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Stereocontrolled Synthesis of α-Trialkylsilyl-β, γ-Unsaturated Aldehydes *via* Palladium (0) Catalysis. Synthetic Usefulness

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Abstract : The reaction of silicon substituted vinyloxiranes in the presence of catalytic amount of palladium (0) catalyst affords the title compounds. This new reaction proceeds smoothly, under very mild conditions and with complete chirality transfer. One-pot addition of selected organometallic nucleophiles to these aldehydes at very low temperature led to a highly selective preparation of the corresponding alcohols in very good yields. Influence of substituents on the silicon atom and of the ligands of palladium have been studied. Copyright © 1996 Elsevier Science Ltd

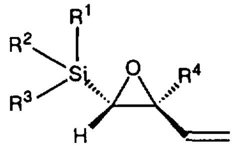
INTRODUCTION

The utility of vinyloxirane derivatives as intermediates in organic synthesis is well recognized and numerous studies have been devoted to the development of methods for the preparation of such compounds.[1, 2] These past fifteen years the reaction of 1,3-diene monoepoxides with nucleophiles in the presence of palladium zerovalent complex as a catalyst under very mild neutral conditions to give 1,4-adducts selectively has known a tremendous development for the preparation of highly functionalized compounds.[3] On the other hand, Muchowski and coworkers have recently shown the interesting behavior of trialkylsilyl substituted oxiranes which gave in the presence of silica gel α-silylated aldehydes.[4] These carbonyl derivatives have heretofore rarely been isolated[5] from acid catalyzed epoxide rearrangements, since protodesilylation usually takes place, and are valuable synthetic intermediates difficult to prepare by conventional methods.[6] We felt that the synthesis of vinyloxiranes having a silicon substituent on the external carbon atom of the small ring should be straightforward, even in optically pure form by taking advantage of the recent development of the catalytic asymmetric Sharpless epoxidation[7] of 3-trialkylsilyl-prop-2-en-1-ol.[8] These reasons prompted us to undertake a general study of the preparation and synthetic behavior of such trialkylsilyl substituted vinyloxiranes. In this paper, we will give full details of a new catalytic rearrangement of silicon substituted epoxides leading in a totally stereoselective manner to α-trialkylsilyl-β,γ-unsaturated aldehydes having in view of their ambident character a great synthetic potential. The influence of substituents on the silicon atom and of the ligands on the catalytic species on the course of 1,2-silicon migration will be adressed. Finally, the diastereoselective one-pot addition of carbon nucleophiles onto the thus generated aldehydes will be described.

RESULTS and DISCUSSION

A- Preparation of Vinyloxiranes 1

We prepared seven silicon substituted vinylepoxides **1** (Figure 1) following two synthetic pathways depending on the nature of the substituent R^4.

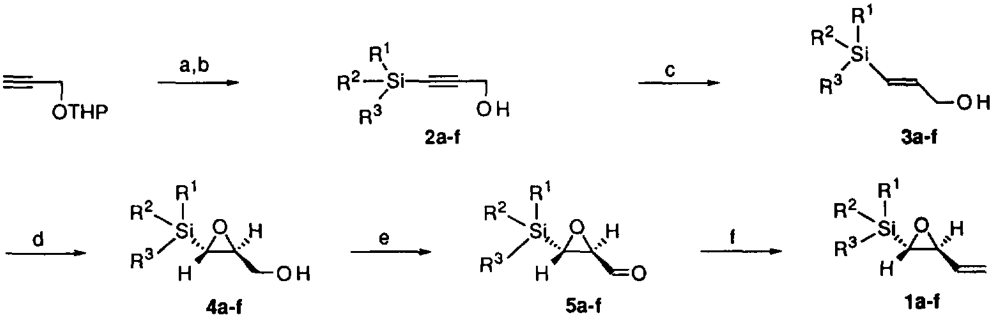


1 a-g

1a : $R^1 = R^2 = Me$; $R^3 = t\text{-}Bu$; $R^4 = H$
1b : $R^1 = R^2 = R^3 = Me$; $R^4 = H$
1c : $R^1 = R^2 = Me$; $R^3 = Ph$; $R^4 = H$
1d : $R^1 = R^2 = R^3 = Et$; $R^4 = H$
1e : $R^1 = R^2 = R^3 = i\text{-}Pr$; $R^4 = H$
1f : $R^1 = R^2 = Ph$; $R^3 = t\text{-}Bu$; $R^4 = H$
1g : $R^1 = R^2 = Me$; $R^3 = t\text{-}Bu$; $R^4 = Me$

Figure 1

When $R^4 = H$, the synthetic approach is depicted in Scheme 1.



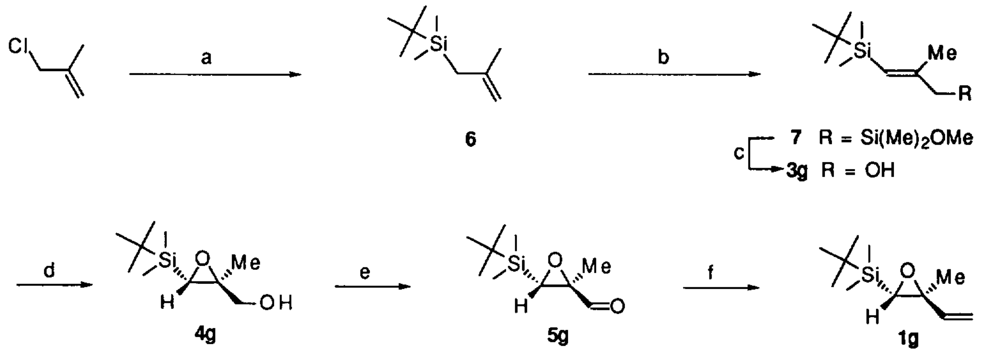
a) *n*-BuLi, $R^1R^2R^3SiCl$, THF ; b) APTS cat., MeOH ; c) 1.6 eq RedAl, Et_2O ; d) 10 mol % $Ti(O\text{-}i\text{-}Pr)_4$, 12 mol % (+)-DIPT, 3.1 eq *t*-BuOOH, CH_2Cl_2, -20°C, 48h ; e) 3 eq $SO_3.C_5H_5N$, 20 eq DMSO, 10 eq Et_3N, CH_2Cl_2, r.t., 2 h f) benzene, 1.2 eq $Ph_3P^+\text{-}CH_3,Br^-$, 1.1 eq $NaOC(CH_3)_2C_2H_5$.

Scheme 1

Starting from the commercially available tetrahydropyranyl ether of the propargylic alcohol, we first introduced various silyl substituents in the acetylenic position. After hydrolysis under mild acidic conditions, the resulting silicon substituted propargylic alcohols were treated with Red-Al to deliver stereoselectively the corresponding *E*-vinylsilanes in high chemical yields.[9] It should be pointed out that reduction using cristal clear solution of lithium aluminium hydride produced stereoselectively the Z isomer.[10] Sharpless asymmetric epoxidation[11] resulted in the formation of silyl substituted epoxyalcohols in high enantiomeric excesses and chemical yields. The catalytic conditions[12] using (+) or (-) diisopropyltartrate as homochiral vector were by far superior to the stoichiometric procedure. It is important to note that by this simple sequence and benefiting of the great performance of the asymmetric Sharpless epoxidation, we could prepare in each cases all the four possible stereomers with high optical purity. (In the following development, we have only carried out the asymmetric epoxidation with (+) DIPT of the *E*-vinylsilane **3**).

Oxidation of **4** by using the Swern procedure[13] or the SO_3-pyridine method[14] delivered the epoxyaldehydes **5** which were readily transformed into the desired vinyloxiranes. The efficiency of this sequence is remarkable : for instance, the preparation of **1a** was performed in five steps from the commercially available tetrahydropyranyl propargyl ether in 43 % overall yield. It is noteworthy that compounds **1** were obtained in enantiomeric excesses varying from 85 % for **1f** to 98 % in the case of **1a** (enantiomeric excesses were determined onto **4**, **5** and **1** by NMR measurements using either Mosher reagents[15] or the chiral shift reagent (tri[3-heptafluoropropyl-hydroxymethylene]-d-camphorato)europium (III) $[Eu(hfc)_3]$.

Surprisingly, if few methods for the selective preparation of *E* and *Z* trisubstituted vinylsilane allylic alcohols have been recorded,[16] they have never been applied to the synthesis of *E*-3-trialkylsilyl-2-methyl-2-propen-1-ol like **3g**. We thus developed a short and efficient synthesis of **1g** (scheme 2). The silyl allyl carbanion generated from the known (2-methylallyl)-*tert*-butyldimethylsilane **6**,[17] reacted with alkoxychlorosilane to regioselectively afford the vinylsilane **7** as the pure *E* isomer. A consecutive chemoselective Tamao oxidation[18] yielded the allylic alcohol **3g** in a 73 % overall yield.



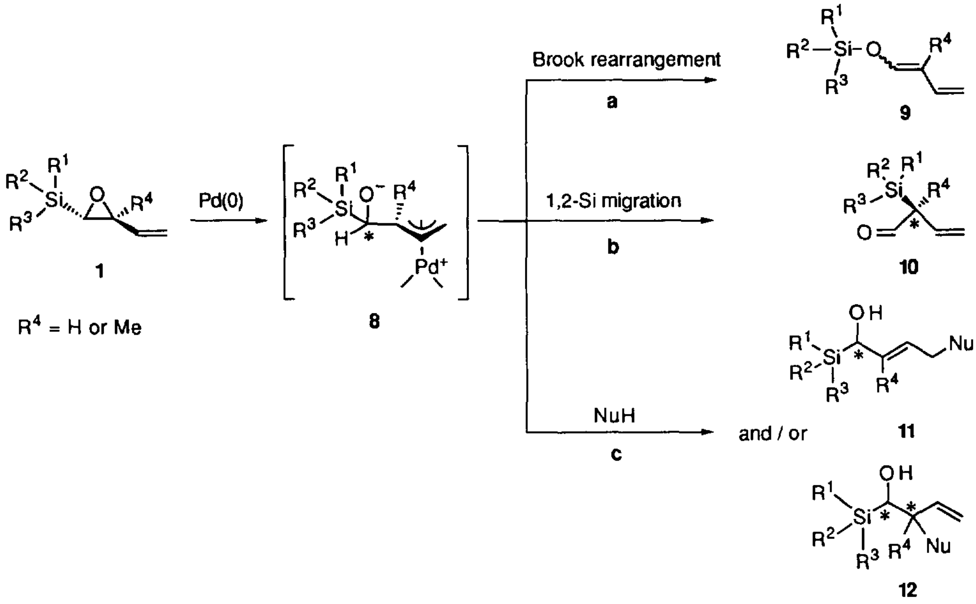
a) *t*-$BuMe_2SiCl$, Mg, THF, 62% ; b) *n*-BuLi/*t*-BuOK, $ClSi(Me)_2OMe$, Et_2O ; c) H_2O_2, $KHCO_3$, MeOH, THF, 73% ; d) L-(+)-DIPT, $Ti(O\text{-}i\text{-}Pr)_4$, *t*-BuOOH, CH_2Cl_2, 78% ; e) DMSO, Et_3N, CH_2Cl_2, 67% ; f) $Ph_3P^+\text{-}CH_3$, Br^-, $NaOC(CH_3)_2C_2H_5$, benzene, 81%

Scheme 2

Following the same procedure as above the vinylepoxide **1g** was obtained from glycidol **4g** in very high yields. The enantiomeric excess of **4g** was determined to be 98 %.

