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Attempt to Rationalize the Diastereoselectivity in the Addition of Ester Enolate to Optically Active α,β-epoxyaldehydes

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Abstract:
Aldol condensations on α,β-epoxyaldehyde having a remote alkoxy group have been realized. A rationalization of the outcome of this condensation is discussed, relying on the dominant conformers revealed by molecular modeling of *anti* and *syn* γ,δ-epoxy β-hydroxyesters and their NMR and IR spectrostroscopic properties.

Keywords: Aldol reactions; γ,δ-epoxy β-hydroxyesters; diastereoselection; energy

Optically active compounds having a 1,3 or 1,2,3 polyhydroxylated frame are useful synthons for the synthesis of natural products.[1] Therefore, their elaboration has received considerable attention. Two general strategies have been developed, the first using existing optically active starting compounds especially carbohydrates and derivatives, the second consisting in the creation of the stereogenic centers of the target molecule.

In connection with a program directed towards the total synthesis of modified deoxysugars, ulosonic acids and deoxynucleosides, a method was developed based on two key reactions: a) Sharpless asymmetric epoxidation of an allylic alcohol and b) stereocontrolled addition of a *tert*-butyl lithioester to an optically active α,β-epoxyaldehyde.[2] The chiral γ,δ-epoxy-β-hydroxyesters thus obtained have been used to synthesize β-hydroxy γ-butyrolactones,[3] tetrahydrofuranyl lactones,[4] heptulosonic ester[5] and modified nucleosides.[6] Concerning the synthesis of modified sugars and deoxysugars we are interested in the synthesis of fucose derivatives bearing alkyl chains of varying lengths and terminal functionalities at the C-5 position. L-fucose is present in many oligosaccharidic structures and it is assumed that enzymes associated with its incorporation may be potential biological indicator of abnormal processes in the human body.[7] Modified compounds may be helpful in understanding their biochemical and biological role.

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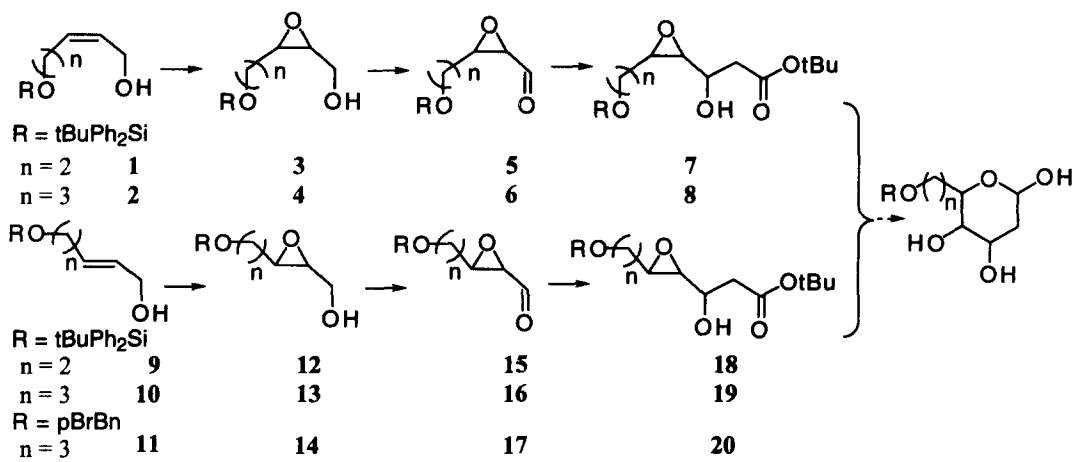
As a first step of our research concerning the potentiality of the epoxyester synthons, we present in this paper the synthesis, spectroscopic properties (IR and NMR) and molecular modeling conformational investigations of optically active γ,δ-epoxy-β-hydroxyesters possessing a remote alkoxy group.

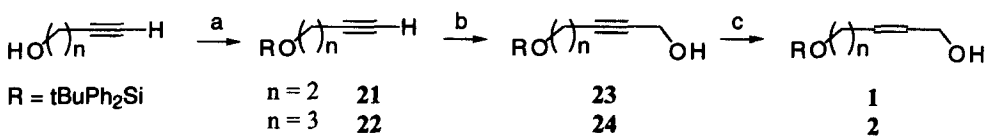
Synthesis of α,β-epoxyaldehydes 5, 6, 15-17

As the corresponding allylic alcohols (scheme 1) are not commercially available, their syntheses have been undertaken.



Scheme 1

Cis allylic alcohols have been synthesized in three steps[8] starting from acetylenic alcohols according to the following scheme 2.



a) imidazole, $tBuPh_2SiCl$, DMF; b) $(CH_2)_nO$, nBuLi, Et_2O, -78°C, then r.t. 12 h; c) $Pd/BaSO_4$, quinoline, H_2, MeOH, -20°C → -10°C, 2h.

Scheme 2

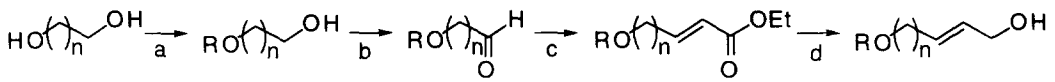
While the two first steps proceeded very well, in 93% and 95% total yield for compounds **23**, **24**, some difficulties arised in the reduction of the triple bond to form the *cis* allylic alcohols **1** and **2**.

Hydrogenation using $Pd/BaSO_4$ as a catalyst in presence of quinoline at low temperature gave the best results. Compound **2** was thus obtained in 83% yield, and **1** was obtained in 85% , using **23** as precursor.

Compounds **9-11** were synthesized by another method, starting from 1,3-propanediol and 1,4-butanediol (scheme 3). *Trans* allylic alcohols **9** and **10** were also synthesized in 89% yield from **1** and **2** according to the procedure previously described,[2] through oxidation isomerization and reduction of the unsaturated aldehyde.

The oxidation of the monoprotected alcohols **26-28** by the Doering's method,[9] leads to the corresponding aldehydes, and was followed by a Horner-Emmons reaction using ethyl diethylphosphonoacetate; subsequent reduction of the corresponding unsaturated esters gave the *trans* allylic alcohols **9-11** in good yields.

Finally, Sharpless asymmetric epoxidation[10] of the allylic alcohols, yielded the corresponding epoxyalcohols which have then been oxidized in good yields to the aldehydes **5**, **6**, **15-17**. The results concerning the epoxidation and the oxidation reactions and the $[\alpha]_D$ values are reported in table 1.



