nature of the substituents on the olefin. With aryl groups (R_E or R_Z) capable of stabilization of a carbocation or a developing positive charge,[12] the *5-endo-trig* cyclization is the preferred pathway (*i.e.* **5**). Alternatively, with alkyl groups which are much less prone to positive charge stablization, the SE' reaction is the major pathway (i.e. **6**), as indicated by the low yield of tetrahydrofurans isolated in these cases. Such a regiochemical outcome was not unexpected and may be rationalized as depicted below (Scheme 5). It is worthy of note that a larger amount of tetrahydrofuran is formed with the methyl analogue (entry 6) than with the corresponding ethyl analogue (entry 7). The hypothesis that a C-H bond is more electron-rich than a C-C bond and hence can stabilize more efficiently a nascent positive charge has been the subject of a long debate and may explain the important difference of regioselectivity observed between **4f** and **4g**.[13]



Scheme 5

The SE' reaction occuring with **4f-h** was found to produce both olefins of *E* and *Z*-configurations in a ratio close to 55:45. It is well known that such reactions occur through the intermediacy of a carbocationic species stabilized through hyperconjugative overlap with the C-Si bond (Silicon-β-effect, Scheme 5).[9,14] As the rotation around the C_1-C_2 bond must be prevented, then the ratio of the two olefins formed during the process must represent roughly the population of the reactive conformations at the time of electrophilic attack, assuming that the electrophile attacks *anti* relative to the silicon group.[9]

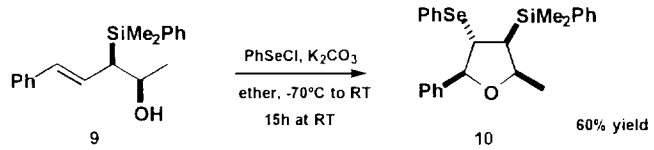
The stereocontrol arising from the *5-endo-trig* cyclisation has been rationalized through the transition state illustrated in scheme 6. If we assume that the cyclisation occurs through a more or less concerted mechanism, then only two conformations at the transition state can be drawn.[2f,5] It is therefore conceivable that the more sterically hindered silicon group will occupy the less sterically congested *outside* position to minimize the steric interactions with R_Z (*i.e.* conformation **A**). Electronic effects will also favour a silicon group in an *outside* position relative to the *inside* one. The co-operativity observed here between steric and electronic effects probably explains the high level of diastereocontrol observed.[15] It is worthy of note that *5-endo-trig* selenoetherification of analogous allylic amino- and thioethers led to the respective tetrahydrofurans with the same stereochemistry as those obtained from allylsilanes **4a-i**, but with somewhat lower stereoselectivity.[7] A similar transition state has hence been proposed. Alternatively, with the corresponding allylic alcohols, a reversal of the topicity was observed and a conformation such as **B** was thus proposed.[7,16,17]

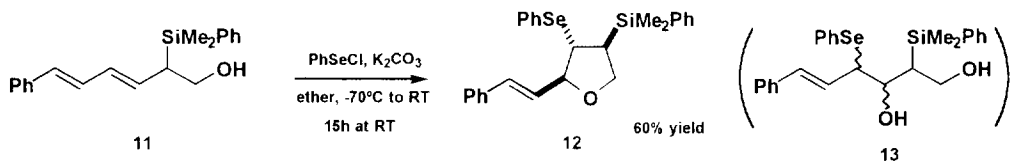


Scheme 6

The cyclisation has also been applied to more challenging systems having a secondary alcohol function as in **9**,[4,5] or a dienyl system as in **11**[4,5] (Scheme 7). Tetrahydrofuran **10** was obtained in reasonable yield as a unique diastereoisomer with 4 chiral centres set up *via* a double 1,2-stereocontrol, in only two steps from the corresponding α-silylketone. Treatment of **11** as above gave the tetrahydrofuran **12** in 60% yield, along with a small quantity of a by-product which structure was tentatively assigned as **13**. The relative configuration of **10** and **12** is the same as that of tetrahydrofurans **5a-i**. It is worth mentioning that in the vinylic tetrahydrofuran **12**, the double bond can be easily functionalized further, which should provide an alternative route for the preparation of alkyl substituted tetrahydrofurans **5f-h**.

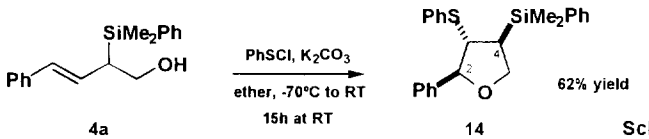
Scheme 7





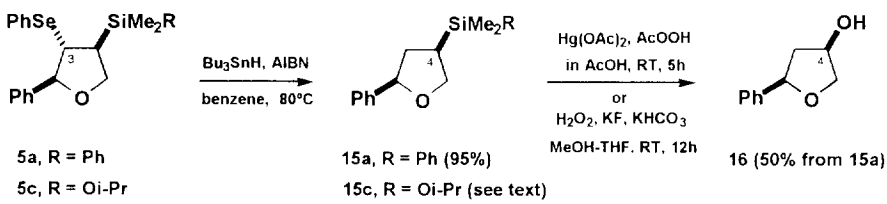
Other electrophiles may advantageously replace toxic and expensive PhSeCl. This is illustrated in Scheme 8 where precursor **4a** was converted in 62% yield into the desired tetrahydrofuran **14** using PhSCl under the same conditions as those employed with PhSeCl. Again, only one diastereoisomer was obtained having the *2,4-cis* relative configuration. The reactive ICl has also been tried but led essentially to degradation of the starting material. Silver salts are known to activate electrophiles such as I_2 or PhSeCl. In our case, the use of CF_3CO_2Ag

(1 eq.) in conjonction with PhSeCl did not improve the yield. As an example, treatment of **4f** under these conditions produced **5f** in 30% yield compared to 44% without the silver salt.



4a 14 **Scheme 8**

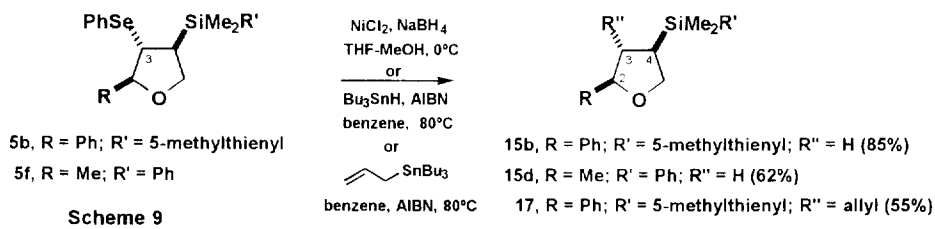
The PhSe or PhS groups, as well as the silicon moiety allow for further functionalizations. The PhSe group can be replaced either by hydrogen through a radical reduction or can serve for radical chain elongation through the well known allylstannane chemistry (Scheme 9).[18] The reduction is carried out using standard conditions, *i.e.*, Bu_3SnH-AIBN, to yield deselenylated products **15a** and **15b** in excellent yields. Alternatively, deselenylation of **5f** was also performed using $NiCl_2$-$NaBH_4$, producing the tetrahydrofuran **15d** in moderate yield. Comparison of the ^1H NMR spectrum of **15d** with that of a sample obtained by an alternative route confirmed the stereochemistry of our tetrahydrofurans **15a-d**.[17a,c] The $PhMe_2Si$ group at C-4 was then oxidized, with retention of configuration, using Fleming's one-pot protocol[6,19] ($Hg(OAc)_2$, AcOOH) to produce **16** in 50% yield. The modest yield obtained during silicon group unmasking may be attributed to the benzylic nature of the substrate rather than to the inefficiency of the oxidation. **15c** was directly converted into the corrresponding alcohol **16** in 52% overall yield (3 steps) starting from the homoallylic alcohol **4c**. Finally, an allyl chain can be introduced at C-3 using allyltributylstannane in the presence of AIBN.[18] The radical reaction proceeds stereoselectively to afford **17** as a unique diastereoisomer in 55% yield after chromatography. The silicon group at C-4 and the phenyl group at C-2, *cis* to each other efficiently direct the incoming allyl group to the opposite face, thus conserving the relative configuration of the selenylated precursor.