B- The 1,2-Carbon to Carbon-Silyl Migration. New Palladium Catalyzed Rearrangement

Having these silicon substituted vinyloxiranes in hand, we started the studies of their behavior in the presence of catalytic amount of palladium zerovalent complexes. Oxidative addition of such a partner onto the metal catalyst would deliver a π-allyl palladium complex intermediate which could evolve *a priori* following three different pathways, as shown in Scheme 3.



Scheme 3

In pathway **a**, we envisaged the Brook rearrangement[19] which involves an intramolecular 1,2-migration of silicon from carbon to oxygen to lead the dienolether **9**. In this process, the initial stereogenic center has been destroyed. On the other hand, if for steric or electronic reasons direct attack of the oxyanion onto the silicon atom was forbidden, and due to the strong electrophilic character of the π-allyl moiety, we could observe (pathway **b**) a more interesting synthetic route consisting in a new 1,2-silicon migration from carbon to carbon. This would deliver the very synthetically promising β,γ-unsaturated aldehyde having a new silicon substituted stereogenic center in the α-position. This derivative exhibits several advantages : its ambident character could allow very useful synthetic transformation by sequential and judicious addition of electrophilic and nucleophilic reagents ; in addition, we could expect high 1,2-asymmetric induction to occur on both the carbonyl and the carbon-carbon double bond, thus allowing the preparation of useful synthetic frameworks with at least three contiguous stereogenic centers formed in a stereoselective manner (Scheme 4).

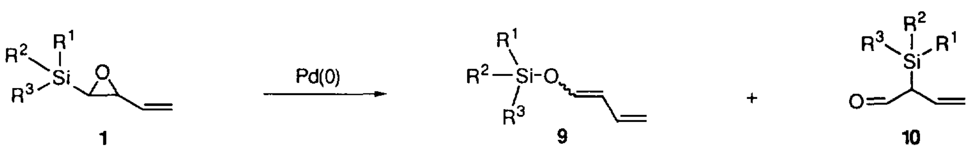
Scheme 4

It is also obvious that the presence of an allylsilane appendage could offer the opportunity to realize stereoselective Sakurai reaction.[20] Finally, in case we found conditions where the π-allyl palladium complex **8** should be stable enough, we could expect addition of external nucleophiles in very mild conditions.

Herein, we will describe the results of our studies devoted to the formation, characterization and illustration of the synthetic utility of compounds **10**.

Exposure of **1a-f** to a catalytic amount of palladium zerovalent species generated *in situ* from 5 mol % of palladium acetate and 20 mol % of triisopropylphosphite in tetrahydrofuran at room temperature afforded in good to excellent chemical yield the adducts **9** and **10**, as summarized in table 1.

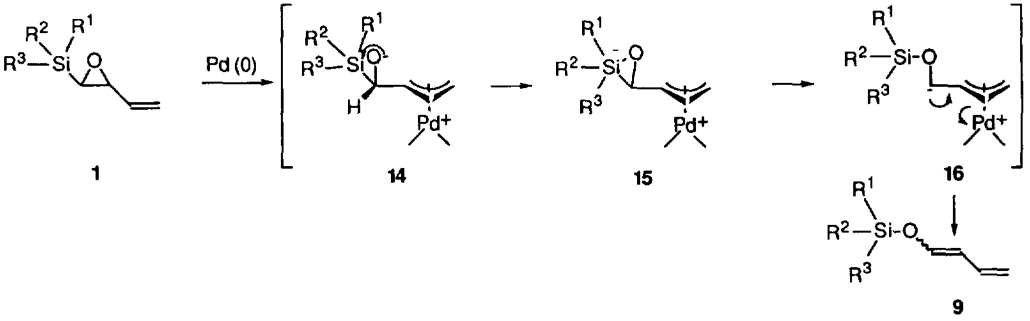
Table 1 : Pd(0)-Rearrangement of Vinyloxiranes **1a-f**



Entry	Compound	R^1	R^2	R^3	9 (%)	10 (%)
1	**1a**	Me	Me	*t*-Bu	-	85
2	**1b**	Me	Me	Me	traces[a]	-
3	**1c**	Me	Me	Ph	67	-
4	**1d**	Et	Et	Et	35[a]	-
5	**1e**	*i*-Pr	*i*-Pr	*i*-Pr	-	81
6	**1f**	Ph	Ph	*t*-Bu	26	71

(a) due to the volatility of the compounds, the yields are low

When the substituents on the silicon atom are *i*-propyl or when a *t*-butyl is present, we were pleased to observe exclusively or mainly the formation of aldehydes **10**. In contrast, vinyloxiranes **1b**, **1c** and **1d** yielded exclusively the corresponding silyldienolethers resulting from the Brook rearrangement. The difference of behavior between these two groups of epoxides could be explained in terms of steric hindrance. As suggested, the Brook rearrangement seems to proceed *via* a pentavalent sp^3d-hybridized silicon intermediate,[21] whose formation in our case is avoided or by a very minor pathway formed, when bulky substituents (like *t*-Bu or *i*-Pr) are present (Scheme 5).



Scheme 5

In entry 6, the minor formation of dienolether may be explained by the stabilization effect of the phenyl groups onto the anionic silicon pentavalent intermediate **15**.

In a typical experiment, after simple filtration of the crude reaction mixture, the isolated aldehyde **10a** was optically active ($[\alpha]_D^{20}$ -40.8 [c = 6.05, EtOH]) meaning that the migration of silicon proceeded with some degree of chirality transfer. But this sort of compound is relatively sensitive to racemization : when **10a** was kept in ether solution at room temperature, the racemization was complete after 48 hours. Because of this problem, we failed to determine the optical purity of **10a**.

In order to circumvent this difficulty, we studied the migration of the silicon group with substrate **1g**. This enantiomerically pure vinyloxirane ($[\alpha]_D^{20}$-6.8 [c = 8.05, EtOH]) was subjected to the palladium catalyzed reaction as described above. The thus generated (π-allyl)-palladium complex intermediate produced aldehyde **10g** ($[\alpha]_D^{20}$ +42.1 [c = 10.2, EtOH]) in 87 % yield. The 1,2-carbon to carbon-silicon shift was here again the exclusive pathway. In this case, as a consequence of the presence of a quaternary stereogenic center, racemization due to an acid or base catalyzed enolization of the present aldehyde was excluded. Compound **10g** was reduced into the corresponding primary alcohol and its enantiomeric excess was determined by ^{1}H and ^{13}C-NMR analyses of Mosher's ester[15] to be 77%. We also demonstrated that this epoxide **1g** was very acid sensitive : in the presence of catalytic amount of *para*-toluenesulfonic acid in a dichloromethane solution it rearranged, albeit in a low chemical yield, to the aldehyde **10g** as the optical antipode ($[\alpha]_D^{20}$-36.9 [c = 6.05, EtOH]). This result drived us to consider that this could be the competitive pathway explaining that the chirality transfer was only 77% and unambiguously demonstrated the dramatic influence of the metal in the rearrangement as well as its stereoselectivity.

Having in mind that in addition to the steric effects of the substituents on the silicon atom, the competition between palladium(0)-catalyzed 1,2-carbon to carbon shift and Brook rearrangement as well as the stereoselectivity could be influenced by electronic effects induced by the metal ligands, we undertook a study in presence of various phosphorous and nitrogen derivatives in the case of vinyloxirane **1f**.

Table 2 : Influence of the Ligands in the Pd-Catalyzed Rearrangement of Vinyloxirane **1f**.

Entry	Ligand	9f^a (%)	10f^a %)	T (° C)	Time (h)
1	TMEDA^b	78	2	67	12
2	dppe^b	66	13	67	60
3	PBu_3	73	16	25	3
4	PPh_3^{b}	39	33	67	12
5	$P(OEt)_3$	41	40	25	3
6	$P(OMe)_3$	31	51	25	3
7	$P(O$*i*$-Pr)_3$	26	71	25	3
8	$P(OCH_2)_3CEt$	24	64	25	3
9	$P(OPh)_3$^{b}	-	90	41	3

(a) Isolated yields after flash chromatography on silica gel ; (b) no reaction occured at 25 °C within 2 hours

Exposure of racemic vinyloxirane **1f** to a catalytic amount of palladium zerovalent species generated *in situ* from 2.6 mol % of palladium acetate and 16 mol % of various ligands, in tetrahydrofuran at different temperatures and reaction times afforded the two rearranged products **9** and **10** in good chemical yields as summarized in table 2.

We observed an interesting change in the product distribution from tetramethylethylenediamine (TMEDA) to triphenylphosphite ($P(OPh)_3$), which can be explained in terms of more or less acceptor properties of the ligands. It is noteworthy that with this electron-acceptor ligands the unique product isolated was the aldehyde **10f**. Åkermark and Vitagliano[22] showed by ^{13}C-NMR measurements that the three carbon atoms of (η^3-allyl) palladium systems were electronically affected by a variation of ligands (Scheme 6).