R = $tBuPh_2Si$ (n = 2, 3)	**26, 27**	**29, 30**	**32, 33**	**9, 10**
R = pBrBn (n = 3)	**28**	**31**	**34**	**11**

a) n-BuLi, $tBuPh_2SiCl$, THF, -78°C ↗ Δ or pBrBnBr, nBu_4NI, NaH, THF, 0°C; b) pyr.SO_3, DMSO, Et_3N, CH_2Cl_2, r.t., 45 min; c) n-BuLi, $EtOOC\text{-}CH_2PO(OEt)_2$, ether, -78°C; d) DIBAH, toluene, -78°C

Scheme 3

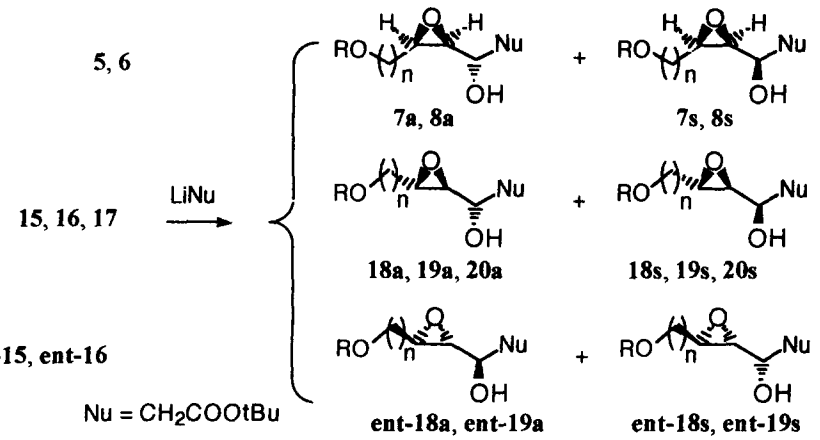
Table 1. Epoxyalcohols[a] and epoxyaldehydes synthesized; yields and $[\alpha]_D$ values[b]

allylic alcohol	epoxy alcohol	yield %	$[\alpha]_D^{25}$	absolute configuration	epoxy aldehyde	yield %	$[\alpha]_D$
1	**3**	88	+2.7	2S 3R	**5**	78	+57.2
2	**4**	82	-2.2	2S 3R	**6**	72	+61.0
9	**12**	88	-19.0	2S 3S	**15**	82	+48.0
9	**ent-12**	86	+19.6	2R 3R	**ent-15**	83	-47.2
10	**13**	93	-16.2	2S 3S	**16**	84	+37.6
10	**ent-13**	92	+15.7	2R 3R	**ent-16**	83	-36.9
11	**14**	75	-21.2	2S 3S	**17**	78	+54.1

Compounds **3**, **4**, **12**, **13** and **14** were epoxidized with (+)DET or (+)DIPT, while **ent-12** and **ent-13** with (-)DET or (-)DIPT. b) $[\alpha]_D$ values were measured in $CHCl_3$; **ent** = enantiomer.

Study of the aldolisation reaction

The α,β-epoxyaldehydes were subjected to the aldolisation reaction with lithium *tert*-butylacetate under various experimental conditions (scheme 4, table 2). Acidic hydrolysis of the reaction medium and usual workup led to a mixture of two adducts which was used to determine the diastereoisomeric ratio measured by analytical chromatography. The two aldol adducts have been purified except for compound **20**. The diastereoisomeric ratio determined by HPLC or on the yields after purification were found in good agreement (±2%).



Scheme 4

Table 2. Diastereoselectivity of the reaction of lithium *tert*-butylacetate with the α,β-epoxyaldehydes

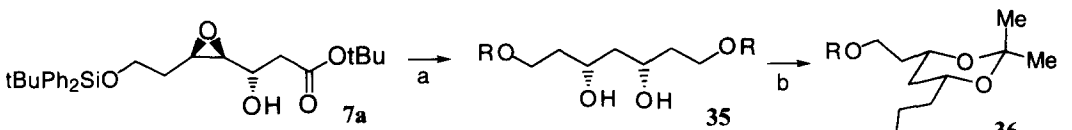
entry	aldehyde	enolate/aldehyde eq.	T°C	yield (%)	*anti:syn*	epoxyester
1	**5**	1	-78	80	80:20	**7a:7s**
2	**5**	2	-78	82	81:19	**7a:7s**
3	**5**	2	-78↗25	84	87:13	**7a:7s**
4	**6**	1	-78	85	82:18	**8a:8s**
5	**6**	1	-78↗25	83	80:20	**8a:8s**
6	**6**	2	-78	93	85:15	**8a:8s**
7	**6**	2	-78↗25	78	96:4	**8a:8s**
8	**15**	1	-78	87	74:26	**18a:18s**
9	**15**	2	-78↗25	88	72:28	**18a:18s**
10	**ent-15**	1	-78	77	73:27	**ent-18a:ent-18s**
11	**ent-15**	2	-78↗25	73	75:25	**ent-18a:ent-18s**
12	**16**	2	-78↗20	67	74:26	**19a:19s**
13	**ent-16**	2	-78	90	76:24	**ent-19a:ent-19s**
14	**ent-16**	2	-78↗25	80	75:25	**ent-19a:ent-19s**
15	**17**	2	-78↗25	82	75:25	**20a:20s**

ent = enantiomer, **a** = *anti*, **s** = *syn*

For *cis*-epoxyaldehydes **5** and **6** the diastereoselectivity was found equal to 4:1 in favour of the *anti* aldol adduct when using a 1:1 ratio of reactants at -78°C (entries 1, 4). No change in the selectivity occurred when varying only the ratio of the reactants (entries 2, 6) or only the temperature of the reaction mixture (entry 5). On the contrary, an improvement was observed by varying both the temperature and the reactant equivalents (entries 3, 7). The best diastereoselectivity was obtained for compound **6**, when 2 eq. of enolate were added at -78°C and the mixture allowed to reach room temperature slowly, a 24:1 selectivity was obtained in favour of the *anti* aldol adduct (entry 7, **8a:8s** 96:4).

Finally, when *trans* α,β-epoxyaldehydes (**15**, **ent-15**, **16**, **ent-16** and **17**) reacted under the same experimental conditions (entries 8-15) the aldol adducts were obtained in good to excellent yields. Nevertheless, no change in selectivity was observed that is 3:1 in favour of the *anti* aldol adducts.

The stereochemical assignment of the aldol products was established for compound **7a** by conversion to the six-membered acetonide (scheme 5), according to a known procedure. The ^{13}C NMR shifts of the acetal carbons were in agreement with our previous results[2] and those reported in the literature,[11] attributing a *cis* configuration to the two hydroxy functions of the acetonide and then an *anti* configuration for the major aldol adduct **7a**.



a) Red.Al, THF 83%; imidazole, ClSiPh$_2$tBu 90%; b) CSA, (MeO)$_2$CMe$_2$ 99%

Scheme 5

The *anti* diastereofacial preference can be explained according to the Felkin-Anh or Conforth type models.[12] In both cases nucleophilic attack occurs from the "Si" face either antiperiplanar to the epoxide bond or from the less hindered face of the carbonyl group. The results on the diastereoselectivity observed for the different epoxyaldehydes is the same with that precedently observed for n = 1.[2] Thus, the diastereoselectivity is not modified when increasing the chain length bearing the alkoxy group.

To explain the diastereoselectivity differences observed when condensing lithium *tert*-butylacetate with *cis* and *trans* α,β-epoxyaldehydes in the conditions previously specified, clues may also be found in the relative stability of the *syn* and *anti* adducts. We thus decided to investigate their physical chemistry properties by IR and NMR spectroscopy, and correlate the findings with molecular modeling energy minimization.

In order to examine if they are common characteristics for the major (*anti*) and minor (*syn*) aldol adducts synthesized, we have studied the infrared spectra of the epoxyhydroxyesters. They were recorded either neat or in CCl_4 solution at two different concentrations M/20 and M/400 (table 3).

Spectra recorded for pure liquids showed broad vibrational bands for νOH at 3443-3458 cm^{-1} indicating principally strong intermolecular interactions between the hydroxy groups. In such conditions the population of the compounds which present intramolecular bonds between the carbonyl oxygen and the hydroxy hydrogen is not important and the major νC=O bands at 1730 cm^{-1} are characteristic of a free carbonyl.