5a, R = Ph
5c, R = Oi-Pr

15a, R = Ph (95%)
15c, R = Oi-Pr (see text)

16 (50% from 15a)



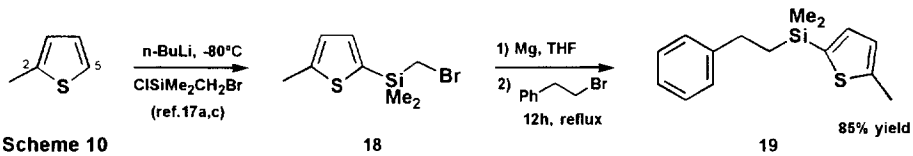
5b, R = Ph; R' = 5-methylthienyl
5f, R = Me; R' = Ph

15b, R = Ph; R' = 5-methylthienyl; R'' = H (85%)
15d, R = Me; R' = Ph; R'' = H (62%)
17, R = Ph; R' = 5-methylthienyl; R'' = allyl (55%)

Scheme 9

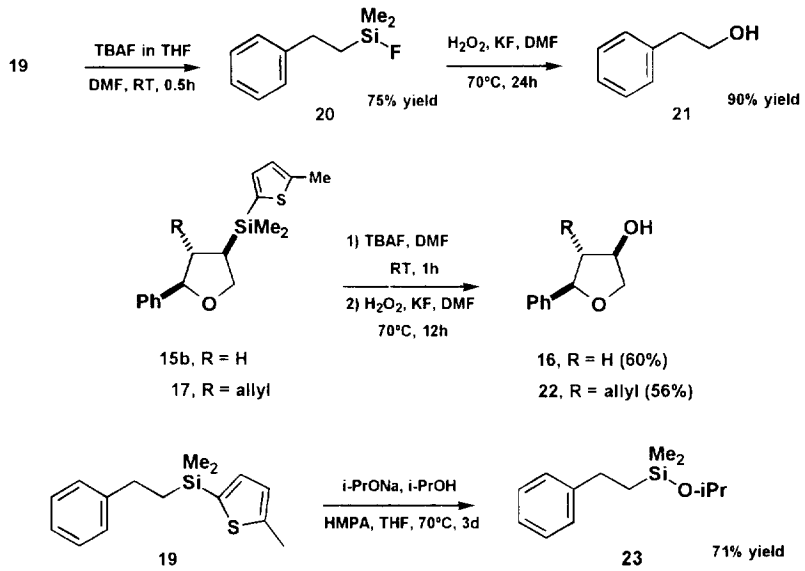
Finally, we have also developed a new organosilicon group which could be used as a latent hydroxy group. The pioneering work of Tamao, Kumada and Fleming has led to the discovery of the C-Si to C-OH conversion which is now recognized as an efficient tool for organic synthetic chemists.[6] Although a plethora of silicon groups has been introduced these last few years, it is difficult in certain cases to combine both the stability of the silicon group and its ability to be oxidized in mild conditions. This drawback is well illustrated with the commonly employed $PhMe_2Si$ group.[19] We found that thiophene derivatives might be particularly useful in this context since they are easy to introduce, relatively stable (compared to the analogous furane[20]) and should be easy to displace using both acidic (and electrophilic) and basic conditions. Electrophilic conditions may be troublesome when one has to deal with sensitive functionalities such as double bonds or ketones. 2-Methylthiophene was choosen since it is commercially available, cheap and can be easily mono-metallated at C-5. We first investigated the oxidation of this silicon group using model **19** prepared in two steps from methylthiophene (Scheme 10). **19**

was also prepared by hydrosilylation of styrene with $RhCl(PPh_3)_3$ as a catalyst, but the product was contaminated with the unseparable vinylsilane analogue.[21]



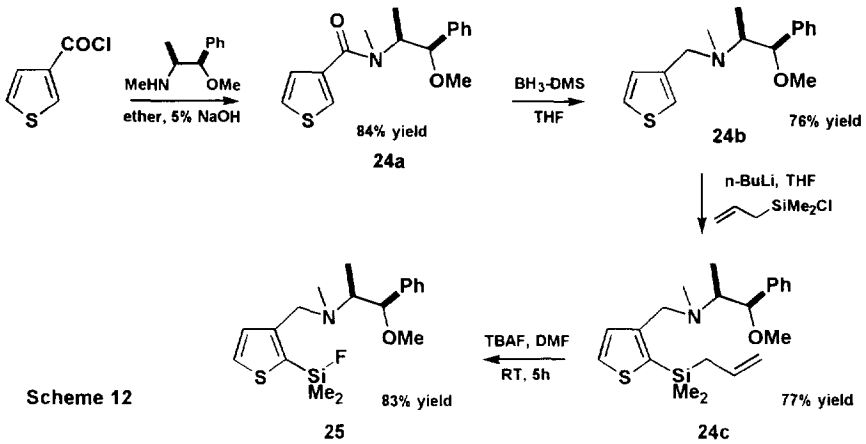
Scheme 10 **18** **19**

Treatment of **19** with TBAF in THF led to smooth displacement of the thienyl moiety to afford the corresponding fluorosilane **20** in 75% yield after purification.[20a] Using CsF in DMF or KF in DMSO gave slightly lower yields and longer reaction times. The fluorosilane was then oxidized using Tamao protocol,[6,22] *i.e.*, H_2O_2, KF in DMF to afford phenethyl alcohol **21** in 90% yield. Interestingly, silane **19** can be converted in one pot into **21** by simply treating the fluorosilane intermediate, without prior purification, with H_2O_2, KF and $KHCO_3$. Noteworthy, Fleming's one-pot procedure[19] using $Hg(OAc)_2$ and AcOOH also affords the alcohol **21** from **19** in 72% yield. The oxidation was also performed on tetrahydrofurans **15b** and **17** described before, affording the alcohols **16** and **22** in 60% and 56% yield respectively (Scheme 11).



Scheme 11

This demonstrates that our thienylsilane can be a useful masked hydroxy group, more stable to electrophiles than a double bond, as demonstrated by its inertness towards PhSeCl (*vide infra*). The mild nucleophilic conditions in which it can be removed should be noticed since they are compatible with numerous functionalities. We also observed that the thienylsilyl moiety can be readily replaced by an alkoxy group (i.e. **23**), although in somewhat drastic conditions (Scheme 11). Interestingly, we have also found that the thienylsilyl group is not as good a leaving group as the allyl group[23] upon treatment with TBAF, *i.e.* fluoride treatment of **24c** gave the thienyl derivative **25** in 83% yield. Model **24c** was prepared in 3 steps following the sequence depicted below (Scheme 12). It was also demonstrated that a phenyl group at the silicon centre is, as expected, inert towards fluoride attack.[23b] Such a difference of reactivity between aryl-, allyl- and thienylsilanes towards nucleophiles may be useful when one has to choose a suitable silicon group for its conversion into a OH group.[6]



Scheme 12

In summary, we have investigated the scope and limitations of the *5-endo-trig*-like cyclisation of 2-silyl-3-alkenols. It appears that the regioselectivity is dependent both of the substituent on the olefin and the geometry of the double bond. Styryl systems afford tetrahydrofurans in good yield and with complete stereocontrol, while the alkyl and *Z*-olefins favour the SE' reaction leading to a mixture of *E* and *Z*-selenylated olefins. However, this apparent limitation can be overcome by using dienyl systems as in precursor **11**. Finally, our tetrahydrofurans can be functionalized further using radical reactions but other processes might also be applicable. We have also demonstrated that the silicon group not only controls efficiently the stereochemistry at the proximal centre (1,2-stereocontrol) but also serves as a masked hydroxy group. A new silicon group having a thienyl fragment attached to the silicon centre has been devised and was shown to be oxidized under both electrophilic and nucleophilic conditions.

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. IR spectra were recorded on a Perkin-Elmer 1710 spectrophotometer. All commercial products were used without further purification. Ether and THF were distilled from sodium and benzophenone.

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).

General Procedure for the reduction of allylsilanes 3. (*E*)-4-Phenyl-2-(dimethylphenylsilyl)but-3-enol 4a. To a solution of silyl ester **3a** (0.2 g, 0.61 mmol) in dry ether (5 ml) was added dropwise at 0°C a 1M solution of $LiAlH_4$ in ether (0.34 ml, 0.34 mmol). The mixture was stirred at 0°C for 30 minutes then treated with 1M HCl. The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. Chromatography (petroleum ether/EtOAc/NEt_3 95:4.5:0.5) gave **4a** as a pale yellow oil (0.16 g, 95%). **^{1}H NMR** (δ ppm) : 7.92-7.17 (10H, m), 6.37 (1H, dd, J 0.6 and 15.8 Hz), 6.10 (1H, dd, J 9.7 and 15.8 Hz), 3.80-3.76 (2H, m), 2.31 (1H, dt, J 4.6 and 9.7 Hz), 0.36 (6H, s). **IR** ($CHCl_3$) (υ_{max}): 3200 (O-H), 2990, 2960 (C-H), 1640 (C=C), 1600 (C=C), 1440, 1250 (Si-C), 1120 cm^{-1}. **MS** (CI, NH_3): 144 (5), 137 (18), 135 (28), 131 (13), 130 (100), 129 (32), 115 (21), 105 (7), 91 (16), 77 (8). **Anal.** Calcd for $C_{21}H_{24}O_2Si$: C, 76.54; H, 7.85; Si, 9.94. Found: C, 76.65; H, 7.93; Si, 9.93.

(*E*)-4-Phenyl-2-(dimethyl-(4-methylthien-2-yl)silyl)but-3-enol 4b. (92%). **^{1}H NMR** (δ ppm) : 7.38-7.22 (5H, m), 7.08 (1H, d, J 3.2 Hz), 6.87 (1H, m), 6.42 (1H, d, J 15.9 Hz), 6.15 (1H, dd, J 9.7 and 15.9 Hz), 3.88-3.76 (2H, m), 2.55 (3H, d, J 0.8 Hz), 2.28 (1H, dt, J 5.7 and 9.7 Hz), 0.38 (3H, s), 0.36 (3H, s). **IR** (film) (υ_{max}): 3350 (O-H), 3020, 2960 (C-H), 2920, 1640 (C=C), 1600 (C=C), 1490, 1440, 1250 (Si-C), 1220, 1050, 1000, 960, 840, 760, 700 cm^{-1}. **MS** (CI, NH_3): 302 (M^+, 1), 285 (6), 205 (19), 187 (8), 172 (12), 157 (17), 155 (27), 131 (68), 130 (41), 115 (12), 92 (100), 75 (99). **Anal.** Calcd for $C_{17}H_{22}OSiS$: C, 67.50; H, 7.33; Si, 9.28; S, 10.60. Found: C, 67.43; H, 7.46; Si, 9.23; S, 10.60.