Scheme 6

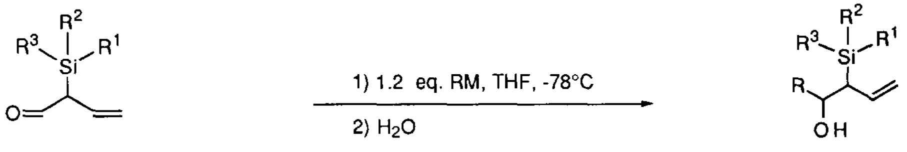
The electronic distribution is responsible for the regioselectivity in the nucleophilic attack of both amines and malonate anions. Acceptor ligands like $P(OPh)_3$ induce greater positive charge at the more substituted (η^3-allyl)-terminus. In this case, the electronic factor predominates and the nucleophilic attack will preferentially occur on this site. Donor ligands like TMEDA contribute to eliminate the difference in electrophilic character between the termini and the steric effect predominates resulting in a higher proportion of nucleophilic attack at the least substituted carbon atom. In our case, the sole effect to consider is the growth in electropositive charge induced on the proximal position of the intermediate which reinforce the 1,2 migration of the « nucleophile » silicon group to the detriment of the Brook rearrangement. Except for PPh$_3$ which should be a more acceptor ligand than P(OMe)$_3$ our results are in good agreement with this Åkermark classification. The best acceptor ligand P(OPh)$_3$ induced the highest degree in the 1,2-carbon to carbon -silicon shift (with the same level of chirality transfer as we will described *infra*) whereas the more donor ligand, TMEDA, was found to favor the Brook rearrangement.

This study led us to find optimized conditions to achieve this new rearrangement in the case where substituents present on the silicon atom allow a possible stereoselective oxidation of the carbon-silicon bond, in order to increase its synthetic usefulness.

C- Stereoselective 'One-Pot' Addition of Nucleophiles

Simple α-trialkylsilylaldehydes[23] possessing crowded silyl groups have been already described but few examples concerning their reactions with organometallic reagents have been reported.(24,25) We previously mentionned that this new class of aldehydes **10** is very sensitive to enolization. Indeed in our initial study, we found that at 0°C nucleophiles like organolithium and Grignard reagents acted as bases and only untractable materials were obtained. However, we showed that the less basic and highly carbonylophile organozirconium reagents[26] could achieve the addition on the carbonyl group albeit in moderate chemical yield (47%) but with a high degree of diastereoselectivity. However, in order to disclose more practical conditions, we eventually found that at lower temperature (-78°C) aldehydes **10** react with 1.2 equivalents of organolithium and Grignard reagents in tetrahydrofuran to furnish the corresponding alcohols **17** in very good yield and with an extremely high level of diastereoselectivity as outlined in table 3.

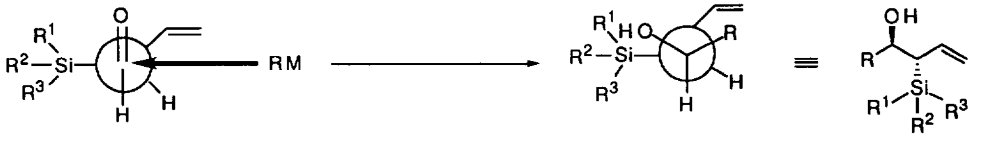
Table 3 : Addition of Organometallic Reagents on Aldehydes **10a** and **10e**.



10a, 10e **17a, 17e**

		17a ($R^1 = R^2$ = Me; R^3 = *t*-Bu)		17e ($R^1 = R^2 = R^3$ = *i*-Pr)	
Entry	**RM**	**yield (%)**	**de (%)**	**yield (%)**	**de (%)**
1	MeLi	67	98	63	98
2	*n*-BuLi	82	98	94	98
3	*t*-BuLi	94	98	84	98
4	PhLi	-	-	88	87
5	CH_2=CH-MgBr	92	76	90	54

Interestingly, no enolization and no decomposition arose at -78°C. In good agreement with the literature,[23] the diastereoselectivity observed resulted of the preferred addition of the nucleophile *anti* to the silicon group, according to the Felkin model[27] (Scheme 7).



10a, 10e **17a, 17e**

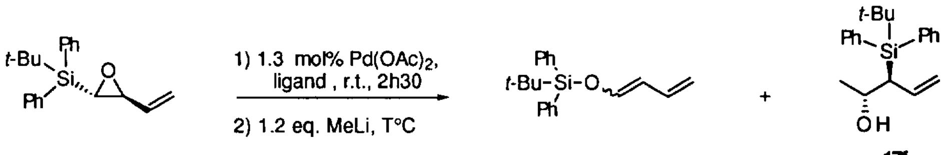
Scheme 7

When less sterically demanding groups like vinyl Grignard or phenyllithium were used, the diastereomeric excess decreased. In addition and more interestingly, we found that both reactions, 1,2-carbon to carbon-silyl migration and addition of nucleophiles could be suitably performed in a one-pot sequence. Thus, the treatment of vinyloxirane **1a** with a catalytic amount of palladium zerovalent complex (generated *in situ* from 1 mol% of $Pd(OAc)_2$ and 4 mol % of $P(Oi\text{-}Pr)_3$) at room temperature followed by addition of 1.2 equivalents of methyllithium, at -78°C, led to the alcohol **17a** in 49% chemical yield and with a diastereomeric excess as high as 98%.

The finding of this new cascade process offered us the opportunity to use the chirality transfer with optimized chances of success.

For synthetic purposes, we then performed the reaction with the vinylepoxide **1f** because the presence of a phenyl group is necessary for the transformation of a silyl group into a hydroxyl group by Fleming oxidation[28] and in addition, the presence of the *tert*-butyl group associated with judicious choice of ligands could impede the Brook rearrangement. The enantiomeric excess of **1f** was found to be 85% by NMR measurements using the chiral shift reagent $Eu(hfc)_3$. The tandem sequence 1,2-migration-addition of nucleophile was performed using the procedure described precedently, the results are presented in table 4.

Table 4 : Enantioselective Cascade Process



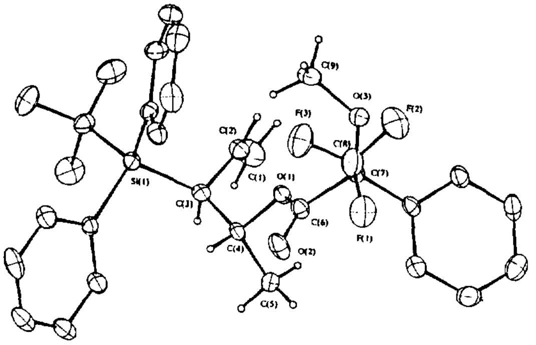
1f **9f** **17f**

T^a (°C)	Ligand	**9f** (%)	**17f** (%)	$[\alpha]_D^{20}$ (c, solv.)	ee (%)
-78	$P(Oi\text{-}Pr)_3$	27	49	30.6 (17, $CHCl_3$)	55
-100	$P(Oi\text{-}Pr)_3$	28	55	48.8 (18, $CHCl_3$)	85
-100	$P(OPh)_3$	-	81	48.9 (15, $CHCl_3$)	85

(a) temperature of the cooling bath.

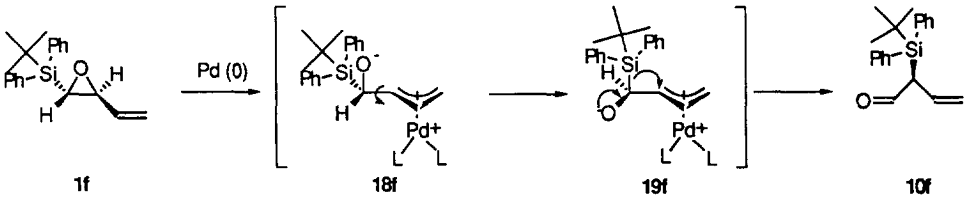
In addition of the ligand effect already disclosed, we showed that the temperature has a dramatic influence on the enantiomeric excess. Indeed at -78°C, the ee of the alcohol **17f**, after its transformation to Mosher ester was typically 55% suggesting a partial racemization of the intermediate aldehyde **10f** which is quite prone to enolization. To insure a complete transfer of chirality, it was necessary to carry out the tandem reaction at -100°C : the enantiomeric excess was found to be essentially identical, within experimental error, with that of the starting vinyloxirane. Besides, we noticed that when aldehyde **10f** was readily separated from the Brook rearrangement adduct **9f** by flash chromatography immediately before adding the nucleophile, the enantiomeric excess fell to an average of 15% confirming the easiness of racemization of this aldehyde.

Finally, the X-ray crystal structure analysis of the major diastereomer of the Mosher ester of **17f** allowed us to determine the absolute configuration of the newly generated stereogenic centers which was found to be 2R, 3S (Scheme 8).



Scheme 8

To conclude, on the basis of the complete chirality transfer here observed and the diastereoselective addition of nucleophile which results from the preferred addition *anti* to the silicon group, according to the Felkin model,[27] we were now authorized to propose the following mechanistic pathway for this Pd(0)-catalyzed rearrangement of vinyloxiranes (Scheme 9).



Scheme 9

The π-allyl palladium complex intermediate was formed by oxidative addition of the vinyloxirane (with the *s-trans* conformation) to palladium(0) with inversion.[29] The steric interaction between the silicon and the palladium would favor the rotation around the carbon-carbon bond to the **19f** conformation and furthermore the silylated group would attack *anti* to the metal. As unambiguously confirmed by the X-ray crystallography data, the stereochemistry of the newly generated stereogenic center : net retention resulted from this double inversion pathway.

CONCLUSION

Palladium zerovalent complex proved to be very efficient catalyst for this unprecedented vinyloxirane rearrangement leading to a new class of carbonyl derivatives : α-silyl-β,γ-unsaturated aldehydes having an interesting ambident character. We have found that ligands on the metal have a tremendous effect on this rearrangement.

A one-pot process : Pd-catalyzed-1,2 rearrangement in tandem with a total diastereoselective addition of organometallic derivatives offered a new entry to synthetic useful homoallylic alcohols[30] having silicon substituted stereogenic center in the allylic position. A dramatic temperature effect allowed this cascade process to proceed with a total chirality transfer .

Finally, synthetic application of this sequence is under active investigation in our laboratory.