When diluted to M/20 and M/400 the aldol adducts show some significant modifications of the IR spectra. Intramolecular bonds are favored; they can take place either between the oxygen of the carbonyl and the C3-hydroxy, or possibly between the oxygen of the epoxide function and the C3-hydroxy. In the first case we expect a change in the νOH value from 3450 to 3540 cm^{-1} and a concomitant decrease of the νC=O from 1730 to ~1710 cm^{-1}; in the second case the νOH will decrease and the νC=O will be unaffected. The results show that these phenomena appear differently, depending on the nature *cis* or *trans* of the initial epoxide engaged in the condensation and on the configuration *syn* or *anti* of the diastereoisomer considered.

For the major aldol adduct **7a**, issued from *cis* epoxyaldehyde, we observe at M/20 two vibrational bands for νC=O (~1713 and 1733 cm^{-1}) and two for νOH (~3533 and 3450 cm^{-1}). The last one, attributed to intermolecular chelation disappeared at M/400 and a free νOH at 3617 cm^{-1} is observed in addition to the intramolecular six-membered structure (3533 cm^{-1}). In the same way, for the major aldol adduct **8a** the frequency at 3434 cm^{-1} is not observed at M/400 while the intramolecular hydrogen bond between the C3 hydroxy group and the carbonyl oxygen is unaffected by a high dilution.

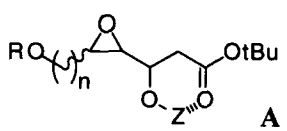
Table 3.

epoxyester	νOH (cm^{-1})			νC=O (cm^{-1})	
	liquid	M/20	M/400	liquid	M/20
7a	3459	3533 > 3450	3533 > 3617	1730 > 1707	1733 < 1713
7s	3443	3605 > 3541	3605 > 3541	1731	1731 >> 1709
8a	3446	3530 > 3434	3530 > 3615	1730 > 1707	1733 << 1713
8s	3452	3605 > 3540	3605 > 3540	1731 > 1711	1731 > 1711**
18a	3456	3548	3548 >> 3624	1730 > 1708	1732 ~ 1714
18s	3458	3554 ~ 3603	3603 ~ 3554	1731	1731 > 1715
19a	3452	3545	3545 >> 3621	1731 > 1710	1731 ~ 1710
19s	3455	3555 ~ 3601	3603 ~ 3554	1732	1732 > 1714

* Solutions in CCl_4; ** In addition a νC=O band at 1719 cm^{-1} was observed

Finally, for all minor aldol adducts we observe that upon dilution the intramolecular hydrogen bond between C3-OH and C=O groups are very weak, indicating that the six-membered chelated forms (**A**) are not predominant as it is evidenced by the presence even at M/20 of a free hydroxy frequency (νOH: 3601-3605 cm^{-1} for **7s**, **8s**, **18s**, **19s**).

According to these IR data it appears that the *anti* epoxy β-hydroxyester, when compared to the *syn* are more stabilized by an intramolecular chelation (type **A**). It may be reasonable to assume that the same effect contributes to the stabilization of the lithio *anti* adducts in the aldolisation step (Z = Li).



A

We have also studied the characteristics of the aldol adducts by NMR spectroscopy. ^1H and ^{13}C NMR spectroscopy has been used in the literature to assign the relative configurations of the aldol compounds. Bäckvall *et al.*[13] have used this direct method to assign the stereochemistry of the components of a diastereoisomeric mixture of epoxyalcohols. Heathcock *et al.*[14] reported also that when intramolecular hydrogen bonds exist in the aldol adducts, then the measure of vicinal coupling constants between two asymmetric carbon atoms may be helpful for stereostructural assignments.

While ^{13}C NMR spectroscopy did not reveal any characteristic trends for the epoxyesters synthesized, ^1H NMR spectroscopy gave some helpful informations. For all the aldol compounds issued from *cis*-epoxyaldehydes, the values of vicinal coupling constants, J_{H3-H4} between an epoxide proton (H4) and the one formed from the aldolisation reaction (H3), are much higher than that observed for compounds issued from *trans* epoxyaldehydes (J_{H3-H4} = 7.4-8.3 Hz and J_{H3-H4} = 4.0-4.9 Hz respectively). On the other hand, in each case values of J_{H3-H4} for the *anti* aldol adducts are higher than that corresponding to the minor adducts.

These trends can be understood by inspection of the three rotamers around the C3-C4 bond of the *anti* and *syn* adducts issued from the different epoxyaldehydes. The energetically more favoured conformers have been calculated by the MMX program[15] for epoxyesters **8a**, **8s** and **19a**, **19s** issued from the *cis* and *trans* α,β-epoxyaldehydes **6** and **16** respectively. The three conformational minima predicted from the calculated rotational profile of each epoxyester are presented in figure 1. Geometrical informations and relative energies calculated are reported in table 4.

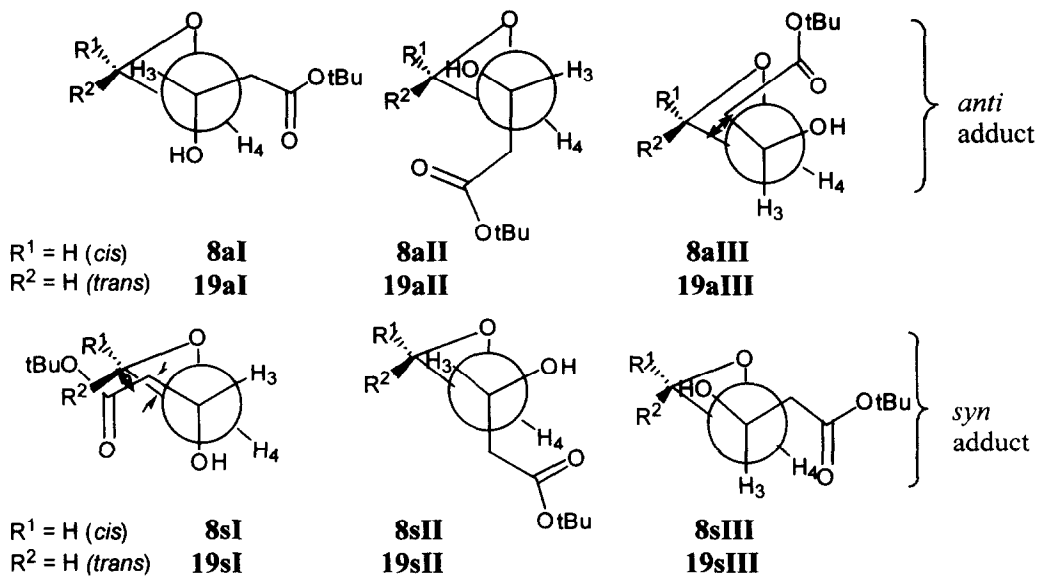


Figure 1. Different rotamers around the C3-C4 bond for the *anti* and *syn* aldol adducts of epoxyesters **8a**, **19a** (**I-III**) and **8s**, **19s** (**I-III**)

Table 4. Geometrical informations and relative energies for the different conformers of compounds **8a**, **19a** (**I-III**) and **8s**, **19s** (**I-III**)