(*E*)-4-Phenyl-2-(isopropyloxydimethylsilyl)but-3-enol 4c. (87%). **^{1}H NMR** (δ ppm) : 7.43-7.16 (5H, m), 6.39 (1H, d, J 16.0 Hz), 6.16 (1H, dd, J 9.6 and 16.0 Hz), 4.04 (1H, sept, J 6.1 Hz), 3.95-3.80 (2H, m), 2.28-2.13 (1H, m), 1.18 (6H, d, J 6.1 Hz), 0.21 (3H, s), 0.18 (3H, s). **IR** (film) (υ_{max}): 3400 (O-H), 3030, 2950 (C-H), 2870, 1630 (C=C), 1590 (C=C), 1440, 1370, 1360, 1250 (Si-C), 1160, 1110, 1020 (Si-O), 880 cm^{-1}. **MS** (CI, NH_3) : 265 (M^++1, 12), 247 (10), 189 (4), 147 (18), 131 (100), 130 (50), 117 (28), 92 (26), 75 (49). **Anal.** Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15; Si, 10.62. Found: C, 68.12; H, 9.09; Si, 10.43.

(*E*)-4-Phenyl-2-(fluorodiisopropylsilyl)but-3-enol 4d. To a solution of **3d** (1.17 g, 3.63 mmol) in dry ether (60 ml) was added dropwise at -100°C, a 1M solution of DIBAH in toluene (7.3 ml, 7.3 mmol). The reaction mixture was stirred at this temperature for 1 h then treated with 1M HCl. The resulting mixture was stirred for 30 minutes at room temperature 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 the solvent was evaporated *in vacuo*. Distillation under vacuum (170°C, 0.06 mbar) gave **4d** as a pale yellow oil (0.66 g, 65%). **^{1}H NMR** (δ ppm) : 7.39-7.19 (5H, m), 6.50 (1H, d, J 15.8 Hz), 6.20 (1H, dd, J 10.0 and 15.8 Hz), 3.97-3.93 (2H, m), 2.57-2.47 (1H, m), 1.62 (1H, s), 1.26-1.04 (14H, m). **IR** (film) (υ_{max}) : 3400 (O-H), 3030, 2950 (C-H), 2870, 1720, 1640 (C=C), 1600 (C=C), 1460, 1250 (Si-C), 1040, 1000, 970, 880 (Si-F), 820, 700 cm^{-1}. **MS** (CI, NH_3) : 298 (M^++NH_4^+, 30), 280 (M^+, 1), 263 (100), 261 (24), 150 (9), 131 (89), 130 (57), 115 (16), 91 (10). **Anal.** Calcd for $C_{16}H_{25}OSiF$: C, 68.52; H, 8.98; Si, 10.01. Found: C, 68.54; H, 8.81; Si, 9.91.

(*E*)-4-Phenyl-2-(dimethylphenylsilyl)pent-3-enol 4e. (85%). **^{1}H NMR** (δ ppm) : 7.55-7.51 (2H, m), 7.46-7.21 (8H, m), 5.66 (1H, dq, J 1.2 and 11.2 Hz), 3.90-3.80 (1H, m), 3.71 (1H, dd, J 10.4 and 10.4 Hz), 2.56 (1H, dd, J 4.2, 10.4 and 11.2 Hz), 1.92 (3H, d, J 1.3 Hz), 0.38 (3H, s), 0.36 (3H, s). **IR** ($CHCl_3$) (υ_{max}) : 3580 (O-H), 3150, 3000, 2960 (C-H), 2870, 1600 (C=C), 1500, 1460, 1440, 1390, 1260 (Si-C), 1120, 1040, 1000, 920, 820 cm^{-1}. **MS** (CI, NH_3) : 201 (4), 152 (5), 145 (20), 144 (92), 143 (15), 137 (57), 135 (62), 129 (100), 91 (11). **Anal.** Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16; Si, 9.47. Found: C, 77.02; H, 8.13; Si, 9.32.

(*E*)-2-(Dimethylphenylsilyl)pent-3-enol 4f. (83%). **^{1}H NMR** (δ ppm) : 7.61-7.44 (2H, m), 7.41-7.33 (3H, m), 5.45 (1H, dq, J 6.1 and 15.2 Hz), 5.27 (1H, ddq, J 1.3, 9.4 and 15.2 Hz), 3.72-3.53 (2H, m), 2.04 (1H, dt, J 4.2 and 9.4 Hz), 1.70 (3H, dd, J 1.3 and 6.1 Hz), 0.30 (3H, s), 0.29 (3H, s). **IR** ($CHCl_3$) (υ_{max}) : 3650 (O-H), 3000, 2970 (C-H), 2940, 1410, 1250 (Si-C), 1110, 970, 910 cm^{-1}. **MS** (CI, NH_3) : 152 (4), 137 (100), 135 (81), 119 (6), 107 (9), 105 (15), 91 (9), 75 (10). **Anal.** Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15; Si, 12.74. Found: C, 70.98; H, 9.08; Si, 12.83.

(*E*)-2-(Dimethylphenylsilyl)hex-3-enol 4g. (85%). **^{1}H NMR** (δ ppm) : 7.52-7.45 (2H, m), 7.41-7.31 (3H, m), 5.47 (1H, dt, J 6.3 and 15.3 Hz), 5.25 (1H, ddt, J 1.3, 9.6 and 15.3 Hz), 3.69 (1H, dd, J 4.2 and 10.7 Hz), 3.59 (1H, dd, J 10.7 and 10.7 Hz), 2.11-1.99 (3H, m), 0.97 (3H, t, J 6.4 Hz), 0.31 (3H, s), 0.30 (3H, s). **IR** ($CHCl_3$) (υ_{max}) : 3570, 3450 (O-H), 3000, 2960 (C-H), 2950, 2870, 1460, 1440, 1260 (Si-C), 1220, 1120, 970, 860, 740 cm^{-1}. **MS** (CI, NH_3): 217 (8), 216 (6), 210 (9), 194 (13), 193 (20), 152 (17), 137 (60), 135 (100), 102 (13), 86 (36), 82 (28). **Anal.** Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46; Si, 11.98. Found: C, 71.68; H, 9.30; Si, 11.89.

(*Z*)-2-(Dimethylphenylsilyl)hex-3-enol 4h. (86%). **^{1}H NMR** (δ ppm) : 7.52-7.47 (2H, m), 7.39-7.33 (3H, m), 5.55 (1H, dt, J 1.7 and 10.9 Hz), 5.17 (1H, ddt, J 1.4, 11.0 and 11.0 Hz), 3.71-3.65 (1H, m), 3.55 (1H, dd, J 10.7 and 10.7 Hz), 2.44 (1H, dt, J 4.0 and 11.0 Hz), 2.11-1.83 (2H, m), 0.91 (3H, t, J 7.5 Hz), 0.32 (3H, s), 0.31 (3H, s). **IR** ($CHCl_3$) (υ_{max}) : 3580, 3450 (O-H), 3050, 3000, 2960 (C-H), 2870, 1600 (C=C), 1460, 1440, 1260 (Si-C), 1220, 1120, 1000, 850 cm^{-1}. **MS** (CI, NH_3): 219 (2), 169 (12), 137 (64), 135 (66), 105 (14), 83 (12), 82 (100). **Anal.** Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46; Si, 11.98. Found: C, 71.83; H, 9.35; Si, 12.00.

(*E*)-5,5-Dimethyl-2-(dimethylphenylsilyl)hex-3-enol 4i. (85%). **^{1}H NMR** (δ ppm) : 7.50-7.44 (2H, m), 7.40-7.33 (3H, m), 5.46 (1H, dd, J 0.6 and 15.6 Hz), 5.14 (1H, dd, J 9.7 and 15.6 Hz), 3.74-3.55 (2H, m), 2.02 (1H, dt, J 4.5 and 9.7 Hz), 0.99 (9H, s), 0.30 (3H, s), 0.29 (3H, s). **IR** (film) (υ_{max}) : 3400 (O-H), 2950 (C-H), 2870, 2830, 1600 (C=C), 1480, 1440, 1360, 1250 (Si-C), 1120, 1050, 970, 820 cm^{-1}. **MS** (CI, NH_3) : 245 (20), 152 (55), 135 (100), 111 (4), 95 (13), 75 (2). **Anal.** Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98. Found: C, 73.27; H, 9.90.