EXPERIMENTAL SECTION

^{1}H-NMR and ^{13}C-NMR spectra were taken on 200 MHz Bruker AC 200, 400 MHz JEOL 65X 400 and Bruker ARX 400 spectrometers. Chemical shifts are reported in ppm referenced to the residual proton resonances of the solvants. Infrared (IR) spectra were recorded by using a Perkin Elmer 1420 spectrometer. Mass spectra (MS) were obtained on GC-MS Hewlett-Packard HP 5971 apparatus. Melting points were measured on a Büchi B-510 apparatus and were uncorrected. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F 254. Silica gel Merck Geduran SI (40-63 µm) was used for column chromatography using Still method.[31]

A- Preparation of Vinyloxiranes 1a-g

1) General Procedure for the preparation of the silylated propargylic alcohols 2 a-f: At -78°C, *n*-butyllithium (1,55 M in hexane ; 68 mmol) was added dropwise to a solution of 3-tetrahydropyranyloxy-prop-1-yne (9.45 g ; 68 mmol) in THF (120 mL). After being stirred at -78°C for 30 min, a solution of the silyl chloride (68 mmol) in THF (40 mL) was added dropwise. The resulting mixture was refluxed for 19h, cooled to room temperature and diluted with ether (200 mL). The organic layer was washed successively with a saturated solution of NH_4Cl (400 mL) and brine (200 mL), dried over Na_2SO_4, filtered and concentrated. The crude residue was dissolved in MeOH (135 mL) and *p*-toluenesulfonic acid (1.35 g) was added. After being stirred for 2-3 h (the completion of the reaction was evidenced by TLC) at room temperature, the reaction mixture was hydrolyzed with a saturated solution of $NaHCO_3$ (200 mL) and extracted with ether (250 mL). The organic layer was washed with brine (2x100 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the residue by flash chromatography (petroleum ether/ether = 90/10) afforded the silylated propargylic alcohols.

3-*tert*-Butyldimethylsilyl-prop-2-yn-1-ol (2a) $R^1 = R^2 = Me$, $R^3 = t$-Bu, 11.6 g, 100%.[32]

3-Trimethylsilyl-prop-2-yn-1-ol (2b) $R^1 = R^2 = R^3 = Me$, 6.8 g, 100%.[33]

3-Dimethylphenylsilyl-prop-2-yn-1-ol (2c) $R^1 = R^2 = Me$, $R^3 = Ph$, 11.4 g, 88%.[32]

3-Triethylsilyl-prop-2-yn-1-ol (2d) $R^1 = R^2 = R^3$ = Et, 11.6 g, 100% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.25 (d, *J* = 5.8 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 9H), 0.58 (q, *J* = 7.5 Hz, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 104.9, 87.7, 51.3, 7.2, 4.1 ; IR (neat) 3300, 2940, 2160, 1460, 1040, 880 cm^{-1}.

3-Triisopropylsilyl-prop-2-yn-1-ol (2e) $R^1 = R^2 = R^3$ = *i*-Pr, 13 g, 87% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.29 (d, *J* = 6.0 Hz, 2H), 1.10-1.02 (m, 21H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 105.7, 86.8, 51.7, 18.5, 11.1 ; IR (neat) 3300, 2940, 2160, 1460, 1040, 880 cm^{-1}. MS (*m/z*) 212, 169, 14. Anal Calcd for $C_{12}H_{24}OSi$: C, 67.85 ; H, 11.39. Found : C, 67.76 ; H, 11.41.

3-*tert*-Butyldiphenylsilyl-prop-2-yn-1-ol (2f) $R^1 = R^2$= Ph, R^3 = *t*-Bu, 18.4 g, 92% ; ^{1}H-NMR (400 Mhz, $CDCl_3$) δ 7.79-7.74 (m, 2H), 7.40-7.30 (m, 3H), 4.42 (s, 2H), 1.08 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 135.5, 133.0, 129.6, 127.7, 107.9, 86.0, 51.8, 27.0, 18.4 ; IR (neat) 3350, 3060, 3040, 2940, 2160, 1420, 1360, 1100, 1030, 815 cm^{-1}.

2) *Preparation of the silylated allylic alcohols 3a-g.* General procedure for 3a-f : To a cooled (0°C), stirred solution of Red-Al (65% wt, 16.6 g, 53.5 mmol) in toluene was added dropwise a solution of the silylated propargylic alcohol (33.5 mmol) in ether (23 mL). The rate of the addition was controlled so that the temperature was maintained above 5°C. After being stirred at room temperature for 3 h, the reaction mixture was cooled at 0°C and H_2SO_4 (3.6 M, 100 mL) was carefully added dropwise. The reaction mixture was extracted with ether (4x100 mL) and washed with brine (4x80 mL), dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography (petroleum ether/ether = 80/20) afforded the corresponding *trans*-allylic alcohols.

(*E*) 3-*tert*-Butyldimethylsilyl-prop-2-en-1-ol (3a) $R^1 = R^2$ = Me, R^3 = *t*-Bu, R^4 = H, 4.91 g, 85%.[32]

(*E*) 3-Trimethylsilyl-prop-2-en-1-ol (3b) $R^1 = R^2 = R^3$ = Me, R^4 = H, 4.05 g, 93% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.15 (dt, *J* = 18.5, 4.5 Hz, 1H), 5.88 (dt, *J* = 18.5, 1.5 Hz, 1H), 4.13 (dd, *J* = 4.5, 1.5 Hz, 2H), 0.04 (s, 9H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 144.9, 129.8, 65.1, −1.0 ; IR (neat) 3300, 2940, 1615, 1240, 975, 860 cm^{-1}.

(*E*) 3-Dimethylphenylsilyl-prop-2-en-1-ol (3c) $R^1 = R^2$ = Me, R^3= Ph, R^4 = H, 5.73 g, 89%.[32]

(*E*) 3-Triethylsilyl-prop-2-en-1-ol (3d) $R^1 = R^2 = R^3$ = Et, R^4 = H, 4.73 g, 82% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.18 (dt, *J* = 19.1, 4.3 Hz, 1H), 5.83 (dt, *J* = 19.1, 1.8 Hz, 1H), 4.17 (d, *J* = 4.3 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 9H), 0.55 (q, *J* = 7.5 Hz, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 146.2, 125.6, 65.6, 7.1, 3.3 ; IR (neat) 3300, 2940, 1620, 1450, 1230, 1070, 1000 cm^{-1}.

(*E*) 3-Triisopropylsilyl-prop-2-en-1-ol (3e) $R^1 = R^2 = R^3$ = *i*-Pr, R^4 = H, 6.3 g, 88% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.24 (dt, *J* = 19.2, 4.4 Hz, 1H), 5.80 (dt, *J* = 19.2, 1.8 Hz, 1H), 4.28 (m, 2H), 1.25-1.10 (m, 21H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 146.9, 123.5, 65.9, 18.6, 10.8 ; IR (neat) 3300, 2940, 1620, 1460, 990, 880cm^{-1}. MS (*m/z*) 214, 171, 143, 129 ; Anal Calcd for $C_{12}H_{26}OSi$: C, 67.21; H, 12.22. Found : C, 67.14; H, 12.25.

(*E*) 3-*tert*-Butyldiphenylsilyl-prop-2-en-1-ol (3f) R^1 = R^2 = Ph, R^3 =*t*-Bu, R^4 = H, 9.44 g, 95% ; white solid, m.p. = 61°C ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60-7.50 (m, 4H), 7.40-7.25 (m, 6H), 6.28 (dt, *J* = 18.7, 1.5 Hz, 1H), 6.15 (dt, *J* = 18.7, 3.8 Hz, 1H), 4.25 (dd, *J* = 3.8, 1.5 Hz, 2H), 1.05 (s, 9H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 150.3, 136.1, 134.4, 129.1, 127.5, 122.1, 65.2, 27.7, 18.0 ; IR (neat) 3600, 3400, 3060, 3000, 2960, 1640, 1420, 1170, 1100, 990 cm^{-1}.

Preparation of **3g** : i) A THF (32 mL) solution of 3-chloro-2-methyl-prop-1-ene (5.64 mL, 57.1 mmol) and *tert*-butyldimethylsilyl chloride (6.47 g, 42.9 mmol) was added dropwise over 3 hours to a suspension of magnesium (1.39 g, 57.1 mmol) and some drops of 1,2-dibromoethane in THF (3 mL). The resulting mixture was heated at reflux for 15 h, cooled to room temperature diluted with ether (100 mL) and poured in H_2O. The organic layer was washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (pentane) afforded (2-methylallyl)-*tert*-butyldimethylsilane **6** (6.30 g, 86%) ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.59 (m, 1H), 4.49 (m, 1H), 1.71 (br t, 3H), 1.54 (br s, 2H), 0.89 (s, 9H), -0.02 (s, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 144.0, 108.1, 26.2, 24.9, 24.0, 16.9, −6.0 ; IR (neat) 3070, 2950, 2920, 2850, 1670, 1465, 1370, 1360, 1250, 865, 835 cm^{-1}. ii) *n*-butyllithium (24.5 mL, 39.2 mmol, 1.6 M in hexane) was added to a cooled (0°C) suspension of potassium *tert*-butoxide (4.40 g, 39.2 mmol) in hexane (30 mL). After being cooled to -78°C, ether (20 mL) and a solution of **6** (6.07 g, 35.6 mmol) in ether (20 mL) were added successively. The reaction mixture was warmed to room temperature and stirred for 4h. The solution was then cooled to -78°C and dimethylmethoxysilyl chloride (5.1 mL, 39.2 mmol) was added. The reaction mixture was stirred at -78°C for 2h and 90 min further at room temperature, diluted with ether (100 mL). The organic layer was washed with saturated solution of NH_4Cl and brine, dried (Na_2SO_4), filtered and concentrated. The crude product **7** was used in the next step without purification. iii) Hydrogen peroxide (43.6 mL, 427.2 mmol, 30% wt in H_2O) was added to a solution of **7** in MeOH (150 mL), THF (150 mL) in presence of $KHCO_3$ (10.69 g, 106.8 mmol). The mixture was heated at reflux for 1h, diluted with ether, washed with 10% $NaHSO_3$ aqueous solution and brine, dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (petroleum ether/ether = 70/30) furnished **(*E*) 3-*tert*-Butyldimethylsilyl-2-methyl-prop-2-en-1-ol (3g)** R^1 = R^2 = Me, R^3 = *t*-Bu, R^4 = Me, 4.84 g, 73% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.52 (s, 1H), 4.02 (s, 1H), 1.77 (s, 3H), 0.87 (s, 9H), 0.09 (s, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 154.1, 118.5, 68.9, 26.3, 18.5, 16.8, −4.1; IR (neat) 3370, 2940, 2920, 1660, 1460, 1370, 1245, 830 cm^{-1}. Anal Calcd for $C_{10}H_{22}OSi$: C, 64.44 ; H, 11.90. Found : C, 64.31 ; H, 11.91.