	8aI	**8aII**	**8aIII**	**8sI**	**8sII**	**8sIII**
energy Kcal/mol	37.8	44.7	40.8	44.9	40.3	46.2
OC3^C4Oep.	148	25	-100	170.4	-75	61
C2C3^C4C5	-156	85	-46	-22	100	-132
C2C3^C4Oep.	-91	151	19	45	165	-65
H3C3^C_4H_4	169	48	-77	59	178	-48
d (OH, C=O) Å	2.31	2.33	2.39	4.03	4.2	4.11
d (OH, Oep.) Å	4.28	3.62	4.01	3.93	2.64	3.35
	19aI	**19aII**	**19aIII**	**19sI**	**19sII**	**19sIII**
energy Kcal/mol	36.2	38.2	38.9	38.9	36.4	38.8
OC3^C4Oep.	160	51	-106	167	-71	52
C2C3^C4C5	-143	108	-48	-21	105	-136
C2C3^C4Oep.	-79	173	18	44	169	-71
H3C3^C4H4	-177	70	-77	59	-175	-54
d (OH, C=O) Å	2.33	2.34	2.29	4.02	4.13	4.08
d (OH, Oep.) Å	4.23	3.64	4.14	3.94	2.58	3.16

d (OH, C=O) = O-H···O=C

Results obtained for epoxyesters **8a**, **8s** showed two privileged conformations **8aI** and **8sII** for *anti* and *syn* adducts respectively. The **8aI** conformation places the hydroxy group almost antiperiplanar to the oxygen atom of the epoxide function and in the same time it minimizes steric interactions between the alkoxy chain and the ester group. For this conformer an intramolecular hydrogen-bond can exist as the distance O-H····O=C is calculated to be d = 2.31-2.39 Å. For conformer **8sII** we have also minimized the steric interactions; a gauche conformation between the oxygen atoms of the epoxide ring and the hydroxy group may be not destabilizing as it was found for other electronegative atoms.[16] For this conformer intramolecular hydrogen bond O-H····O=C might be much less pronounced as the hydrogen atom can also interact with the oxygen of the epoxide ring.

For *trans* epoxyesters **19**, **19aI** and **19sII** are relatively the most stable conformers where the same trends apply as before. Nevertheless, the differences in energy between conformers are less pronounced for **19a**, **19s** than for **8a**, **8s**. This is due mainly to less steric interactions in the former case between the alkoxy and the ester groups. Rotation around the C3-C4 bond is less energy demanding for the *trans* epoxyesters, thus increasing the population of conformers where H3, H4 atoms are not strictly antiperiplanar. Relative free rotation around the C3-C4 bond results in a decrease of the vicinal coupling constants $J_{H3\text{-}H4}$ as it is observed experimentally.

Looking back to the aldolisation reaction, we can observe that the same *anti* diastereoface preference is obtained if we operate at −78°C (1 or 2 eq. of enolate) or −78↗25°C (1 eq. of enolate). This could be in agreement with the fact that among the possible conformations for the lithiated adducts issued from the *cis* and *trans* α,β-epoxyaldehydes those equivalent to **aI/sII** might prevail, indicating that the *anti* adducts are thermodynamically more stable than the *syn* adducts; that being more pronounced for the *cis* epoxyesters for the reasons we developed before.

In conclusion, we have further studied the aldolisation reaction of lithium ester *tert*-butylacetate with various α,β-epoxyaldehydes. An attempt has been made to rationalize the spectroscopical characteristics of the epoxyesters synthesized and the results concerning the diastereoselectivity of the reaction. Its also appears that remote alkoxy group does not noticeably influence the aldol distributions.

In a next paper we will develop our findings concerning the intramolecular cyclization of these compounds leading to optically active polyhydroxylated lactones.

EXPERIMENTAL SECTION

Reactions were run in oven-dried glassware, sealed with a rubber septum, and stirred with a magnetic stirring bar under argon or nitrogen if required. Materials were obtained from commercial suppliers and were used without purification, unless otherwise stated. The solvents used are Aldrich anhydrous grade if required or unless noted. Tetrahydrofuran (THF) was freshly distilled from sodium wire, diethyl ether (Et_2O) was distilled from sodium and kept on sodium. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride and kept on dark on 4 Å molecular sieves. Reactions were monitored by thin-layer chromatography carried out on Riedel-de-Haën 60 f_{254} special (0.2 mm) thin layer plates using UV light as visualizing agent and an phosphomolybdic acid solution in ethanol and heat as developing agents. NMR spectra were recorded on Bruker AC-200 or AC-250 instrument and calibrated using deuterated solvent as internal reference. The following abbreviations were used to explain the multiplicities: s = single, d = doublet, t = triplet, q = quartet, quint = quintuplet, sext = sextuplet, hept = heptuplet, m = multiplet, b = broad. IR spectra were recorded on a Perkin-Elmer model 883 Series FTIR spectrometer. Optical rotations were recorded on a Perkin-Elmer model 141 polarimeter. All measures were made at 25°C. Mass spectra were recorded on Nermag R10-10 mass spectrometer under electronic impact or chemical ionization conditions. Liquid chromatography purifications were performed in the following conditions classified according to an increasing purification difficulty: **A** Gravity chromatography using silica particle size of 70-200 μm supplied by Amicon; **B** Flash chromatography

using silica particle size of 35-70 μm supplied by Amicon; **C** Medium pressure chromatography with an axial compression Jobin-Yvon apparatus using silica particle size of 6-35 μm supplied by Amicon or 15 μm Merck. Enantiomeric excess were measured by high performance liquid chromatography on the following set: Kratos Spectroflow 400 pump, abl 759A UV detector and Chiracel OD L = 25 cm, Ø = 0.46 cm chiral column. The same apparatus set with a Waters Nova-Pak normal phase silica column (L = 15 cm, Ø = 0.39 cm) was used for diastereoisomeric ratio measurement performed on the crude product of the aldolisation reaction and also for the product purity monitoring. Melting points were measured with a Kofler apparatus and are uncorrected. 4 Å molecular sieves heated to dryness at 150°C for four hours under 0.1 torr vacuum. Zinc chloride was dried in the same conditions.

NB: Reagent amounts in mL/mmol or % are expressed relatively to the starting material.

cis Allylic Alcohol Synthesis

Protection protocol of butynol and pentynol with $tBuPh_2SiCl$. To a solution of the alcohol to be protected in DMF (4 mL/mmol), was added 2.2 eq of imidazole, and 1.1 eq of *tert*-butyldiphenylsilane chloride. After 5 h stirring at r.t. the reaction mixture was diluted with diethyl ether (2 times DMF volume), and a saturated aqueous solution of NH_4Cl (0.8 mL/mmol). The organic layer was washed 3 times with water (0.8 mL/mmol), dried over $MgSO_4$, filtered and concentrated.

1-but-3-ynyloxy-2,2-dimethyl-1,1-diphenyl-1-silapropane **21**. Starting from 0.5 g (6.92 mmol) of 3-butynol we have isolated 2.13 g (6.92 mmol) of compound **21** after liquid chromatography purification according to method **A** eluting with PE 100% then PE/Et_2O: 95/5 (TLC, PE 100%, Rf = 0.20), yield 100%. IR (neat), ν cm^{-1}: 3307 (≡C-H), 3073-2935 (C-H), 1111 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.70 and 7.41 (m, 10H), 3.80 (t, 2H, J = 7.07 Hz), 2.47 (td, 2H, J = 7.07; 2.67 Hz), 1.96 (t, 1H, J = 2.67 Hz), 1.07 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.6, 129.7, 127.7, 81.6, 69.4, 62.3, 26.8, 22.6, 19.2.