General procedure for the *5-endo-trig* selenocyclisation. 5a. To a stirred solution of **4a** (0.61 g, 2.17 mmol) in dry ether (20 ml) was added, under nitrogen at -70°C, K_2CO_3 (0.45 g, 3.26 mmol) then dropwise a solution of PhSeCl (0.63 g, 3.26 mmol) in dry ether (5 ml). The solution was slowly allowed to warm to room temperature (2 h) 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 the solvent was evaporated *in vacuo*. Chromatography (petroleum ether/EtOAc/NEt_3 98:1.5:0.5) gave **5a** (386 mg, 71%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.52-7.08 (15H, m), 4.73 (1H, d, J 8.4 Hz), 4.03 (1H, dd, J 8.7 and 9.1 Hz), 3.99 (1H, dd, J 8.7 and 9.1 Hz), 3.14 (1H, dd, J 8.4 and 10.4 Hz), 1.90 (1H, dt, J 8.9 and 10.4 Hz), 0.40 (3H, s), 0.39 (3H, s). **^{13}C NMR** (δ ppm) : 140.2 (s), 136.7 (s), 135.1 (d, J 164 Hz), 133.9 (d, J 158 Hz), 129.4, 128.8, 128.2, 127.9, 127.7, 127.6, 126.6, 88.5 (d, J 149 Hz), 70.5 (t, J 148 Hz), 50.5 (d, J 146 Hz), 33.9 (d, J 123 Hz), -3.5 (q, J 120 Hz), -4.4 (q, J 120 Hz). **IR** (film) (υ_{max}) : 2920 (C-H), 1600 (C=C), 1440, 1260

(Si-C), 1130, 1040, 960, 770 cm^{-1}. **MS** (CI, NH_3) : 438 (M^++1, 2), 292 (14), 281 (20), 205 (7), 135 (100), 105 (9), 75 (21). **Anal.** Calcd for $C_{24}H_{26}OSiSe$: C, 65.89; H, 5.99; Se, 18.05; Si, 6.42. Found: C, 65.73; H, 5.45; Se, 18.00; Si, 6.44.

5b. **^{1}H NMR** (δ ppm) : 7.29-7.10 (10H, m), 7.05 (1H, d, J 3.2 Hz), 6.85-6.83 (1H, m), 4.74 (1H, d, J 8.3 Hz), 4.13-4.01 (2H, m), 3.20 (1H, dd, J 8.4 and 10.4 Hz), 2.54 (3H, d, J 0.8 Hz), 1.88 (1H, m), 0.40 (6H, s). **^{13}C NMR** (δ ppm) : 146.0 (s), 140.0 (s), 135.5 (d, J 164 Hz), 135.0 (d, J 163 Hz), 133.5, 132.2, 128.7, 128.0, 127.6, 127.5, 126.9, 126.5, 88.3 (d, J 149 Hz), 70.3 (t, J 147 Hz), 50.2 (d, J 146 Hz), 34.1 (d, J 123 Hz), 15.0 (q, J 130 Hz), -1.5 (q, J 120 Hz), -2.2 (q, J 120 Hz). **IR** (film) (υ_{max}) : 3050, 2950 (C-H), 2870, 1650 (C=C), 1600 (C=C), 1480, 1250 (Si-C), 1210, 1080, 1020, 1000, 960, 820, 760, 700 cm^{-1}. **MS** (CI, NH_3) : 458 (M^++1, 2), 301 (11), 227 (15), 155 (100), 115 (11), 75 (14). **Anal.** Calcd for $C_{23}H_{26}OSiSeS$: C, 60.37; H, 5.73; Se, 17.26; Si, 6.14. Found: C, 60.45; H, 5.84; Se, 17.28; Si, 6.08.

5c. This sensitive tetrahydrofuran was directly converted into the alcohol **16** without further purifications.

5d. **^{1}H NMR** (δ ppm): 7.41-7.10 (10H, m), 4.75 (1H, d, J 8.3 Hz), 4.15 (1H, dd, J 8.2 and 14.6 Hz), 4.12 (1H, dd, J 8.4 and 15.3 Hz), 3.40 (1H, dd, J 8.3 and 10.7 Hz), 2.04-1.94 (1H, m), 1.35-1.02 (14H, m). **^{13}C NMR** (δ ppm): 140 (s), 135.2 (d, J 154 Hz), 128.8, 128.4, 128.3, 127.9, 126.6, 88.3 (d, J 148 Hz), 69.1 (t, J 146 Hz), 48.7 (d, J 144 Hz), 31.8 (d, J 122 Hz), 17.0 (q, J 123 Hz), 12.4 (d, J 123 Hz). **IR** (film) (υ_{max}) : 2950 (C-H), 2870, 1580 (C=C), 1460, 1360, 1240 (Si-C), 1060, 1020, 880 (Si-F), 830, 740, 700 cm^{-1}. **MS** (CI, NH_3) : 279 (40), 235 (3), 129 (100), 117 (14), 115 (18), 105 (34), 91 (14), 77 (78). **Anal.** Calcd for $C_{22}H_{29}OSiSeF$: C, 60.67; H, 6.71; Si, 6.45. Found: C, 60.75; H, 6.67; Si, 6.37.

5e. **^{1}H NMR** (δ ppm) : 7.51-6.97 (15H, m), 4.05 (1H, dd, J 9.0 and 9.0 Hz), 3.82 (1H, dd, J 8.8 and 10.3 Hz), 3.40 (1H, d, J 11.3 Hz), 2.06 (1H, ddd, J 9.2, 10.4 and 11.3 Hz), 1.64 (3H, s), 0.29 (3H, s), 0.22 (3H, s). **^{13}C NMR** (δ ppm): 146.0 (s), 136.7 (s), 133.0 (d, J 163 Hz), 129.2 (d, J 163 Hz), 128.9 (d, J 161 Hz), 128.1 (d, J 159 Hz), 127.8 (d, J 160 Hz), 127.0 (d, J 159 Hz), 126.7 (d, J 161 Hz), 86.5 (s), 68.5 (t, J 146 Hz), 57.2 (d, J 144 Hz), 34.3 (d, J 123 Hz), 25.0 (q, J 128 Hz), -3.4 (q, J 120 Hz), -4.5 (q, J 120 Hz). **IR** ($CHCl_3$) (υ_{max}) : 2960 (C-H), 2870, 1600 (C=C), 1480, 1440, 1260 (Si-C), 1060, 940 cm^{-1}. **MS** (CI, NH_3) : 332 (5), 292 (6), 143 (29), 135 (100), 105 (5). **Anal.** Calcd for $C_{25}H_{28}OSiSe$: C, 66.50; H, 6.25; Se, 17.49; Si, 6.22. Found: C, 66.62; H, 6.22; Se, 17.51; Si, 6.18.

5f. **^{1}H NMR** (δ ppm) : 7.55-7.22 (10H, m), 3.91-3.71 (3H, m), 2.82 (1H, dd, J 8.0 and 9.9 Hz), 1.71 (1H, ddd, J 8.3, 9.0 and 9.8 Hz), 1.06 (3H, d, J 7.1 Hz), 0.41 (3H, s), 0.38 (3H, s). **^{13}C NMR** (δ ppm) : 136.8 (s), 135.5 (d, J 163 Hz), 133.9 (d, J 163 Hz), 129.3 (d, J 159 Hz), 129.0 (d, J 153 Hz), 128.0 (d, J 161 Hz), 127.8 (d, J 159 Hz), 83.3 (d, J 148 Hz), 69.0 (t, J 147 Hz), 48.3 (d, J 144 Hz), 33.1 (d, J 123 Hz), 18.6 (q, J 126 Hz), -0.1 (q, J 120 Hz), -0.8 (q, J 120 Hz). **IR** ($CHCl_3$) (υ_{max}) : 3030, 3000, 2950 (C-H), 2870, 1590 (C=C), 1480, 1440, 1260 (Si-C), 1120, 1080, 830 cm^{-1}. **MS** (CI, NH_3) : 292 (12), 225 (6), 219 (12), 135 (100), 105 (7), 75 (14). **Anal.** Calcd for $C_{19}H_{24}OSiSe$: C, 60.78; H, 6.44; Se, 21.03; Si, 7.48. Found: C, 60.88; H, 6.44; Se, 20.95; Si, 7.54.

5g. **^{1}H NMR** (δ ppm) : 7.56-7.23 (10H, m), 3.89 (1H, dd, J 8.7 and 8.7 Hz), 3.79-3.72 (1H, m), 3.74 (1H, dd, J 8.5 and 8.5 Hz), 2.95 (1H, dd, J 7.6 and 9.5 Hz), 1.73 (1H, ddd, J 8.7, 8.7 and 9.5 Hz), 1.53 (1H, ddq, J 3.7, 7.4 and 14.0 Hz), 1.26 (1H, ddq, J 0.8, 7.5 and 14.0 Hz), 0.85 (3H, t, J 7.4 Hz), 0.42 (3H, s), 0.38 (3H, s). **^{13}C NMR** (δ ppm) : 136.9 (s), 135.5 (d, J 146 Hz), 133.9 (d, J 153 Hz), 129.3 (d, J 160 Hz), 129.0 (d, J 160 Hz), 128.4 (s), 128.0 (d, J 160 Hz), 127.9 (d, J 160 Hz), 88.3 (d, J 148 Hz), 69.1 (t, J 150 Hz), 46.3 (d, J 140 Hz), 33.3(d, J 143 Hz), 26.1 (t, J 123 Hz), 10.3 (q, J 124 Hz), -3.5 (q, J 120 Hz), -4.2 (q, J 120 Hz). **IR** ($CHCl_3$) (υ_{max}) : 3020, 2950 (C-H), 2870, 1590 (C=C), 1480, 1260 (Si-C), 1220, 1120, 1030, 940 cm^{-1}. **MS** (CI, NH_3) : 390 (M^++1, 1), 292 (11), 233 (9), 135 (100), 105 (7), 97 (7), 75 (13). **Anal.** Calcd for $C_{20}H_{26}OSiSe$: C, 61.68; H, 6.73; Se, 20.27; Si, 7.21. Found: C, 61.75; H, 6.79; Se, 20.29; Si, 7.26.