3) General procedure for the preparation of the silylated epoxyalcohols ***4a-g***. Catalytic enantioselective epoxidation : The reaction was carried out in a flame-dried flask, under argon. To a cooled (-20°C), stirred suspension of molecular sieves in powder (4 Å ; 600 mg ; dried 12h at 250°C under 2 mm Hg) in CH_2Cl_2 (75 mL) was added titanium (IV) isopropoxide (0.426 g, 1.5 mmol) and (+) diisopropyl tartrate (0.387 g, 1.85 mmol). After being stirred for 30 min, *tert*-butyl hydroperoxide (3M in isooctane, 46 mmol) and 5 min after, a solution of allylic alcohol (15 mmol) in CH_2Cl_2 (25 mL) were added dropwise and the stirring was maintained, at -20°C, for 48 h. At -20°C, the reaction mixture was diluted with ether (100 mL), hydrolyzed with a saturated solution of Na_2SO_4 (2 mL), warmed up to room temperature and stirred for 1 h, filtered on celite and concentrated. The crude residue was purified by flash chromatography (petroleum ether/ether = 50/50) and afforded the silylated epoxyalcohols. Racemic epoxidation : At room temperature, to a stirred solution of silylated allylic alcohol (15 mmol) in CH_2Cl_2 (60 mL) was added MCPBA (5.17 g, 30 mmol). After being stirred at room temperature for 90 min, the reaction mixture was diluted with CH_2Cl_2 and neutralized with saturated solution of $NaHCO_3$. The organic layer was washed with brine, dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (petroleum ether/ether = 50/50) gave the corresponding silylated epoxyalcohols.

(2S, 3S) 3-*tert*-Butyldimethylsilyl-2,3-epoxy-propan-1-ol (4a) $R^1 = R^2 =$ Me, $R^3 =$ *t*-Bu, $R^4 =$ H, 2.43 g, 86% ; $[\alpha]_D^{20}$ -26.9 (c = 11.85, $CHCl_3$).[32]

2,3-Epoxy-3-trimethylsilyl-propan-1-ol (4b) $R^1 = R^2 = R^3 =$ Me, $R^4 =$ H, 1.15 g, 52% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.98 (br d, *J* = 12.0 Hz, 1H), 3.58 (br d, *J* = 12.0 Hz, 1H), 3.02 (m, 1H), 2.27 (d, *J* = 4.0 Hz, 1H), 0.03 (s, 9H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 63.0, 56.1, 48.0, -4.0 ; IR (neat) 3400, 2950, 1245, 1050, 835 cm^{-1}.

(2S, 3S) 3-Dimethylphenylsilyl-2,3-epoxy-propan-1-ol (4c) $R^1 = R^2 =$ Me, $R^3 =$ Ph, $R^4 =$ H, 2.25 g, 71% ; $[\alpha]_D^{20}$ -11.6 (c = 12.85, $CHCl_3$).[32]

2,3-Epoxy-3-triethylsilyl-propan-1-ol (4d) $R^1 = R^2 = R^3 =$ Et, $R^4 =$ H, 2.6 g, 92% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.96 (dd, *J* = 12.6, 2.2 Hz, 1H), 3.52 (dd, *J* = 12.6, 4.9 Hz, 1H), 3.05 (m, 1H), 2.29 (d, *J* = 3.8 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 9H), 0.57 (q, *J* = 7.4 Hz, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 63.6, 55.7, 46.6, 7.1, 1.7; IR (neat) 3380, 2940, 1450, 1050, 860 cm^{-1}.

(2S, 3S) 2,3-Epoxy-3-triisopropylsilyl-propan-1-ol (4e) $R^1 = R^2 = R^3 =$ *i*-Pr, $R^4 =$ H, 3.11 g, 90% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.98 (ddd, *J* = 12.1, 6.1, 2.2 Hz, 1H), 3.55 (ddd, *J* = 12.1, 6.1, 5.0 Hz, 1H), 3.16 (ddd, *J* = 5.0, 3.9, 2.2 Hz, 1H), 2.34 (d, *J* = 3.9 Hz, 1H), 1.15-1.00 (m, 21H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 63.7, 55.5, 46.2, 18.5, 10.4 ; IR (neat) 3400, 2940, 1460, 1050, 880 cm^{-1}. MS (*m/z*) 230, 187, 131, 103, 75, 61. Anal Calcd for $C_{12}H_{26}O_2Si$: C, 62.55 ; H,11.37. Found : C, 62.59 ; H, 11.48. $[\alpha]_D^{20}$-15.01 (c = 12.85, $CHCl_3$).

(2S, 3S) 3-*tert*-Butyldiphenylsilyl-2,3-epoxy-propan-1-ol (4f) $R^1 = R^2 = Ph$, $R^3 = t$-Bu, $R^4 = H$, 4.12 g, 88% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.63-7.56 (m, 4H), 7.47-7.31 (m, 6H), 3.99 (ddd, *J* = 12.6, 5.3, 2.2 Hz, 1H), 3.67 (ddd, *J* = 12.6, 7.3, 4.1 Hz, 1H), 2.91-2.85 (m, 2H), 1.18 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.0, 135.9, 132.2, 131.9, 129.8, 129.7, 127.9, 127.7, 62.7, 55.6, 45.1, 27.8 , 18.6 ; IR (neat) cm^{-1}. $[\alpha]_D^{20}$ -25.0 (c = 19.00, $CHCl_3$).

(2S, 3S) 3-*tert*-Butyldimethylsilyl-2,3-epoxy-2-methyl-propan-1-ol (4g) $R^1 = R^2 = Me$, $R^3 = t$-Bu, $R^4 = Me$, 2.36 g, 78% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.68 (d, *J* = 12.0 Hz, 1H), 3.54 (d, *J* = 12.0 Hz, 1H), 2.45 (s, 1H), 1.32 (s, 3H), 0.95 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 66.5, 61.3, 51.9, 26.5, 17.5, 16.9, –5.9, –6.5 ; IR (neat) 3410, 2950, 1465, 1385, 1360, 1030, 830 cm^{-1}. Anal Calcd for $C_{10}H_{22}O_2Si$: C, 59.35 ; H, 10.96. Found : C, 59.04 ; H, 10.91. $[\alpha]_D^{20}$-24.9 (c = 9.55, $CHCl_3$).

4) General procedure for the preparation of the silylated epoxyaldehydes 5a-g: Dimethylsulfoxide (14.2 mL, 200 mmol), sulfur trioxide pyridine complex (4.78 g, 30 mmol), triethylamine (13.9 mL, 100 mmol) and the silylated epoxyalcohol (10 mmol) in CH_2Cl_2 (15 mL) were stirred, at room temperature, for 2 h. The reaction mixture was diluted with CH_2Cl_2, washed with a saturated solution of NH_4Cl and brine, dried (Na_2SO_4) and concentrated. Purification by flash chromatography (petroleum ether/ether = 90/10) yielded the corresponding silylated epoxyaldehydes.

(2S, 3S) 3-*tert*-Butyldimethylsilyl-2,3-epoxy-propan-1-al (5a) $R^1 = R^2 = Me$, $R^3 = t$-Bu, $R^4 = H$, 1.68 g, 90% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.80 (d, *J* = 6.5 Hz, 1H), 3.14 (dd, *J* = 6.5, 3.5 Hz, 1H), 2.54 (d, *J* = 3.5 Hz, 1H), 0.95 (s, 9H), -0.02 (s, 3H), -0.03 (s, 3H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 200.0, 56.1, 46.0, 25.9, 17.1, -8.0, -8.5 ; IR (neat) 2950, 1730, 1470, 1250, 1030, 840 cm^{-1}. Anal Calcd for $C_9H_{18}O_2Si$: C, 58.01 ; H, 9.74.Found : C, 57.62 ; H, 9.49.

2,3-Epoxy-3-trimethylsilyl-propan-1-al (5b) $R^1 = R^2 = R^3 = Me$, $R^4 = H$, 1.20g, 82% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 6.5 Hz, 1H), 3.11 (dd, *J* = 6.5, 3.5 Hz, 1H), 2.47 (d, *J* = 3.5 Hz, 1H), 0.07 (s, 9H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 199.0, 56.1, 47.9, -4.0 ; IR (neat) 2940, 1725, 1245, 1025, 870, 840 cm^{-1}.

(2S, 3S) 3-Dimethylphenylsilyl-2,3-epoxy-propan-1-al (5c) $R^1 = R^2 = Me$, $R^3 = Ph$, $R^4 = H$, 1.96 g, 95% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.82 (d, *J* = 6.5 Hz, 1H), 7.56-7.52 (m, 2H), 7.43-7.37 (m, 3H), 3.15 (dd, *J* = 6.5, 3.5 Hz, 1H), 2.67 (d, *J* = 3.5 Hz, 1H), 0.42 (s, 3H), 0.39 (s, 3H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 198.3, 134.5, 134.0, 129.9, 128.1, 56.1, 48.0, -5.0 ; IR (neat) 3060, 2950, 1720, 1420, 1245, 1025, 830 cm^{-1}.

2,3-Epoxy-3-triethylsilyl-propan-1-al (5d) $R^1 = R^2 = R^3 = Et$, $R^4 = H$, 1.23 g, 86% ; ^1H-NMR (200 MHz, $CDCl_3$) δ 8.75 (d, *J* = 6.6 Hz, 1H), 3.16 (dd, *J* = 6.6, 3.4 Hz, 1H), 2.51 (d, *J* = 3.4 Hz, 1H), 0.95 (t, *J* = 7.7 Hz, 9H), 0.60 (q, *J* = 7.7 Hz, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 198.8, 56.1, 46.6, 7.1, 1.8 ; IR (neat) 2940, 1725, 1450, 1260, 1210, 1140, 1000, 850 cm^{-1}.

(2S, 3S) 2,3-Epoxy-3-triisopropylsilyl-propan-1-al (5e) $R^1 = R^2 = R^3 = i\text{-Pr}$, $R^4 = H$, 1.78g, 78% ; ^1H-NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 6.6 Hz, 1H), 3.31 (dd, *J* = 6.6, 3.3 Hz, 1H), 2.58 (d, *J* = 3.3 Hz, 1H), 1.2-1.0 (m, 21H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.2, 56.1, 46.1, 18.6, 10.5 ; IR (neat) 2940, 1725, 1460, 1025, 880 cm^{-1}. MS (*m/z*) 228, 213, 185, 115. Anal Calcd for $C_{12}H_{24}O_2Si$: C, 63.10 ; H, 10.59. Found : C, 63.12 ; H, 10.61.