1-pent-4-ynyloxy-2,2-dimethyl-1,1-diphenyl-1-silapropane **22**. Starting from 5.0 g (59.44 mmol) of 4-pentynol we have isolated 18.89 g (58.66 mmol) of compound **22** after liquid chromatography purification according to method **A** eluting with PE 100% then EP/Et_2O: 9/1, (TLC, EP/Et_2O: 9/1, Rf = 0.49), yield 99%. IR (neat), ν cm^{-1}: same as **21**. ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.70 and 7.41 (m, 10H), 3.76 (t, 2H, J = 6.0 Hz), 2.36 (td, 2H, J = 7.0; 2.5 Hz), 1.92 (t, 1H, J = 2.5 Hz), 1.79 (m, 2H, J = 7.0; 6.0 Hz), 1.07 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.8, 129.6, 127.7, 84.3, 68.3, 62.3, 31.5, 26.9, 19.3, 15.0.

Addition procedure of lithiated acetylenide derivative on paraformaldehyde. To the alcyne solution in diethyl ether at -78°C was added dropwise butyllithium (1 eq). This mixture was stirred for 20 min at -78°C and for an additional 20 min at a temperature between -78°C and r.t. Paraformaldehyde (equal weight as the starting material) solution in ether was added at -78°C and the suspension stirred for 2 h. The cooling bath was removed followed by 12 h agitation at r.t. The reaction was quenched by adding a saturated aqueous solution of $NaHCO_3$ (0.4 mL/mmol). The aqueous phase was extracted 3 times with ether, the organic layers were gathered, dried over $MgSO_4$, filtered and concentrated.

5-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)pent-2-yn-1-ol **23**. Starting from 13.2 g (42.75 mmol) of 1-silyloxybutynol compound **21** we have obtained 10.35 g (30.62 mmol) of compound **23** after liquid chromatography purification according to method **A** eluting with PE/Et_2O: 6/4 (TLC, Rf = 0.25), yield 72%. IR (neat), ν cm^{-1}: 3355 (O-H), 3073-2935 (C-H), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.70 and 7.41 (m, 10H), 4.20 (td, 2H, J = 7.8; 2.1 Hz), 3.78 (t, 2H, J = 7.1 Hz), 2.49 (tt, 2H, J = 7.0; 2.1 Hz), 1.51 (t, 1H, J = 6.0 Hz). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.6, 129.7, 127.7, 83.5, 79.5, 62.4, 51.4, 26.8, 22.9, 19.2.

6-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)hex-2-yn-1-ol **24**. Starting from 18.89 g (53.66 mmol) of 1-silyloxypentynol compound **22** we have isolated 13.6 g (38.64 mmol) of compound **24** and 4.54 g (14.1 mmol) of the starting material after liquid chromatography purification according to method **A** eluting with PE/EA: 8/2 (TLC, Rf = 0.20), yield 72%. IR (neat), ν cm^{-1}: 3356 (O-H), 3073-2861 (C-H), 1109 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.66 and 7.42 (m, 10H), 4.20 (td, 2H, J = 5.7; 2.0 Hz), 3.73 (t, 2H, J = 6.0 Hz), 2.37 (tt,

2H, J = 7.0; 2.0 Hz), 1.76 (m, 2H), 1.66 (m, 1H), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.7, 133.9, 129.7, 127.7, 86.1, 78.6, 62.4, 51.4, 31.5, 26.9, 19.3, 15.3.

Hydrogenation of acetylenic compounds. To a solution of the alcyne in methanol (7 mL/mmol) was successively added 2% weight of 5% palladium/C/$BaSO_4$ and 4% weight of quinoline. This mixture was cooled to -20°C and H_2 was bubble into the reaction mixture. The reaction was stopped after 2 h while the cooling bath temperature has evolved from -20°C to -10°C, by filtering off the palladium through a short pad of celite. The filtrate was concentrated to dryness and the residue was used in the next step without further treatment.

(Z)-5-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)pent-2-en-1-ol **1**. Starting from 11.8 g (34.9 mmol) of **23** we obtained 12.3 g of the crude alcene **1** (including 4% of quinoline), eluant EP/Et_2O: 6/4 (CCM, Rf = 0.17). IR (film) ν cm^{-1}: 3331 (O-H); 3073-2935 (C-H); 1111 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.68 and 7.41 (m, 10H), 5.76 and 5.61 (m, 2H), 4.15 (t, 2H, J = 6.0 Hz), 3.66 (t, 2H, J = 6.5 Hz), 2.36 (q, 2H, J = 6.5 Hz), 1.74 (t, 1H, J = 5.7), 1.05 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.5, 130.7, 129.7, 129.5, 127.7, 63.2, 58.4, 30.8, 26.8, 19.2.

(Z)-6-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)hex-2-en-1-ol **2**. Starting from 10.9 g (30.9 mmol) of **24** we obtained 11.5 g of the crude alcene **2** (including 4% of quinoleine), eluant EP/Et_2O: 8/2 (CCM, Rf = 0.19). IR (neat) ν cm^{-1}: 3331 (O-H); 3072-2935 (C-H); 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.68 and 7.41 (m, 10H), 5.61 and 5.56 (m, 2H), 4.19 (dd, 2H, J = 5.70 Hz,), 3.66 (t, 2H, J = 6.12 Hz), 2.20 (td, 2H, J = 7.39 Hz), 1.62 (m, 2H), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 129.6, 127.7, 133.9, 132.5, 129.0, 62.9, 58.4, 32.2, 23.6, 26.8, 19.2.

trans Allylic Alcohols Synthesis

3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propan-1-ol **26**. To a stirred propanediol solution of 2.9 g (36.70 mmol) in 60 mL (1.6 mL/mmol) of anhydrous THF at -78°C under argon, 23 mL (36.80 mmol, 1 eq) of 1.6 M solution of butyllithium in hexane and 9.57 mL (36.80 mmol, 1 eq) *tert*-butyldiphenylsilyl chloride were added dropwise. After 15 min at -78°C, the reaction mixture was warmed to 25°C, stirred for 30 min, then was refluxed for 3 h. The THF was evaporated under reduced pressure to give a white residue which was purified according to method **A** eluting with PE/Et_2O: 5/5 (TLC, Rf = 0.35) to afford 11.50 g (36.62 mmol) of the desired compound, yield 100%. IR (neat), ν cm^{-1}: 3386 (C-OH), 2935-2861 (C-H), 1110 (C-O). ^1H NMR (250 $CDCl_3$) δ ppm: 7.70 and 7.46 (m, 10H), 3.87 (t, 4H, J = 5.5 Hz), 2.48 (m, 1H), 1.83 (q, 2H, J = 5.5 Hz), 1.07 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.0, 129.8, 127.8, 63.3, 61.9, 34.3, 26.9, 19.1. MS, EI (m/z, relative intensity): 179 (73.2%), 257 (M-tBu, 30.8%), 315 (MH^+, 0.2%).