5i. Prepared according to the general procedure, except that the reaction mixture was stirred under reflux for 2 days. **^{1}H NMR** (δ ppm) : 7.50-7.25 (10H, m), 3.80 (1H, dd, J 8.5 and 8.5 Hz), 3.70 (1H, d, J 7.3 Hz), 3.63 (1H, dd, J 8.7 and 8.7 Hz), 3.19 (1H, dd, J 7.3 and 9.0 Hz), 1.84 (1H, ddd, J 8.7, 8.7 and 8.7 Hz), 0.86 (9H, s), 0.39 (3H, s), 0.28 (3H, s). **^{13}C NMR** (δ ppm) : 136.0 (d, J 155 Hz), 133.9 (d, J 158 Hz), 129.2, 129.0, 128.1, 127.8, 93.2 (d, J 148 Hz), 70.2 (t, J 149 Hz), 41.9 (d, J 142 Hz), 35.4 (d, J 123 Hz), 35.2 (s), -3.5 (q, J 120 Hz), -4.0 (q, J 120 Hz). **IR** (film) (υ_{max}) : 3070, 2960 (C-H), 2870, 1590 (C=C), 1470, 1360, 1250 (Si-C), 1110, 1060, 970, 830, 820, 740, 700 cm^{-1}. **MS** (CI, NH_3) : 292 (5), 261 (17), 135 (100), 109 (28), 105 (6), 77 (13). **Anal.** Calcd for $C_{22}H_{30}OSiSe$: C, 63.29; H, 7.24; Se, 18.91; Si, 6.73. Found: C, 63.33; H, 7.40; Se, 18.84; Si, 6.76.

(*Z*)-4-Phenylselenylpent-2-enol 6a. **^{1}H NMR** (δ ppm): 7.62-7.53 (2H, m), 7.37-7.24 (3H, m), 5.54-5.42 (2H, m), 3.88-3.82 (1H, m), 3.68-3.64 (2H, m), 1.67 (3H, d, J 4.8 Hz). **IR** (film) (υ_{max}): 3380 (O-H), 2950 (C-H), 2870, 1590 (C=C), 1480, 1440, 1030, 980 cm^{-1}. **MS** (CI, NH_3): 183 (1), 158 (24), (9), 117 (4), 98 (37), 85 (8), 84 (11), 81 (100), 77 (17).

(*E*)-4-Phenylselenylpent-2-enol 6b. **^{1}H NMR** (δ ppm) : 7.55-7.51 (2H, m), 7.35-7.26 (3H, m), 5.77 (1H, ddt, J 1.3, 8.4 and 15.3 Hz), 5.36 (1H, ddt, J 0.9, 5.9 and 15.3 Hz), 4.0 (2H, dd, J 1.3 and 5.9 Hz), 3.95-3.83 (1H, m), 1.50 (3H, d, J 6.9 Hz). **IR** (film) (υ_{max}): 3400 (O-H), 3070, 2920 (C-H), 2870, 1580 (C=C), 1480, 1440, 1370, 1040, 1020, 970, 740 cm^{-1}. **MS** (CI, NH_3) : 242 (M^++1, 6), 158 (47), 135 (10), 85 (61), 84 (100), 78 (48), 77 (25). **Anal.** Calcd for $C_{11}H_{14}OSe$: C, 54.78; H, 5.85. Found : C, 54.76; H, 5.76.

(*Z*)-4-Phenylselenylhex-2-enol 6c. **^{1}H NMR** (δ ppm) : 7.57-7.53 (2H, m), 7.31-7.27 (3H, m), 5.51-5.44 (2H, m), 3.92-3.83 (1H, m), 3.68-3.60 (2H, m), 2.08-1.96 (2H, m), 0.92 (3H, d, J 7.4 Hz). **IR** (film) (υ_{max}) : 3400 (O-H), 2970 (C-H), 2870, 1590 (C=C), 1480, 1440, 1380, 1060, 980, 750, 700 cm^{-1}. **MS** (CI, NH_3): 255 (M^+, 2), 239 (24), 237 (13), 217 (9), 170 (7), 152 (60), 135 (100), 116 (5), 99 (10), 81 (20).

7. Prepared according to the general procedure, except that the reaction mixture was stirred at room temperature for 15 h. Flash chromatography (petroleum ether/EtOAc/NEt_3 98:1.5:0.5) gave 7 (23%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.69-7.25 (10H, m), 6.08-6.05 (1H, m), 5.82-5.79 (1H, m), 4.98 (1H, ddd, J 2.2, 5.1 and 12.6 Hz), 4.86 (1H, ddd, J 1.4, 3.6 and 12.6 Hz), 0.45 (6H, s). **IR** (film) (υ_{max}) : 3070, 2950 (C-H), 2850, 1600 (C=C), 1490, 1460, 1440, 1260 (Si-C), 1150, 1120, 1100, 1080, 930, 840, 790 cm^{-1}. **MS** (CI, NH_3) : 298 (M^++NH_4^+, 24), 281 (M^++1, 100), 280 (M^+, 11), 279 (42), 263 (13), 203 (7), 152 (8), 135 (41), 105 (6), 75 (10). **Anal.** Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19; Si, 10.01. Found: C, 77.04; H, 7.09; Si, 9.86.

10. **^{1}H NMR** (δ ppm) : 7.56-7.09 (15H, m), 4.79 (1H, d, J 8.5 Hz), 4.34 (1H, dq, J 6.6 and 7.1 Hz), 3.37 (1H, dd, J 8.7 and 8.7 Hz), 2.07 (1H, dd, J 7.6 and 9.3 Hz), 1.23 (3H, d, J 6.6 Hz), 0.43 (3H, s), 0.37 (3H, s). **^{13}C NMR** (δ ppm) : 141.4 (s), 140.3, 135.0, 134.0, 133.8, 129.1, 128.8, 128.4, 128.1, 127.9, 127.7, 127.6, 126.8, 126.5, 88.1 (d, J 149 Hz), 50.9 (d, J 144 Hz), 39.6 (d, J 123 Hz), 20.5 (q, J 123 Hz), -1.4 (q, J 120 Hz), -2.6 (q, J 120 Hz). **IR** (film) (υ_{max}) : 3070, 2970 (C-H), 2900, 2860, 1590 (C=C), 1580 (C=C), 1480, 1440, 1370, 1250 (Si-C), 1110, 1050, 1020, 910, 820, 740, 700 cm^{-1}. **MS** (CI, NH_3): 295 (7), 251 (3), 152 (6), 143 (8), 136 (15), 135 (100), 115 (4), 105 (7), 91 (6), 77 (6). **Anal.** Calcd for $C_{25}H_{28}OSiSe$: C, 66.50; H, 6.25. Found: C, 66.66; H, 6.12.

(*3E,5E*)-6-Phenyl-2-(dimethylphenylsilyl)hex-3,5-dienol 11[4] (90%). **^{1}H NMR** (δ ppm) : 7.53-7.18 (10H, m), 6.79 (1H, dd, J 10.3 and 15.6 Hz), 6.44 (1H, d, J 15.6 Hz), 6.21 (1H, dd, J 10.3 and 15.2 Hz), 5.72 (1H, dd, J 9.7 and 15.2 Hz), 3.76-3.67 (2H, m), 2.26 (1H, dt, J 4.9 and 9.7 Hz), 0.35 (6H, s). **IR** (film) (υ_{max}) : 3400 (O-H), 3020, 2920 (C-H), 2870, 1640 (C=C), 1600 (C=C), 1440, 1260 (Si-C), 1120, 820 cm^{-1}. **MS** (CI, NH_3) : 291 (40), 213 (6), 158 (14), 157 (100), 135 (60), 91 (24), 78 (6), 75 (7). **Anal.** Calcd for $C_{20}H_{24}OSi$: C, 77.87; H, 7.84; Si, 9.10. Found: C, 77.14; H, 7.76; Si, 9.25.

12. (60%). **^{1}H NMR** (δ ppm) : 7.59-7.19 (15H, m), 6.53 (1H, d, J 15.9 Hz), 5.87 (1H, dd, J 6.7 and 15.9 Hz), 4.45 (1H, ddd, J 1.1, 6.8 and 7.9 Hz), 4.03 (1H, dd, J 8.7 and 8.7 Hz), 3.88 (1H, dd, J 8.7 and 8.7 Hz), 3.13 (1H, dd, J 7.9 and 10.3 Hz), 1.84 (1H, dt, J 8.9 and 10.3 Hz), 0.48 (3H, s), 0.46 (3H, s). **^{13}C NMR** (δ ppm) : 136.7 (s), 135.6 (d, J 153 Hz), 134.0 (d, J 147 Hz), 131.8, 129.5, 129.0, 128.3, 128.0, 127.9, 127.8, 127.5, 126.5, 87.9 (d, J 154 Hz), 69.9 (t, J 148 Hz), 47.8 (d, J 147 Hz), 33.6 (d, J 123 Hz), -3.4 (q, J 120 Hz), -4.2 (q, J 120 Hz). **IR** ($CHCl_3$) (υ_{max}) : 3050, 2950 (C-H), 2850, 1590 (C=C), 1440, 1380, 1260 (Si-C), 1220, 1070, 1030, 840, 740 cm^{-1}. **MS** (CI, NH_3) : 465 (16), 463 (M^+, 9), 313 (66), 311 (34), 309 (20), 307 (80), 233 (9), 155 (25), 152 (39), 136 (13), 135 (100), 115 (6), 91 (13), 78 (6), 75 (9). **Anal.** Calcd for $C_{26}H_{28}OSiSe$: C, 67.37; H, 6.09; Se, 17.03; Si, 6.06. Found: C, 67.41; H, 6.09; Se, 16.94; Si, 6.13.