(2S, 3S)) 3-*tert*-Butyldiphenylsilyl-2,3-epoxy-propan-1-al (5f) $R^1 = R^2 = Ph$, $R^3 = t\text{-Bu}$, $R^4 = H$, 2.55 g, 82% ; ^1H-NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 6.5 Hz, 1H), 7.60-7.30 (m, 10H), 3.10 (d, *J* = 3.3 Hz, 1H), 3.05 (dd, *J* = 6.5, 3.3 Hz, 1H), 1.23 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.0, 135.9, 135.8, 130.9, 130.7, 130.2, 130.1, 128.1, 127.9, 56.2, 45.6, 27.7, 18.7 ; IR (neat) 3060, 3040, 2920, 1720, 1460, 1100, 1020, 810 cm^{-1}.$[\alpha]_D^{20}$ -18.60 (c = 10.00, $CHCl_3$).

(2S, 3S) 3-*tert*-Butyldimethylsilyl-2,3-epoxy-2-methyl-propan-1-al (5g) $R^1 = R^2 = Me$, $R^3 = t\text{-Bu}$, $R^4 = Me$, 1.73 g, 86% ; ^1H-NMR (200 MHz, $CDCl_3$) δ 8.65 (s, 1H), 2.48 (s, 1H), 1.43 (s, 3H), 0.97 (s, 9H), 0.13 (s, 3H), 0.07 (s, 3H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 200.2, 61.1, 51.2, 25.9, 16.8, 12.0, –5.9, –6.5 ; IR (neat) 2940, 2920, 1725, 1460, 1360, 1245, 830 cm^{-1}.

*5) General procedure for the preparation of the silylated vinyloxiranes **1a-g*** : To a solution of methylphosphonium bromide (2.16 g, 6.05 mmol) in benzene (25 mL) was added a 2.8 M benzene solution of sodium *tert*-amylate (2 mL, 5.55 mmol). The mixture was refluxed and a solution of the silylated epoxyaldehyde (5.05 mmol) in benzene (12 mL) was added. After being slowly cooled at room temperature, the benzene was removed in vacuo. The residue was diluted in ether (100 mL) and neutralized with a saturated solution of NH_4Cl (80 mL). The organic layer was washed with brine (2x50 mL), dried (Na_2SO_4), filtered and concentrated. The crude residue was purified by flash chromatography (petroleum ether/ether = 98/2) to afford the silylated vinyloxiranes.

(1S, 2S) 1-*tert*-Butyldimethylsilyl-1,2-epoxy-but-3-ene (1a) $R^1 = R^2 = Me$, $R^3 = t\text{-Bu}$, $R^4 = H$, 0.77 g, 82% ; Eb_{760} = 165°C ; ^1H-NMR (200 MHz, C_6D_6) δ 5.55 (ddd, *J* = 17.0, 9.0, 7.0 Hz, 1H), 5.42 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.21 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.13 (dd, *J* = 7.0, 3.5 Hz, 1H), 2.18 (d, *J* = 3.5 Hz, 1H), 0.93 (s, 9H), -0.01 (s, 3H), -0.07 (s, 3H) ; ^{13}C-NMR (50 MHz, C_6D_6) δ 137.9, 118.1, 56.1, 51.2, 26.0, 16.9, -8.0, -8.5 ; IR (neat) 3080, 2950, 1640, 1470, 1360, 1250, 910, 830 cm^{-1}. Anal Calcd for $C_{10}H_{20}OSi$: C, 65.15 ; H, 10.95. Found : C, 64.77 ; H, 11.10. $[\alpha]_D^{20}$ -5.2 (c = 10.30, EtOH).

1,2-Epoxy-1-trimethylsilyl-but-3-ene (1b) R^1 = R^2 = R^3 = Me, R^4= H, 0.039 g, 5% ; ^{1}H-NMR (400 MHz, C_6D_6) δ 5.57 (ddd, *J* = 17.0, 10.5, 7.5 Hz, 1H), 5.34 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.08 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.17 (dd, *J* = 7.5, 3.5 Hz, 1H), 2.05 (d, *J* = 3.5 Hz, 1H), 0.0 (s, 9H) ; ^{13}C-NMR (100 MHz, C_6D_6) δ 139.0, 117.9, 56.1, 53.0, -3.5. Anal Calcd for $C_7H_{14}OSi$: C, 59.10 ; H, 9.92 . Found : C, 59.22 ; H, 10.12.

(1S, 2S) 1-Dimethylphenylsilyl-1,2-epoxy-but-3-ene (1c) R^1 = R^2 = Me, R^3 = Ph, R^4= H, 0.878 g, 78% ; ^{1}H-NMR (400 MHz, C_6D_6) δ 7.70-7.55 (m, 2H), 7.26-7.24 (m, 3H), 5.24 (ddd, *J* = 17.0, 10.5, 7.5 Hz, 1H), 5.28 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.04 (dd, *J* = 10.5, 1.0 Hz, 1H), 3.21 (dd, *J* = 7.5, 3.5 Hz, 1H), 2.24 (d, *J* = 3.5 Hz, 1H), 0.27 (s, 3H), 0.23 (s, 3H) ; ^{13}C-NMR (50 MHz, C_6D_6) δ 138.0, 136.2, 134.0, 130.1, 128.2, 118.8, 56.2, 52.9, -5.0, -5.5 ; IR (neat) 3060, 2950, 1635, 1425, 1245, 1110, 915, 850 cm^{-1}. Anal Calcd for $C_{12}H_{16}OSi$: C, 70.53 ; H, 7.89. Found : C, 70.89 ; H, 7.65. $[\alpha]_D^{20}$+15.80 (c = 10.85, EtOH).

1,2-Epoxy-1-triethylsilyl-but-3-ene (1d) R^1 = R^2 = R^3 = Et, R^4= H, 0.73 g, 71% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.50-5.40 (m, 2H), 5.22 (m, 1H), 3.19 (m, 1H), 2.19 (d, *J* = 3.5 Hz, 1H), 0.99 (t, *J* = 7.5 Hz, 9H), 0.59 (q, *J* = 7.5 Hz, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 138.1, 118.1, 55.7, 51.5, 7.1, 1.7 ; IR (neat) 3080, 2950, 1640, 1450, 1370, 1230, 910, 850 cm^{-1}. MS (*m/z*) 184, 155, 127, 115, 99, 87, 75, 59. Anal Calcd for $C_{10}H_{20}OSi$: C, 65.15 ; H, 10.93. Found : C, 65.11 ; H, 10.93.

(1S, 2S) 1,2-Epoxy-1-triisopropylsilyl-but-3-ene (1e) R^1 = R^2 = R^3 = *i*-Pr, R^4 = H, 0.95g, 83% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.60-5.40 (m, 2H), 5.24 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.31 (dd, *J* = 6.8, 3.3 Hz, 1H), 2.24 (d, *J* = 3.3 Hz, 1H), 1.20-1.00 (m, 21H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 138.2, 118.4, 55.9, 51.2, 18.5, 10.4 ; IR (neat) 2930, 1640, 1460, 880 cm^{-1}. MS (*m/z*) 226, 183, 141, 113, 99. Anal Calcd for $C_{13}H_{26}OSi$: C, 68.95 ; H, 11.57 . Found : C, 68.81 ; H, 11.51. $[\alpha]_D^{20}$ + 9.50 (c = 10.00, EtOH).

(1S, 2S)) 1-*tert*-Butyldiphenylsilyl-1,2-epoxy-but-3-ene (1f) R^1 = R^2 = Ph, R^3 = *t*-Bu, R^4 = H, 1.64 g, 96% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.65-7.55 (m, 4H), 7.45-7.30 (m, 6H), 5.63 (ddd, *J* = 17.4, 10.4, 7.6 Hz, 1H), 5.42 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.26 (dd, *J* = 10.4, 1.4 Hz, 1H), 3.05 (dd, *J* = 7.6, 3.4 Hz, 1H), 2.74 (d, *J* = 3.4 Hz, 1H), 1.21 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.3, 135.9, 135.8, 132.2, 131.8, 129.6, 129.5, 127.9, 127.8, 118.9, 55.8, 50.1, 27.7, 18.6 ; IR (neat) 3060, 3040, 2940, 1460, 1420, 1100, 850, 810 cm^{-1}. Anal Calcd for $C_{20}H_{24}OSi$: C, 77.86 ; H, 7.84. Found : C, 77.59 ; H, 7.99. $[\alpha]_D^{20}$ -20.50 (c = 13.00, $CHCl_3$).

(2S, 3S) 3-*tert*-Butyldimethylsilyl-2,3-epoxy-2-methyl-but-3-ene (1g) R^1 = R^2 = Me, R^3 =*t*-Bu, R^4 = Me, 0.85g, 84% ; ^{1}H-NMR (200 MHz, C_6D_6) δ 5.61 (dd, *J* = 17.5, 10.5 Hz, 1H), 5.28 (dd, *J* = 17.5, 1.0 Hz, 1H), 5.15 (dd, *J* = 10.5, 1.0 Hz, 1H), 2.21 (s, 1H), 1.41 (s, 3H), 0.95 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.9, 114.8, 58.9, 57.2, 25.9, 17.9, 16.8, –5.9, –6.5 ; IR (neat) 3080, 2940, 2850, 1630, 1410, 1245, 830 cm^{-1}. Anal Calcd for $C_{11}H_{22}OSi$: C, 66.59 ; H, 11.18. Found : C, 66.86 ; H, 11.10 . $[\alpha]_D^{20}$ -6.8 (c = 8.05, EtOH).

B- The 1,2-Carbon to Carbon-Silyl Migration. New Palladium Catalyzed Rearrangement

To a stirred solution of $Pd(OAc)_2$ (6 mg, 0.03 mmol) and ligand (0.16 mmol) in THF (5 mL), under argon, was added the silylated vinyloxiranes **1** (1 mmol). After being stirred for 2 h at room temperature or at reflux (see table 2), the solvent was removed and the residue was purified by flash chromatography (petroleum ether/ether = 90/10) to give the silyldienolethers **9** and/or the α-trialkylsilyl-β,γ-unsaturated aldehydes **10**. The yields are listed in the tables 1 and 2.