4-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)butan-1-ol **27**. Starting from 3.5 g (36.34 mmol) butanediol the same procedure and proportions as above were applied. The purification was performed according to method **A** eluting with PE/Et_2O (TLC, Rf = 0.27) to give 10.7 g (32.74 mmol) of the monoprotected product, yield 90%. IR (neat), ν cm^{-1}: 3362 (O-H), 3073-2936 (C-H), 1658 (C=C), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.70 and 7.45 (m, 10H), 3.70 (t, 2H, J = 5.5 Hz), 3.69 (q, 2H, J = 5.5 Hz), 2.1 (t, 1H, J = 5.5 Hz), 1.69 (m, 4H), 1.07 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.7, 129.7, 127.7, 64.1, 62.8, 29.9, 29.3, 26.9, 19.2. MS, EI, (m/z, relative intensity): 199 (100%), 229 (15.3%), 271 (M-tBu).

Standard procedure for monoprotection with 4-bromobenzyl bromide. To a suspension of sodium hydride in anhydrous THF (4 mL/mmol) at 0°C was added dropwise 6 eq of the diol to be monoprotected. This mixture was stirred for 30 min, the cooling bath was removed then, tetrabutylammonium iodide (0.01 eq) and 4-bromobenzyl bromide were added. The reaction was quenched 3 h later by adding dropwise water (0.1 mL/mmol). The THF was evaporated under reduce pressure and the residue diluted with diethyl ether (4 mL/mmol). The organic layer was washed 3 time with water (1/3 of the diethyl ether volume), dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford a residue which purification will be specified for each case.

4-((4-bromophenyl)methoxy)butan-1-ol **28**. Starting from 2.44 g (27.08 mmol) of butanediol and 1.4 g (5.60 mmol) of 4-bromobenzyl bromide we have isolated 1.25 g (4.83 mmol) of the monoprotected compound by liquid chromatography purification according to method **A** eluting with PE/Et_2O (TLC, Rf = 0.26), yield 86%. IR (neat), ν cm^{-1}: 3392 (O-H), 2941-2865 (C-H), 1591 (C=C), 1069 and 1012 (C-O). ^1H NMR (200 MHz, $CDCl_3$) δ ppm: 7.45 and 7.20 (2d, 4H, J = 8.4 Hz) 4.45 (s, 2H), 3.63 (t, 2H), 3.51 (m, 2H), 2.18 (s, 1H), 1.68 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm: 137.3, 131.6, 121.6, 129.4, 72.3, 70.5, 62.7, 30.1, 26.6.

Standard oxidation procedure. To a stirred solution of the alcohol to be oxidized in anhydrous CH_2Cl_2 (1.6 mL/mmol) under argon, DMSO (2 mL/mmol) and Et_3N (5 eq) were added successively. SO_3.pyridine (5 eq) complex was added portionwise. After 1 h the reaction was diluted with diethyl ether (7 times CH_2Cl_2 volume). This organic solution was washed 3 times with water (1/3 of CH_2Cl_2 volume), dried with $MgSO_4$, filtered and concentrated. The purification will be specified for each case.

3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propanal **29**. Starting from 10.0 g (31.85 mmol) of compound **26**, 8.4 g (26.84 mmol) of aldehyde **29** were isolated after gravity chromatography according to method **A** eluting with PE/Et_2O: 7/3 (TLC, Rf = 0.38), yield 84 %. IR (neat), ν cm^{-1}: 3073-2960-2935 (C-H), 1729 (C=O), 1588 (C=C), 1107 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 9.83 (t, 1H, J = 2.3 Hz), 7.65 et 7.45 (m, 10H), 4.03 (t, 2H, J = 6.0 Hz), 2.62 (td, 2H, J = 6.0; 2.3 Hz), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 202.0, 135.6, 133.3, 129.8, 127.8, 58.3, 46.4, 26.8, 19.2. MS, DCI/NH_3, (m/z, relative intensity): 330 (M+18, 100%), 313 (M+1, 26.5%).

3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)butanal **30**. Starting from 9.0 g (27.45 mmol) of compound **27**, 7.6 g (23.38 mmol) of aldehyde **30** were isolated after gravity chromatography according to method **A** eluting with PE/Et_2O: 7/3 (TLC, Rf = 0.38), yield 85 %. IR (neat), ν cm^{-1}: 2935-2861 (C-H), 1725 (C=O), 1589 (C=C), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 9.80 (t, 1H, J = 1.8 Hz), 7.64 and 7.45 (m, 10H), 3.70 (t, 2H, J = 6.0 Hz), 2.56 (td, 2H, J = 7.3; 1.8 Hz), 1.90 (dd, 2H, J = 7.3; 6.0 Hz), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 202.6, 135.6, 129.7, 127.7, 133.6, 62.9, 40.8, 26.8, 25.3, 19.2. MS, DCI/NH_3, (m/z, relative intensity): 327 (M+1, 100%), 344 (M+18, 40.6%).

(E)-ethyl 5-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)pent-2-enoate **32**. A stirred and cooled to -78°C solution of triethyl phosphonoacetate (747 µL, 3.6 mmol, 1 eq) in 3 mL of diethyl ether was treated with 2.25 mL of n-butyllithium (3.6 mmol, 1 eq) 1.6 M solution in hexane. After 2 h stirring at -78°C 1.0 g (3.21 mmol) of aldehyde **29** in 3 mL of Et_2O was transferred on the ylide solution prepared as described above. The reaction mixture was diluted with 10 mL of Et_2O followed by the addition of 1 mL of H_2O. The organic layer was successively washed with 3 mL of a saturated aqueous solution of $NaHCO_3$, 3 mL of H_2O, dried over $MgSO_4$ filtered and concentrated. The residue was purified by gravity liquid chromatography using as eluant EP/Et_2O: 8/2 (TLC, Rf = 0.47) to give 0.9 g (2.36 mmol) of the allylic ester **32**, yield 74%. IR (neat), ν cm^{-1}: 2935-2861 (C-H), 1721 (C=O), 1655-1590 (C=C), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.67 and 7.42 (m, 10H), 7.00 (td, 1H, J = 15.5; 7.0 Hz), 5.86 (td, 1H, J = 15.5; 1.5 Hz), 4.21 (q, 2H, J = 7.0 Hz), 3.77 (qd, 2H, J = 7.0; 1.5 Hz), 1.29 (t, 3H, J = 7.0 Hz, 1.05 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 166.5, 145.9, 135.6, 133.6, 129.7, 127.7, 123.1, 62.3, 60.2, 35.5, 26.8, 19.2, 14.3. MS, DCI/NH_3, (m/z, relative intensity): 383 (M+1, 64%), 400 (M+18, 100%).