13. (18%). **^{1}H NMR** (δ ppm): 7.58-7.21 (15H, m), 6.63 (1H, d, J 15.9 Hz), 6.31 (1H, dd, J 6.6 and 15.9 Hz), 4.57-4.52 (2H, m), 4.25-4.14 (2H, m, J 8.4 and 8.4 Hz), 2.27-2.17 (1H, ddd, J 4.1, 9.3 and 15.2 Hz), 0.52 (3H, s), 0.45 (3H, s). **^{13}C NMR** (δ ppm) : 137.5 (s), 137.2 (s), 133.7 (s), 133.4 (s), 132.9, 129.4, 129.0, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 126.7, 126.2, 128.5, 85.0 (d, J 145 Hz), 69.2 (t, J 148 Hz), 67.8 (d, J 162 Hz), 37.8 (d, J 126 Hz), -2.7 (q, J 122 Hz), -3.1 (q, J 122 Hz). **IR** (film) (υ_{max}) : 3400 (O-H), 3060, 2950 (C-H), 2870, 1660 (C=C), 1420, 1250 (Si-C), 1110, 970, 740 cm^{-1}. **MS** (CI, NH_3) : 360 (48), 307 (38), 281 (8), 193 (48), 135 (100), 91 (25).

14. To a solution of **4a** (0.43 g, 1.52 mmol) in dry ether (35 ml) was added at -70°C, K_2CO_3 (0.316 g, 2.3 mmol) then a solution of PhSCl (0.33 g, 2.3 mmol) in ether (15 ml). The reaction mixture was stirred 1 h at -70°C then allowed to warm to room temperature and stirred for 1 h. The mixture was 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 the solvent was evaporated *in vacuo*. Chromatography (petroleum ether/EtOAc 95:5) gave **14** (0.369 g, 62%) as a colourless oil. **^{1}H NMR** (δ ppm): 7.60-6.91 (15H, m), 5.13 (1H, s), 4.42 (1H, dd, J 8.2 and 8.2 Hz), 4.27 (1H, dd, J 8.2 and 12.3 Hz), 3.74 (1H, dd, J 1.4 and 6.4 Hz), 2.09 (1H, ddd, J 6.4, 8.2 and 12.3 Hz), 0.54 (3H, s), 0.52 (3H, s). **^{13}C NMR** (δ ppm) : 142.8 (s), 137.8 (s), 135.0 (s), 133.8, 132.9, 129.3, 129.2, 128.1, 127.8, 127.6, 127.0, 125.0, 87.5 (d, J 150 Hz), 71.6 (t, J 147 Hz), 60.2 (d, J 150 Hz), 31.2 (d, J 117 Hz), -2.1 (q, J 119 Hz), -2.5 (q, J 120 Hz). **IR** (film) (υ_{max}): 3050, 3020, 2950 (C-H), 2870, 1580 (C=C), 1480, 1430, 1250 (Si-C), 1200, 1110, 1030, 930, 820, 700 cm^{-1}. **MS** (CI, NH_3) : 284 (15), 239 (2), 152 (5), 136 (28), 135 (100), 129 (4), 110 (11), 105 (6), 91 (4), 77 (4). **Anal.** Calcd for $C_{24}H_{26}OSiS$: C, 73.80; H, 6.71; S, 8.21; Si, 7.19. Found: C, 73.93; H, 6.75; S, 8.34; Si, 7.21.

15a. A solution of **5a** (0.99 g, 2.28 mmol), Bu_3SnH (1.21 ml, 4.55 mmol) and AIBN (19 mg, 0.11 mmol) in dry benzene (30 ml) was refluxed for 7 days (an additional amount of AIBN was added regularly over the week). The solvent was then evaporated *in vacuo* and chromatography of the residue (petroleum ether/EtOAc/NEt_3 99:0.5:0.5) afforded **15a** (0.61 g, 95%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.47-7.15 (10H, m), 4.76 (1H, dd, J 5.4 and 9.8 Hz), 4.13 (1H, dd, J 8.8 and 8.8 Hz), 3.86 (1H, dd, J 8.8 and 11.0 Hz), 2.36-2.28 (1H, m), 1.90-1.74 (1H, m), 1.62-1.47 (1H, m), 0.26 (6H, s). **^{13}C**

NMR (δ ppm) : 143.2 (s), 137.5 (s), 133.6 (d, J 148 Hz), 129.2, 128.3, 127.9, 127.1, 125.7, 82.0 (d, J 146 Hz), 71.1 (t, J 146 Hz), 38.7 (t, J 131 Hz), 28.3 (d, J 120 Hz), -4.5 (q, J 120 Hz), -4.6 (q, J 120 Hz). **IR** (film) (υ_{max}) : 3070, 2960 (C-H), 2870, 1600 (C=C), 1480, 1440, 1340, 1240 (Si-C), 1100, 1080, 1020, 970, 910, 810, 730 cm^{-1}. **MS** (CI, NH_3) : 300 (M^++NH_4^+, 14), 265 (4), 203 (5), 189 (4), 167 (6), 152 (7), 135 (64), 132 (17), 131 (100), 105 (5), 91 (5). **Anal.** Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85; Si, 9.94. Found: C, 76.63; H, 7.76; Si, 9.77.

15b. (85%). **^{1}H NMR** (δ ppm) : 7.37-7.21 (5H, m), 7.07 (1H, d, J 3.3 Hz), 6.86-6.84 (1H, m), 4.84 (1H, dd, J 5.4 and 9.8 Hz), 4.21 (1H, dd, J 8.4 and 8.4 Hz), 3.95 (1H, dd, J 8.1 and 10.8 Hz), 2.54 (3H, d, J 0.5 Hz), 2.49-2.38 (1H, m), 1.95-1.79 (1H, m), 1.70-1.56 (1H, m), 0.34 (3H, s), 0.33 (3H, s). **^{13}C NMR** (δ ppm) : 146.0 (s), 143.1 (s), 135.1 (d, J 169 Hz), 134.6 (s), 128.3, 127.2, 126.9, 125.7, 82.1 (d, J 146 Hz), 71.0 (t, J 148 Hz), 38.5 (t, J 127 Hz), 28.8 (d, J 119 Hz), 15.0 (q, J 131 Hz), -3.2 (q, J 120 Hz), -3.3 (q, J 120 Hz). **IR** (film) (υ_{max}) : 3020, 2960 (C-H), 2940, 2870, 1600 (C=C), 1480, 1440, 1340, 1250 (Si-C), 1200, 1080, 1060, 1000, 950, 800, 750 cm^{-1}. **MS** (CI, NH_3) : 320 (M^++NH_4^+, 11), 222 (5), 206 (19), 205 (100), 187 (8), 155 (12), 131 (43), 75 (9), 74 (7). **Anal.** Calcd for $C_{17}H_{22}OSiS$: C, 67.50; H, 7.33; Si, 9.28; S, 10.60. Found: C, 67.48; H, 7.46; Si, 9.34; S, 10.63.

15d. To a stirred solution of **5f** (153 mg, 0.41 mmol) and $NiCl_2.6H_2O$ (387 mg, 1.63 mmol) in a 1:1 mixture of THF and MeOH (16 ml), $NaBH_4$ (154 mg, 4.1 mmol) was added cautiously at 0°C. The reaction mixture was stirred at 0°C for 1 h. After filtration through celite and evaporation of the solvents *in vacuo*, chromatography of the residue (petroleum ether/EtOAc/NEt_3 98:1.5:0.5) afforded **15d** (56 mg, 62%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.53-7.48 (2H, m), 7.41-7.35 (3H, m), 4.01-3.86 (2H, m), 3.72 (1H, dd, J 8.2 and 10.6 Hz), 2.08 (1H, ddd, J 5.1, 7.0 and 12.0 Hz), 1.72 (1H, dddd, J 7.1, 8.8, 9.6 and 12.4 Hz), 1.32-1.16 (1H, m), 1.22 (3H, d, J 6.0 Hz), 0.31 (3H, s), 0.30 (3H, s). **^{13}C NMR** (δ ppm) : 133.6 (d, J 157 Hz), 129.2 (d, J 160 Hz), 127.8 (d, J 164 Hz), 76.2 (d, J 150 Hz), 69.7 (t, J 147 Hz), 36.8 (t, J 132 Hz), 27.7 (d, J 120 Hz), 20.5 (q, J 125 Hz), 0.36 (q, J 120 Hz), 0.25 (q, J 120 Hz). **IR** ($CHCl_3$) (υ_{max}) : 3030, 2970 (C-H), 2920, 2870, 1600 (C=C), 1440, 1390, 1260 (Si-C), 1220, 1120, 950, 910, 830 cm^{-1}. **MS** (CI, NH_3) : 220 (M^+, 2), 219 (M^+-1, 6), 203 (6), 179 (4), 161 (5), 152 (6), 137 (35), 135 (100), 127 (13), 105 (9), 75 (6). **Anal.** Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15; Si, 12.74. Found: C, 70.92; H, 9.14; Si, 12.65.