1-Trimethylsilyloxy-but-1,3-diene (9b) $R^1 = R^2 = R^3$ = Me, traces ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.72 (dt, *J* = 17.5, 11.0, 11.0 Hz, 1H), 6.15 (d, *J* = 6.0 Hz, 1H), 5.22 (dd, *J* = 11.0, 6.0 Hz, 1H), 5.06 (d, *J* = 17.5 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 0.20 (s, 9H).

1-Dimethylphenylsilyloxy-but-1,3-diene (9c) $R^1 = R^2$ = Me, R^3 = Ph ; ^{1}H-NMR (400 MHz, $(CD_3)_2CO$) δ 7.68-7.58 (m, 2H), 7.45-7.33 (m, 3H), 6.77 (dt, *J* = 17.5, 10.5, 10.5 Hz, 1H), 6.28 (d, *J* = 6.0 Hz, 1H), 5.25 (dd, *J* = 10.5, 6.0 Hz, 1H), 5.05 (d, *J* = 17.5 Hz, 1H), 4.88 (d, *J* = 10.5 Hz, 1H), 0.48 (s, 6H) ; ^{13}C-NMR (100 MHz, $(CD_3)_2CO$) δ 141.2, 134.5, 133.8, 131.5, 131.1, 129.3, 113.7, 112.9, 1.1, –1.7 ; IR (neat) 3060, 2950, 2850, 1640, 1580, 1435, 1425, 1250, 1070, 830 cm^{-1}.

1-Triethylsilyloxy-but-1,3-diene (9d) $R^1 = R^2 = R^3$ = Et ; mixture of *Z* and *E* isomers ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.80 (m, 1H), 6.52 (m, 1H), 6.32 (m, 1H), 6.12 (m, 1H), 5.79 (m, 1H), 5.63 (m, 1H), 5.20 (m, 2H), 4.71 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 9H), 0.70 (q, *J* = 7.5 Hz, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 145.2, 140.4, 133.4, 129.9, 114.2, 112.8, 11.7, 111.4, 6.4, 6.3, 4.4, 4.3 ; IR (neat) 2940, 2850, 1640, 1590, 1465, 1250, 1070, 1000, 820 cm^{-1}.

1-*tert*-Butyldiphenylsilyloxy-but-1,3-diene (9f) $R^1 = R^2$ = Ph, R^3 = *t*-Bu ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90-7.71 (m, 4H), 7.62-7.39 (m, 6H), 7.12 (dt, *J* = 17.2, 10.6, 10.6 Hz, 1H), 6.28 (d, *J* = 5.8 Hz, 1H), 5.33 (dd, *J* = 10.6, 5.8 Hz, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.6 Hz, 1H), 1.22 (s, 9H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 140.7, 135.4, 132.4, 130.0, 129.8, 127.9, 113.6, 111.2, 26.5, 19.3; IR (neat) 3060, 3040, 2940, 2920, 2840, 1640, 1465, 1250, 1170, 1100, 1070, 820 cm^{-1}.

2-*tert*-Butyldimethylsilyl-but-3-en-1-al (10a) $R^1 = R^2$ =Me, R^3 = *t*-Bu, R^4 = H ; ^{1}H-NMR (200 MHz, C_6D_6) δ 9.52 (d, *J* = 3.0 Hz, 1H), 6.12 (dt, *J* = 17.0, 10.0 Hz, 1H), 4.88 (dd, *J* = 10.0, 1.0 Hz, 1H), 4.78 (dd, *J* = 17.0, 1.0 Hz, 1H), 3.02 (dd, *J* = 10.0, 3.0, 1H), 0.79 (s, 9H), -0.10 (s, 6H) ; ^{13}C-NMR (50 MHz,

C_6D_6) δ 198.1, 133.0, 115.1, 54.9, 27.9, 18.1, -6.0, -7.0 ; IR (neat) 3080, 2970, 1700, 1630, 1470, 1250, 1100, 1000, 950, 860 cm^{-1}. $[\alpha]_D^{20}$ -40.8 (c = 6.05, EtOH).

2-Triisopropylsilyl-but-3-en-1-al (10e) $R^1 = R^2 = R^3 = i$-Pr, R^4 = H ; ^{1}H-NMR (200 MHz, C_6D_6) δ 9.75 (d, J = 3.1 Hz, 1H), 6.23 (dt, J = 17.1, 10.3 Hz, 1H), 5.04 (dd, J = 10.3, 1.3 Hz, 1H), 5.00 (dd, J = 17.1, 1.3 Hz, 1H), 3.58 (dd, J = 10.3, 3.1 Hz, 1H), 1.21-1.10 (m, 21H) ; ^{13}C-NMR (50 MHz, C_6D_6) δ 199.8, 131.6, 114.9, 53.2, 18.6, 18.5, 11.5 ; IR (neat) 2950, 2850, 1700, 1460, 1000, 880 cm^{-1}. MS (*m/z*) 211, 199, 131, 115, 103, 87, 75, 59, 45.

2-*tert*-Butyldiphenylsilyl-but-3-en-1-al (10f) $R^1 = R^2$ = Ph, $R^3 = t$-Bu, R^4 = H ; ^{1}H-NMR (200 MHz, C_6D_6) δ 9.73 (d, J = 3.1 Hz, 1H), 7.71-7.29 (m, 10H), 6.13 (dt, J = 17.1, 10.1 Hz, 1H), 6.13 (dt, J = 17.1, 10.1 Hz, 1H), 5.02 (d, J = 10.1 Hz, 1H), 4.88 (d, J = 17.1 Hz, 1H), 3.96 (dd, J = 10.1, 3.1 Hz, 1H), 1.19 (s, 9H) ; ^{13}C-NMR (50 MHz, C_6D_6) δ 199.7, 136.3, 131.9, 131.7, 130.8, 129.8, 127.8, 117.0, 53.0, 28.2, 19.7; IR (neat) 3060, 3040, 2940, 2920, 2840, 1700, 1460, 1000, 870 cm^{-1}.

2-*tert*-Butyldimethylsilyl-2-methyl-but-3-en-1-al (10g) $R^1 = R^2$ = Me, $R^3 = t$-Bu, R^4 = Me, 0.175g, 87% ; ^{1}H-NMR (200 MHz, C_6D_6) δ 9.60 (s, 1H), 6.33 (dd, J = 17.5, 11.0 Hz, 1H), 4.89 (dd, J = 11.0, 1.0 Hz, 1H), 4.71 (dd, J = 17.5, 1.0 Hz, 1H), 1.22 (s, 3H), 0.79 (s, 9H), -0.11 (s, 3H), -0.12 (s, 3H) ; ^{13}C-NMR (50 MHz, C_6D_6) δ 200.1, 137.8, 111.9, 55.2, 27.8, 18.7, 14.9, –6.9, –7.8; IR (neat) 3080, 2950, 2850, 1700, 1625, 1465, 1250, 1020, 830 cm^{-1}. $[\alpha]_D^{20}$+42.1 (c = 10.20, EtOH).

C- Stereoselective 'One-Pot' Addition of Nucleophiles

1) General Procedure for the Addition of Organometallic Reagents on Aldehydes ***10a*** *and* ***10e****.* Organolithium or vinyl Grignard reagent (1.2 mmol) was added dropwise, at -78°C, to a solution of the aldehyde **10a** or **10e** (1 mmol) in THF (5 mL). After completion of the reaction evidenced by TLC (usually after being stirred for 1h at -78°C), the reaction mixture was partitionned between ether and saturated solution of NH_4Cl. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. Purification by flash chromatography (petroleum ether/ether = 95/5) afforded the alcohols $\mathbf{17a_n}$ and $\mathbf{17e_n}$.

3-*tert*-Butyldimethylsilyl-pent-4-en-2-ol ($\mathbf{17a_1}$) $R^1 = R^2$ = Me, $R^3 = t$-Bu, **R** = Me, 0.134 g, 67% ; ^{1}H-NMR (400 MHz, C_6D_6) δ 5.91 (dt, J = 17.0, 11.0, 11.0 Hz, 1H), 5.07 (dd, J = 11.0, 2.0 Hz, 1H), 4.94 (dd, J = 17.0, 2.0 Hz, 1H), 3.94 (dq, J = 6.0, 3.5 Hz, 1H), 1.65 (dd, J = 11.0, 3.5 Hz, 1H), 1.07 (d, J = 6.0 Hz, 3H), 1.00 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H) ; ^{13}C-NMR (100 MHz, C_6D_6) δ 136.8, 115.9, 67.9, 41.3, 26.9, 24.0, 16.8, –5.5, –5.9 ; IR (neat) 3440, 3060, 2950, 2850, 1620, 1465, 1245, 1045, 1000, 830 cm^{-1}. Anal Calcd for $C_{11}H_{24}OSi$: C, 65.93 ; H, 12.07 . Found : C, 66.15 ; H, 11.85. $[\alpha]_D^{20}$ +12.9 (c = 10.65, $CHCl_3$).

3-*tert*-Butyldimethylsilyl-oct-1-en-4-ol (17a$_2$) $R^1 = R^2 =$ Me, $R^3 =$ *t*-Bu, **R = *n*-Bu**, 0.198 g, 82% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.84 (dt, *J* = 10.5, 3.6 Hz, 1H), 5.04 (dd, *J* = 10.5, 2.2 Hz, 1H), 4.94 (dd, *J* = 17.1, 2.2 Hz, 1H), 3.82 (m, 1H), 1.83 (dd, *J* = 10.5, 3.6 Hz, 1H), 1.55-1.20 (m, 6H), 0.95-0.80 (s overlapped with m, 12H), 0.01 (s, 3H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 136.2, 115.9, 72.0, 39.1, 37.2, 28.2, 27.2, 22.7, 17.8, 14.1, –5.8, –5.9; IR (neat) 3440, 3040, 2920, 1610, 1450, 1235, 880 cm^{-1}. MS (*m*/*z*) 241, 185, 110, 95, 81, 75, 73, 54, 45, 41. Anal Calcd for $C_{14}H_{30}OSi$: C, 69.35 ; H, 12.47. Found : C, 69.38 ; H, 12.54.