(E)-5-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)pent-2-en-1-ol **9** was synthesized starting from compound **26** without purifying the intermediates (compounds **29** and **32**). Compound **26** (20.0 g, 63.69 mmol) was oxidized according to the standard oxidation procedure to give 17.3 g of the crude aldehyde, used as it is in Wittig-Horner reaction: To a solution of triethyl phosphonoacetate (13.8 mL, 75.0 mmol, 1.3 eq) in 40 mL of toluene at -78°C was added 43.0 mL of n-BuLi (69 mmol, 1.25 eq). This mixture was stirred for 2 hours then the aldehyde solution in toluene was added dropwise at -78°C followed by an additional 2 hours stirring. Reduction: Dibal H (128 mL, 128 mmol; 2.3 eq), was added dropwise to the reaction mixture at -60°C. The reaction was quenched 1 h 30 min later with the dropwise addition at -60°C of 20 mL of saturated aqueous solution of NH_4Cl. After being warmed to r.t. the aqueous layer was extracted 2 times with 60 mL of ether. The organic phases were gathered and washed 3 times with 20 mL of brine, dried over $MgSO_4$, filtered through a pad of celite and concentrated to afford 20 g of the crude allylic alcohol. The residue was purified by

flash chromatography (method **B**) eluting with PE/Et_2O: 1/1 (TLC, Rf = 0.33) to give 13.63 g (40.09 mmol) of compound **9**, overall yield 63% for the 3 steps. IR (neat), ν cm^{-1}: 3348 (O-H), 2934-2861 (C-H), 1587 (C=C), 1109 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.68 and 7.43 (m, 10H), 5.68 (m, 2H), 4.07 (m, 2H), 3.72 (t, 2H, J = 6.5 Hz), 2.31 (m, 2H), 1.29 (m, 1H), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.9, 131.0, 129.6, 127.7, 129.6, 63.8, 63.5, 35.6, 26.9, 19.3.

(E)-6-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)hex-2-en-1-ol **10**. To a solution of 12 g (36.59 mmol) of 4 *tert*-butyldiphenylsilyloxy butanol in 59 mL (1.6 mL/mmol) of anhydrous dichloromethane at r.t. were added 73 mL of DMSO (2 mL/mmol), 25.5 mL (183.30 mmol, 5 eq) of triethylamine and 29 g (182.21 mmol, 5 eq) of sulfur trioxide pyridine complex. The reaction mixture was diluted 35 min later with 400 mL of Et_2O. The organic phase was washed 2 times with 100 mL of H_2O, dried over $MgSO_4$, filtered and concentrated to afford 12 g of the crude oxidation product used as it is in the Wittig reaction. To a 32 mL of triethyl phosphonoacetate (51.2 mmol, 1.40 eq) in 60 mL of toluene at -78°C were added dropwise 11 mL of n-butyllilthium (17.6 mmol). After 2 h 30 min stirring the crude aldehyde solution in 26 mL of toluene was added dropwise at -78°C and stirred for 3 h 45 min. Dibal H (84 mL, 84 mmol, 2.3 eq) was added dropwise to the reaction mixture at -78°C and agitated for 1 h, then MeOH (2 mL) was added, the cooling bath removed followed by 2 h agitation at r.t. To this mixture a solution of 0.7 M sodium potassium tartrate (160 mL, 112 mmol, 3.1 eq) was added and stirred for 2 h. The organic layer was extracted 2 times with 300 mL of diethyl ether. The organic layers were gathered and dried with $MgSO_4$, filtered and concentrated; Rf(**30**) = 0.39 (PE/Et_2O: 7/3), Rf(**33**) = 0.54 (PE/Et_2O: 7/3), Rf(**10**) = 0.28 (PE/Et_2O: 6/4).
The residue was purified according to method **B** eluting with PE/Et_2O: 6/4 (TLC, Rf = 0.28) to give 8.44 g of allylic alcohol **10**, overall yield 65% for 3 the steps. IR (neat), ν cm^{-1}: 3329 (O-H), 3051-2935 (C-H), 1109 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.68 and 7.41 (m, 10H), 5.64 (m, 2H), 4.04 (m, 2H), 3.68 (t, 2H, J = 7.5 Hz), 2.20 (m, 2H), 1.66 (m, 3H), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 134.0, 133.9, 129.6, 129.2, 127.6, 63.8, 63.2, 32.0, 28.5, 27.0, 19.2. Anal. for $C_{22}H_{30}O_5Si$, (calculated/found): %C 74.53 (74.52), %H 8.53 (8.42).

(E)-6-((4-bromophenyl)methoxy)hex-2-en-1-ol **11**. The synthesis procedure, reagents and proportions are identical to those used for compound **10** above. Rf(**31**) = 0.21 (PE/Et_2O: 7/3), Rf(**34**) = 0.38 (PE/Et_2O: 7/3), Rf(**11**) = 0.28 (PE/Et_2O: 4/6). Starting from 15 g (61.73 mmol) of 4-bromobenzyloxybutanol, we obtained 9.64 g (33.82 mmol) of 4-bromobenzyloxy-2-hexenol, overall yield 55% for the 3 steps. IR (neat), ν cm^{-1}: 3381 (O-H), 2937-2861 (C-H), 1097-1010 (C-O). ^1H NMR: (250 MHz, $CDCl_3$) δ ppm: 7.46 (d, 2H, J = 8.4 Hz), 7.20 (d, 2H, J = 8.4 Hz), 5.66 (m, 2H), 4.44 (s, 2H), 4.07 (d, 2H, J = 4.2 Hz), 3.46 (t, 2H, J = 6.4 Hz), 2.14 (m, 2H), 1.70 (q, J = 6.6 Hz), 1.39 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 137.6, 132.4, 131.5, 129.5, 129.3, 121.0, 72.1, 69.8, 63.7, 29.1, 28.8. Anal. for $C_{13}H_{17}O_2Br$ (calculated/found): %C 54.75 (54.79), %H 6.01 (6.06).

General epoxidation procedure. To a suspension of 4 Å molecular sieves powder (30 mg/mmol) in dichloromethane at -20°C, was injected 12% of a chiral agent (+/-DET or +/-DIPT), 0.1 eq of Titanium isopropoxide, and 2 eq *tert*-butylhydroperoxide. After 30 min stirring at -20°C the allylic alcohol solution in CH_2Cl_2 was added. The epoxidation reaction was quenched by adding 1.9 eq of 30% solution of sodium hydroxide in a saturated solution of NaCl the mixture was then warmed to 0°C, stirred for 30 min, filtered through a short pad of celite, dried over $MgSO_4$ and concentrated under reduced pressure. The residue purification will be precised for each case.

Allylic alcohol	amount g: (mmol)	chirality agent	time	eluant	Rf	Puri	epoxy-alcohol	amount: g: (mmol)	yield %
9	3.0: (8.82)	(-)DIPT	18h30	PE/Et_2O: 6/4	0.15	**C**	**ent-12**	2.7: (7.58)	86
9	1.0: (5.88)	(+) DET	16	PE/Et_2O: 4/6	0.31	**C**	**12**	1.85: (5.20)	88
10	5.0: (14.12)	(-)DET	3h	PE/EA: 6/4	0.28	**A**	**ent-13**	4.83: (13.1)	92
10	5.0: (14.12)	(+)DET	1h	PE/EA: 7/3	0.27	**A**	**13**	4.77: (12.89)	91
11	6.0: (21.05)	(+)DET	4h	PE/EA: 4/6	0.17	**B**	**14**	4.77: (15.85)	75
1	12.25: (34.79)	(+)DIPT	18h30	PE/Et_2O: 6/4	0.11	**C**	**3**	12.54	88
2	11.40: (34.79)	(+)DET	24h	PE/EA: 8/2	0.21	**C**	**4**	12.21	82

(2S,3R)-(3-2(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl)-2-oxiranyl)methan-1-ol **3**.
IR (neat), ν cm^{-1}: 3436 (O-H), 2936-2864 (C-H), 1101 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.67 and 7.40 (m, 10H), 3.79 (m, 2H), 3.74 (dd, 2H, J = 5.5 Hz), 3.21 (m, 2H), 2.27 (m, 1H), 1.86 (m, 2H), 1.07 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.57, 133.17, 129.87, 127.81, 61.37, 60.83, 56.28, 54.91, 30.80, 26.86, 19.14. $[\alpha]_D$ = +2.7° (c = 2.7, $CHCl_3$). Anal. for $C_{21}H_{28}O_3Si$, (calculated/found): %C 70.74 (70.91), %H 7.92 (8.16).