16. To a solution of **15a** (58 mg, 0.2 mmol) in a mixture of acetic anhydride (0.2 ml) and peracetic acid (32% in acetic acid) (1 ml) was added at 0°C, $Hg(OAc)_2$ (98 mg, 0.3 mmol). The reaction mixture was stirred at room temperature for 24 h and the solvent was evaporated *in vacuo*. The residue was dissolved in ether and filtered through celite. Evaporation of the solvent *in vacuo* followed by chromatography (CH_2Cl_2/MeOH 98:2) afforded **16** (16 mg, 50%). **^{1}H NMR** (δ ppm) : 7.44-7.28 (5H, m), 4.91 (1H, dd, J 7.5 and 7.5 Hz), 4.59-4.53 (1H, m), 4.08-4.02 (1H, m), 3.90 (1H, dd, J 4.5 and 9.9 Hz), 2.67 (1H, ddd, J 6.5, 8.0 and 13.5 Hz), 1.92 (1H, dddd, J 1.3, 3.1, 4.4 and 7.0 Hz), 1.85 (1H, s). **^{13}C NMR** (δ ppm) : 142.5 (s), 128.5 (d, J 159 Hz), 127.5 (d, J 152 Hz), 125.8 (d, J 160 Hz), 80.2 (d, J 145 Hz), 76.2 (t, J 144 Hz), 72.9 (d, J 154 Hz), 43.9 (t, J 132 Hz). **IR** (film) (υ_{max}) : 3400 (O-H), 2950 (C-H), 2870, 1600 (C=C), 1490, 1330, 1240, 1160, 1130, 980, 910, 760, 700 cm^{-1}. **MS** (CI, NH_3) : 164 (M^+, 33), 163 (39), 146 (8), 133 (6), 120 (31), 115 (13), 107 (28), 105 (100), 103 (18), 92 (58), 91 (49), 89 (11), 79 (35), 78 (35), 77 (41). **Anal.** Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37; Found: C, 72.94; H, 7.20.

Preparation of 16 from 5c. To a solution of **5c** (0.263 g, 0.63 mmol) in degassed benzene (16 ml) was added Bu_3SnH (0.5 ml, 1.9 mmol), and AIBN (8 mg, 0.05 mmol). The reaction mixture was refluxed overnight then an additional amount of AIBN (8 mg) and Bu_3SnH (0.5 ml) were added and the mixture was refluxed for 7 h. Evaporation of the solvent afforded the desired deselenylated product (^{1}H NMR) which was directly oxidized without further purification. The residue was dissolved in a 1:1 mixture of MeOH and THF (10 ml) then $KHCO_3$ (0.151 g, 1.5 mmol) and KF (87 mg, 1.5 mmol) were added at 0°C. A 30% solution of H_2O_2 (1 ml) was then added at 0°C and the reaction mixture was stirred at room temperature overnight. The excess of H_2O_2 was decomposed using $Na_2S_2O_3$ and the mixture was stirred for 30 minutes, then diluted with ether, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give an oil which was purified by flash chromatography (CH_2Cl_2/MeOH 98:2) to afford **16** (53 mg, 52%). Spectroscopic data of this material were found to be identical with those obtained from **15a**.

17. A solution of **5b** (0.44 g, 0.96 mmol), allyl tri-n-butyltin (0.44 ml, 1.44 mmol) and AIBN (8 mg, 0.05 mmol) in dry benzene (25 ml) was refluxed for 7 days (an additionnal amount of AIBN was added over the week). The solvent was evaporated *in vacuo* and chromatography of the residue (petroleum ether/EtOAc 98:2) afforded **17** (0.18 g, 55%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.36-7.18 (5H, m), 7.07 (1H, d, J 3.2 Hz), 6.85 (1H, d, J 3.2 Hz), 5.74-5.62 (1H, m), 5.02-4.98 (2H, m), 4.48 (1H, d, J 8.1 Hz), 4.13 (1H, dd, J 8.8 and 8.8 Hz), 4.05 (1H, dd, J 8.7 and 8.7 Hz), 2.54 (3H, s), 2.23-2.19 (2H, m), 2.15-2.06 (1H, m), 1.65 (1H, dt, J 9.2 and 9.2 Hz), 0.36 (3H, s), 0.35 (3H, s). **^{13}C NMR** (δ ppm) : 142.1 (s), 135.2 (d, J 162 Hz), 128.2, 127.7, 126.9, 126.5, 117.2 (t, J 155 Hz), 86.1 (d, J 141 Hz), 70.6 (t, J 146 Hz), 49.8 (d, J 134 Hz), 35.6 (t, J 120 Hz), 32.1 (d, J 120 Hz), 15.0 (q, J 128 Hz), -2.7 (q, J 120 Hz), -2.9 (q, J 120 Hz). **IR** (film) (υ_{max}) : 3050, 2960 (C-H), 2920, 2860, 1640 (C=C), 1600 (C=C), 1490, 1250 (Si-C), 1210, 1060, 1020, 960, 800, 700

cm^{-1}. **MS** (CI, NH_3) : 360 (M^++NH_4^+, 27), 342 (M^+, 4), 263 (100), 262 (90), 246 (32), 245 (39), 203 (15), 187 (21), 172 (19), 155 (94), 115 (14), 91 (25). **Anal.** Calcd for $C_{20}H_{26}OSiS$: C, 70.12; H, 7.65. Found: C, 70.23; H, 7.74.

19. To a suspension of magnesium (0.5 g, 20.5 mmol) in anhydrous THF (5 ml) was added an aliquot of a solution of **18**[17a,c] (4 g, 19.5 mmol) in THF (20 ml). The mixture was heated under reflux for a few minutes then the remaining of the solution of the bromide was added dropwise in order to maintain a gentle reflux. The mixture was then refluxed for 1 h then cooled to 0°C and a solution of phenetyl bromide (3.34 g, 19.5 mmol) in THF (2 ml) was added dropwise. The resulting mixture was refluxed for 12 h then poured into ice 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 the solvent was evaporated *in vacuo* to give an oil which was chromatographed on silica gel (petroleum ether/EtOAc 98:2) affording **19** (4.3 g, 85%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.28-7.18 (5H, m), 7.08 (1H, d, J 1.0 Hz), 6.85 (1H, d, J 1.0 and 3.2 Hz), 2.67 (2H, dt, J 4.9 and 8.7 Hz), 2.54 (3H, d, J 1.0 Hz), 1.12 (2H, dt, J 4.9 and 8.2 Hz), 0.30 (6H, s). **IR** ($CHCl_3$) (υ_{max}) : 2950 (C-H), 2920 (C-H), 1600 (C=C), 1490, 1440, 1250 (Si-C), 1000, 960, 840 cm^{-1}. **MS** (CI, NH_3) : 260 (M^+, 17), 245 (3), 163 (83), 162 (100), 155 (86), 147 (34), 141 (25), 115 (23), 91 (49).

2-Phenylethylfluorodimethylsilane 20. To a solution of **19** (0.5 g, 1.92 mmol) in DMF (10 ml) was added at room temperature, a 1M solution of TBAF in THF (2.1 ml, 2.1 mmol). The resulting mixture was then stirred for 30 minutes then quenched with a saturated solution of NaCl and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give an oil which was chromatographed on silica gel (petroleum ether/EtOAc 98:2) affording **20** (0.293 g, 75%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.31-7.17 (5H, m), 2.66 (2H, dt, J 5.0 and 8.7 Hz), 0.91 (2H, dt, J 5.1 and 8.2 Hz), 0.10 (6H, s). **IR** ($CHCl_3$) (υ_{max}) : 2950 (C-H), 2920 (C-H), 1600 (C=C), 1490, 1450, 1250 (Si-C), 1060 (Si-F), 1000, 840 cm^{-1}. **MS** (CI, NH_3) : 238 (100), 237 (96), 223 (7), 208 (5), 193 (6), 163 (8), 148 (10), 133 (66), 119 (14), 91 (26).

2-Phenylethanol 21. To a solution of **20** (129 mg, 0.71 mmol) in DMF (3 ml) was added at room temperature, KF (123 mg, 2.12 mmol) then a 30% solution of H_2O_2 (1.4 ml, 14.16 mmol). The mixture was then heated at 70°C for 24 h then treated with a saturated solution of NaCl and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give an oil which was purified by chromatography on silica gel (petroleum ether/EtOAc 9:1) affording **21** (50 mg, 90%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.37-7.21 (5H, m), 3.88 (2H, t, J 6.6 Hz), 2.89 (2H, t, J 6.6 Hz). **IR** ($CHCl_3$)(υ_{max}) : 3420 (O-H), 2990 (C-H), 2930 (C-H), 1490, 1380 cm^{-1}.