4-*tert*-Butyldimethylsilyl-2,2-dimethyl-hex-5-en-3-ol (17a$_3$) $R^1 = R^2 =$ Me, $R^3 =$ *t*-Bu, **R = *t*-Bu**, 0.228 g, 94% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.05 (dt, *J* = 17.2, 10.7 Hz, 1H), 4.95 (dd, *J* =.10.7, 2.1 Hz, 1H), 4.90 (dd, *J* = 17.2, 2.1 Hz, 1H), 3.60 (br s, 1H), 2.25 (d, *J* = 10.7 Hz, 1H), 0.95 (s, 9H), 0.94 (s, 9H), 0.07 (s, 3H), 0.01 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.4, 113.6, 78.7, 37.8, 35.4, 27.4, 26.8, 18.0, –6.1 ; IR (neat) 3600, 3500, 2980, 2850, 1620, 1460, 1360, 1250, 1100, 830 cm^{-1}. Anal Calcd for $C_{14}H_{30}OSi$: C, 69.35 ; H, 12.47. Found : C, 69.32 ; H, 12.43.

4-*tert*-Butyldimethylsilyl-hexa-1,5-dien-3-ol (17a$_5$) $R^1 = R^2 =$ Me, $R^3 =$ *t*-Bu, **R = CH_2=CH-**, 0.195 g, 92% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.00-5.80 (m, 2H), 5.17 (d, *J* = 16.1 Hz, 1H), 5.10 (d, *J* = 9.0 Hz, 1H), 5.07 (dd, *J* = 8.4, 1.5 Hz, 1H), 4.96 (dd, *J* = 17.1, 1.5 Hz, 1H), 4.35 (br s, 1H), 1.90 (dd, *J* = 10.9, 4.5 Hz, 1H), 0.90 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.6, 136.4, 115.9, 114.2, 73.4, 40.2, 27.2, 17.6, –5.7, –5.9; IR (neat) 3480, 2900, 1620, 1470, 1250, 1000, 900, 800 cm^{-1}. Anal Calcd for $C_{12}H_{24}OSi$: C, 67.86 ; H, 11.39. Found : C, 67.79 ; H, 11.15.

3-Triisopropylsilyl-pent-4-en-2-ol (17e$_1$) $R^1 = R^2 = R^3 =$ *i*-Pr, **R = Me**, 0.153 g, 63% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.90 (dt, *J* = 17.6, 10.6 Hz, 1H), 5.09 (dd, *J* = 10.6, 2.2 Hz, 1H), 5.00 (dd, *J* = 17.6, 2.2 Hz, 1H), 4.05 (m, 1H), 1.95 (dd, *J* = 10.6, 5.0 Hz, 1H), 1.25 (d, *J* = 5.0 Hz, 1H), 1.10-0.80 (m, 21H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 137.0, 116.5, 66.9, 41.5, 23.7, 19.2, 19.0, 11.8 ; IR (neat) 3440, 3060, 2950, 2850, 1620, 1465, 1245, 1045, 1000, 880 cm^{-1}. MS (*m*/*z*) 199, 157, 131, 115, 103, 75. Anal Calcd for $C_{14}H_{30}OSi$: C, 69.35 ; H, 12.47. Found : C, 69.47 ; H, 12.29.

3-Triisopropylsilyl-oct-1-en-4-ol (17e$_2$) $R^1 = R^2 = R^3 =$ *i*-Pr, **R =*n*-Bu**, 0.267 g, 94% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.94 (dt, *J* = 16.5, 10.0 Hz, 1H), 5.05 (dd, *J* = 10.0, 2.2 Hz, 1H), 4.95 (dd, *J* = 16.5, 2.2 Hz, 1H), 3.83 (m, 1H), 2.04 (dd, *J* = 10.0, 3.5 Hz, 1H), 1.50-0.80 (m, 30H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 136.5, 115.7, 71.0, 38.8, 37.4, 29.7, 28.5, 19.2, 19.0, 11.7 ; IR (neat) 3600, 2920, 2860, 1620, 1450, 1240, 880, 830 cm^{-1}. MS (*m*/*z*) 241, 157, 131, 115, 103, 87, 75, 59. Anal Calcd for $C_{17}H_{36}OSi$: C, 73.76 ; H, 12:75. Found : C, 73.83 ; H, 12.73.

2,2-Dimethyl-4-triisopropylsilyl-hex-5-en-3-ol **($17e_3$)** $R^1 = R^2 = R^3$ = *i*-Pr, **R =*t*-Bu**, 0.239 g, 84% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.11 (dt, *J* = 17.0, 10.8 Hz, 1H), 4.95 (d, *J* = 17.0 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 3.55 (d, *J* = 5.8 Hz, 1H), 2.48 (dd, *J* = 10.8, 5.8 Hz, 1H), 1.30-0.90 (m, 30H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 137.7, 112.9, 77.7, 38.1, 34.4, 27.1, 19.2, 19.0, 12.3 ; IR (neat) 3600, 3500, 2900, 1610, 1460, 1360, 1050, 1000, 880 cm^{-1}. MS (*m/z*) 241, 227, 157, 131, 115, 103, 95, 75, 59. Anal Calcd for $C_{17}H_{36}OSi$: C, 71.75 ; H, 12.75. Found : C, 71.68 ; H, 12.71.

1-Phenyl-2-triisopropylsilyl-but-3-en-1-ol **($17e_4$)** $R^1 = R^2 = R^3$ = *i*-Pr, **R =Ph**, 0.268 g, 88% ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50-7.10 (m, 5H), 6.10 (dt, *J* = 17.2, 11.0 Hz, 1H), 5.07 (t, *J* = 3.2 Hz, 1H), 4.96 (dd, *J* = 11.0, 2.1 Hz, 1H), 4.75 (dd, *J* = 17.2, 2.1 Hz, 1H), 2.30 (dd, *J* = 11.0, 3.2 Hz, 1H), 1.10-0.80 (m, 21H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 145.3, 135.5, 127.9, 127.0, 126.1, 73.5, 22.3, 19.1, 19.0, 11.5 ; IR (neat) 3600, 2940, 2850, 1620, 1450, 880 cm^{-1}. MS (*m/z*) 261, 157, 130, 115, 103, 75. Anal Calcd for $C_{19}H_{32}OSi$: C, 74.93 ; H, 10.59. Found : C, 74.87 ; H, 10.75.

4-Triisopropylsilyl-hexa-1,5-dien-3-ol **($17e_5$)** $R^1 = R^2 = R^3$ = *i*-Pr, **R = CH_2=CH-**, 0.229 g, 90% ; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.10-5.80 (m, 2H), 5.20 (dt, *J* = 18.2, 1.4 Hz, 1H), 5.10 (dt, *J* = 9.6, 1.4 Hz, 1H), 5.05 (dd, *J* = 10.5, 2.0 Hz, 1H), 5.00 (dd, *J* = 18.2, 2.0 Hz, 1H), 4.39 (t, *J* = 5.8 Hz, 1H), 2.10 (dd, *J* = 11.1, 5.8 Hz, 1H), 1.30-0.90 (m, 21H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.4, 136.4, 116.2, 114.6, 72.4, 29.5, 19.2, 19.0, 11.6 ; IR (neat) 3460, 2960, 2850, 1610, 1450 ,880 cm^{-1}. MS (*m/z*) 209, 157, 131, 115, 103, 80, 75, 61. Anal Calcd for $C_{15}H_{30}OSi$: C, 70.79 ; H, 11.88. Found : C, 70.72 ; H, 12.03.

2) Enantioselective Cascade Process. To a stirred solution of $Pd(OAc)_2$ (6 mg, 0.026 mmol) and $P(Oi\text{-}Pr)_3$ (26 µL, 0.104 mmol) in THF (10 mL), under argon, was added **1f** (616 mg, 2 mmol). After being stirred for 2 h at room temperature, the temperature was cooled to -100°C and MeLi (2 mL, 2.4 mmol, 1.2 M in ether) was added. The reaction mixture was stirred 1h at -100°C and then was partitionned between ether and saturated solution of NH_4Cl. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. Purification by flash chromatography (petroleum ether/ether = 95/5) afforded **$17f_1$** (0.357 g, 55%) and **9f** (0.174g, 28%). **2-*tert*-Butyldiphenylsilyl-pent-4-en-2-ol** **($17f_1$)** $R^1 = R^2$ = Ph, R^3 = *t*-Bu, **R** = **Me**; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.90-7.30 (m, 10H), 6.14 (dt, *J* = 17.2, 10.4 Hz, 1H), 5.29 (dd, *J* = 10.4, 1.9 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.9 Hz, 1H), 4.20-4.00 (m, 1H), 2.51 (dd, *J* = 10.4, 3.4 Hz, 1H), 1.30-1.10 (m, 12H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 136.6, 136.4, 135.7, 134.7, 133.7, 129.3, 129.1, 127.6, 127.5, 117.8, 67.1, 40.7, 28.3, 23.0, 19.2 ; IR (neat) 3560, 3300, 3050, 2940, 2900, 2840, 1620, 1440, 1100, 700 cm^{-1}. MS (*m/z*) 267, 239, 223, 199, 181, 135, 121, 105. Anal Calcd for $C_{21}H_{28}OSi$: C, 77.72 ; H, 8.69. Found : C, 77.85 ; H, 8.46. $[\alpha]_D^{20}$+48.8 (c = 18.0, $CHCl_3$).

Preparation of the Mosher ester of **$17f_1$**: To a solution of pyridine (400 µL, 5 mmol) and (R)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (57 µL, 0.3 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of **$17f_1$** (95 mg, 0.29 mmol) in CH_2Cl_2 (1.5 mL). After being stirred 12h at room temperature, the reaction mixture was diluted with CH_2Cl_2, washed with brine, dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (petroleum ether/ether = 80/20) afforded the Mosher ester. $R^1 = R^2$ = Ph, R^3 = *t*-Bu, R = Me, 0.150 g, 95 % ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80-7.60 (m, 4H), 7.50-7.30 (m, 11H), 6.05 (dt, *J* = 17.1, 10.3 Hz, 1H), 5.38 (q, *J* = 7.0 Hz, 1H), 5.53 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.3, 1.5 Hz, 1H), 3.39 (s, 3H), 2.78 (dd, *J* = 10.3, 7.0 Hz, 1H), 1.10 (s, 9H), 1.05 (d, *J* = 7.0 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.0, 136.4, 136.3, 135.9, 133.9, 132.4, 132.1, 129.5, 129.3, 128.1, 127.7, 127.5, 75.5, 5.4, 39.1, 28.2, 20.8, 19.4 ; IR (neat) 3060, 2920, 2870, 1730, 1420, 1260, 1170, 1100, 1010, 690 cm^{-1}.

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