2-Phenylethanol 21. **One-pot procedure**. To a solution of **19** (0.41 g, 1.58 mmol) in DMF (8 ml) was added at room temperature a 1M solution of TBAF in THF (3.15 ml, 3.15 mmol). The resulting mixture was then stirred for 30 minutes, then KF (275 mg, 4.74 mmol), $KHCO_3$ (237 mg, 2.37 mmol) and a 30% solution of H_2O_2 (3.2 ml, 31.5 mmol) were added. The mixture was then heated at 70°C for 24 h then treated as above to give an oil which was chromatographed on silica gel (petroleum ether/EtOAc 9:1) affording **21** (77 mg, 87%) as a colourless oil, which ^{1}H NMR and IR data were identical with those of the compound obtained above.

22. To a stirred solution of **17** (185 mg, 0.54 mmol) in DMF (3 ml) was added at room temperature a 1M solution of TBAF in THF (0.6 ml, 0.59 mmol). The mixture was stirred at room temperature for 20 minutes then treated with brine. The solution was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. To the residue in DMF (9 ml) was added at room temperature, KF (96 mg, 1.65 mmol) and a 30% solution of H_2O_2 (1.08 ml, 10.8 mmol). The reaction mixture was stirred at 70°C for 15 h then treated with a saturated solution of NH_4Cl and the solution was extracted with ether. The combined extracts were washed with a saturated solution of NaCl, dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. Chromatography of the residue (CH_2Cl_2/MeOH 95/5) gave **22** (62 mg, 56%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.43-7.25 (5H, m), 5.90-5.73 (1H, m), 5.30-5.06 (2H, m), 4.47 (1H, d, J 6.9 Hz), 4.27-4.24 (1H, m), 4.01 (2H, d, J 4.2 Hz), 2.35-2.10 (3H, m), 1.96 (1H, s). **^{13}C NMR** (δ ppm) : 141.3 (s), 135.8 (d, J 162 Hz), 128.4 (d, J 160 Hz), 127.7 (d, J 160 Hz), 126.2 (d, J 160 Hz), 117.1 (t, J 158 Hz), 85.8 (d, J 143 Hz), 77.4, 74.6 (t, J 145 Hz), 56.0 (d, J 133 Hz), 35.3 (t, J 129 Hz). **IR** (film) (υ_{max}) : 3420 (O-H), 2980, 2920 (C-H), 2860, 1660 (C=C), 1590 (C=C), 1490, 1440, 1390, 1100, 1000, 920, 700 cm^{-1}. **MS** (CI, NH_3) : 204 (M^+, 3), 175 (51), 163 (23), 162 (58), 146 (25), 145 (100), 129 (11), 128 (12), 115 (20), 107 (54), 105 (51), 91 (43), 79 (32), 77 (29).

2-Phenylethylisopropyloxydimethylsilane 23. To a solution of **19** (0.15 g, 0.58 mmol) in anhydrous THF (3 ml) and HMPA (0.15 ml) was added a solution of sodium isopropylate (2.56 ml, 0.69 mmol) in isopropanol (1 ml) and THF (1ml). The mixture was then heated under reflux for 3 days then quenched with a saturated solution of NaCl and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give an oil which was chromatographed on silica gel (petroleum ether/EtOAc 95:5) affording **23** (90 mg, 71%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.31-7.17 (5H, m), 4.06 (1H , sept, J 6.1 Hz), 2.68 (2H, dt, J 5.1 and 8.7 Hz), 1.18 (6H, d, J 6.1 Hz), 0.97 (2H, dt, J 5.0 and 8.5 Hz), 0.13 (6H, s). **IR** ($CHCl_3$)(υ_{max}) : 2950 (C-H), 2920 (C-H), 1600 (C=C), 1490, 1450, 1250 (Si-C), 1170, 1060 cm^{-1}.

24a. A solution of thiophene-3-carboxylic acid chloride (4.5 g, 30.7 mmol) in ether (60 ml) was added dropwise at 0°C to a solution of methoxyephedrine (5 g, 27.9 mmol) in a mixture of ether (75 ml) and 5% NaOH solution (45 ml). The reaction mixture was stirred at room temperature for 3 h and the organic layer was decanted. The aqueous layer was extracted with ether and the combined extracts were washed successively with 5% NaOH, 0.5M HCl, brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give an oil which was chromatographed on silica gel (petroleum ether/EtOAc 8:2) affording **24a** (6.8 g, 84%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.35-6.75 (8H, m), 4.67-4.60 (1H, m), 4.39 (1H, d, J 5.8 Hz), 3.20 (3H, s), 3.12 (3H, s), 2.93 (3H, s), 2.82 (3H, s), 1.31 (3H, d, J 6.6 Hz). **IR** ($CHCl_3$) (υ max) : 2980, 2930, 2870, 2820 (C-H), 2240, 1630 (C=O), 1520, 1480, 1450, 1260, 1150, 1070, 900 cm^{-1}. **MS** (CI, NH_3) : 291 (M^++1, 12), 258 (7), 168 (26), 111 (100), 83 (7), 77 (10). **Anal.** Calcd for $C_{16}H_{19}SNO_2$: C, 66.41; H, 6.62; S, 11.08; N, 4.84. Found : C, 66.50; H, 6.73; S, 11.07; N, 4.86.

24b. The amide **24a** (6.25 g, 21.6 mmol) in solution in anhydrous THF (250 ml) was treated under reflux with a solution of BH_3-Me_2S (18.5 ml, 0.19 mol). Me_2S was then distilled off the reaction mixture and the resulting solution was heated under reflux for 3.5 h then quenched at 0°C with a 6M HCl solution. The heterogeneous mixture was refluxed for 1 h then treated with a 20% NaOH solution (pH 7). The organic layer was decanted and the aqueous layer was extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give an oil which was chromatographed on silica gel (petroleum ether/EtOAc 9:1) affording **24b** (4.52 g, 76%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.45-7-30 (5H, m), 7.22 (1H, dd, J 3.0 and 4.9 Hz), 6.94 (1H, dd, J 1.0 and 3.0 Hz), 6.81 (1H, dd, J 1.2 and 4.9 Hz), 4.31 (1H, d, J 5.9 Hz), 3.70 (1H, d, J 13.8 Hz), 3.63 (1H, d, J 13.8 Hz), 3.30 (3H, s), 2.96 (1H, dq, J 5.9 and 6.7 Hz), 2.31 (3H, s), 1.19 (3H, d, J 6.7 Hz). **^{13}C NMR** (δ ppm) : 141.4 (s), 141.3 (s), 128.1 (d, J 182 Hz), 128.0 (d, J 164 Hz), 127.4 (d, J 164 Hz), 125.0 (d, J 186 Hz), 121.7 (d, J 184 Hz), 85.9 (d, J 141 Hz), 65.8 (t, J 141 Hz), 62.9 (d, J 137 Hz), 56.7 (q, J 140 Hz), 37.7 (q, J 131 Hz), 8.6 (q, J 126 Hz). **IR** (CH_2Cl_2) (υ max): 3000, 2980, 2930, 2820 (C-H), 1490, 1450, 1090 cm^{-1}. **MS** (EI) : 276 (M^++1, 15), 154 (25), 97 (100). **Anal.** Calcd for $C_{16}H_{21}SNO$: C, 69.78; H, 7.69; S, 11.64; N, 5.09. Found : C, 69.82; H, 7.66; S, 11.61; N, 5.02.

24c. To a solution of **24b** (1 g, 3.64 mmol) in dry THF (8 ml) was added dropwise at -80°C, a 1.6 M solution of n-BuLi in hexane (2.7 ml, 4.36 mmol). The resulting solution was stirred for 1 h at -80°C then allyldimethylchlorosilane (0.66 ml, 4.36 mmol) in dry THF (2 ml) was added dropwise. The reaction mixture was stirred at -80°C for 2 h 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 brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give an oil which was chromatographed on silica gel (petroleum ether/EtOAc 95:5) affording **24c** (1.04 g, 77%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.42-7-22 (6H, m), 6.79 (1H, d, J 4.8 Hz), 5.85-5.67 (1H, m), 4.94-4.82 (2H, m), 4.26 (1H, d, J 5.9 Hz), 3.63 (2H, s), 3.24 (3H, s), 2.91 (1H, m), 2.18 (3H, s), 1.80 (2H, m), 1.13 (3H, d, J 6.7 Hz), 0.32 (6H, s). **Anal.** Calcd for $C_{21}H_{31}SSiNO$: C, 67.51; H, 8.36; S, 8.58; N, 3.75. Found : C, 67.64; H, 8.42; S, 8.53; N, 3.80.

25. To a solution of **24c** (0.1 g, 0.28 mmol) in dry DMF (2 ml) was added at room temperature, a 1M solution of TBAF in THF (0.38 ml, 0.28 mmol). The reaction mixture was stirred for 5 h then quenched with a saturated solution of NaCl and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give an oil which was chromatographed on silica gel (petroleum ether/EtOAc 8:2) affording **25** (78 mg, 83%) as a colourless oil. **^{1}H NMR** (δ ppm) : 7.37-7.15 (5H, m), 6.87 (1H, d, J 4.7 Hz), 4.23 (1H , d, J 5.9 Hz), 3.59 (2H, d, J 4.1 Hz), 3.23 (3H, d, J 1.2 Hz), 2.86 (1H, dq, J 6.6 Hz), 2.23 (3H, s), 1.09 (3H, dd, J 1.1 and 6.7 Hz), 0.16-0.08 (6H, m). **IR** ($CHCl_3$)(υ_{max}) : 2930 (C-H), 2820 (C-H), 1450, 1260 (Si-C), 1090 cm^{-1}.

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