(2S,3R)-(3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl)-2-oxiranyl)methan-1-ol **4**.
IR (neat) ν cm^{-1}: 3433 (O-H), 3073 -2934 (C-H), 1589 (C=C), 1110 (C-O). ^1H NMR (250 MHz, CDCl3) δ ppm: 7.67 and 7.41 (m, 10H), 3.76 (m, 2H, J = 4.5; 6.5; 12.0 Hz, Part AB of ABX(Y)), 3.68 (m, 2H), 3.15 (ddd, 1H, J = 6.5; 4.5; 4.5 Hz part X of ABX(Y)), 3.02 (t d, 1H, J = 6.0; 4.5 Hz), 2.25 (m, 1H, OH part Y of ABX(Y)) 1.68 (m, 4H), 1.05 (s, 9H). ^{13}C NMR (63 MHz, CDCl3), δ ppm: 135.59, 135.57, 133.65, 129.73, 127.72, 63.17, 60.62, 57.02, 56.81, 29.36, 24.23, 26.88, 19.20. $[\alpha]_D$ = -2.2° (c = 1.2, $CHCl_3$). Anal. for $C_{22}H_{30}O_3Si$, (calculated/found): %C 71.31 (72.14), %H 8.16 (8.44).

((2S,3S)-(3-2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl)-2-oxiranyl)methan-1-ol **12**.
IR, NMR are identical to those of compound **ent-12**. $[\alpha]_D$ = -19.0° (c = 2.2, $CHCl_3$).

((2R,3R)-(3-2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl)-2-oxiranyl)methan-1-ol **ent-12**. IR (neat), ν cm^{-1}: 3438 (O-H), 2934-2860 (C-H), 1582 (C=C), 1109 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.67 and 7.42 (m, 10H), 3.92 and 3.63 (ddd, 2H, J = 12.5; 7.0; 5.5; 4.5; 2.5 Hz), 3.62 (2t, 2H, J = 6.5; 5.5 Hz), 3.14 (td, 1H, J = 5.5; 2.5 Hz), 2.99 (ddd, 1H, J = 4.5; 2.5; 2.5 Hz), 1.84 (dd, 2H, J = 5.5; 6.5 Hz), 1.82 (q, 1H, J = 6.5 Hz). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.6, 129.7, 127.7, 61.7, 60.8, 58.7, 53.7, 34.8, 26.8, 19.2. $[\alpha]_D$ = +19.6° (c = 2.2, $CHCl_3$).

(2S,3S)-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl)-2-oxiranyl)methan-1-ol **13**.
IR (neat), ν cm^{-1}: 3435 (O-H), 3073-2935 (C-H), 1109 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.67 and 7.44 (m, 10H), 3.72 (ddd, 1H, J = 12.5; 5.5; 2.5 Hz, part A of ABXY), 3.59 (ddd, 1H, J = 12.5; 7.3; 4.5 Hz, part B of ABXY), 3.60 (m, 2H), 2.95 (m, 1H), 2.90 (td, 1H, J = 4.5; 2.5: 2.5 Hz, part X of ABXY), 1.82 (dd, 1H, J = 7.25; 5.5 Hz, part Y of ABXY, 1.69 (m, 4H), 1.05 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.8, 129.7, 127.7, 63.3, 61.7, 58.5, 55.7, 28.9, 28.1, 26.9, 19.2. $[\alpha]_D$ = -16.2° (c = 4.5, $CHCl_3$). Anal. for $C_{22}H_{30}O_3Si$ (calculated/found): %C 71.31 (71.22), %H 8.16 (8.25).

(2R,3R)-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl)-2-oxiranyl)methan-1-ol **ent-13**. IR, NMR and EA are identical to those of compound **13**. $[\alpha]_D$ = +15.7° (c = 1.8, $CHCl_3$).

(2R,3R)-(3-(3-((4-bromophenyl)methoxy)propyl)-2-oxiranyl)methan-1-ol **14**. IR (neat), ν cm^{-1}: 3435 (O-H), 2934-2864 (C-H), 1102 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.47 (d, 2H, J = 8.4 Hz), 7.20 (d, 2H, J = 8.5 Hz), 4.44 (s, 2H), 3,87 (ddd, 1H, J = 12.5; 5.4; 2.7 Hz part A of ABXY), 3.61 (ddd, 1H, J = 12.5; 7.2; 4.3 Hz, part B of ABXY), 3.50 (m, 2H), 2.99 (m, 1H), 2.91 (ddd, 1H, J = 4.3; 2.7; 2.1 Hz, part X of ABXY), 1.86 (dd, 1H, J = 7.2; 5.4 Hz, part Y of ABXY), 1.71 (m, 4H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 137.4, 131.5, 129.3, 121.5, 72.2, 69.8, 61.7, 58.5, 55.7, 28.5, 26.2. $[\alpha]_D$ = -21.2° (c = 2.7, $CHCl_3$), ee = 98%. Anal. for $C_{13}H_{17}OBr$, (calculated/found): %C 51.84 (51.80), %H 5.69 (5.64).

Epoxyalcohol standard oxidation procedure. To a stirred solution of the alcohol to be oxidized in anhydrous CH_2Cl_2 (1.6 mL/mmol) under argon, DMSO (2 mL/mmol) and Et_3N (5 eq) were added successively. Then, SO_3 pyridine complex (5 eq) was added portionwise. After 1 h the reaction was diluted with diethyl ether (7 times CH_2Cl_2 volume). This organic solution was washed 3 times with water (1/3 of CH_2Cl_2 volume) dried over $MgSO_4$ filtered and concentrated. The purification will be precised for each case.

(2R,3R)-3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl)oxirane-2-carbaldehyde **5**.
Starting from 10.61 g (29.80 mmol) of epoxyalcohol **3** we have isolated 8.18 g (23.10 mmol) of epoxyaldehyde **5** by MPLC purification (method **C**) eluting with PE/Et_2O 8/2, (TLC, Rf = 0.20). yield 78%. IR (neat) ν cm^{-1}: 3073-2934 (C-H); 1724 (C=O); 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 9.42 (d,

1H, J = 4.9 Hz); 7.67 and 7.42 (m, 10H); 3.83 (m, 2H); 3.47 (ddd, 1H, J = 4.5; 4.5; 6.0 Hz); 3.40 (t, 1H, J = 4.7 Hz); 1.94 (m, 2H); 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 198.58, 135.56, 133.25, 129.86, 127.82, 60.86, 57.65, 57.02, 30.96, 26.82, 19.16. $[\alpha]_D$ = +57.2° (c = 0.84, $CHCl_3$). Anal. for $C_{21}H_{26}O_3Si$, (calculated/found): %C 71.15 (71.09), %H 7.39 (7.39).

(2R,3R)-3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl)oxirane-2-carbaldehyde **6**
Starting from 9.13 g (24.68 mmol) of epoxyalcohol **4** we have isolated 6.55 g (17.80 mmol) of epoxyaldehyde **6** by gravity liquid chromatography purification (method **A**) eluting with PE/Et_2O 8/2, (TLC, Rf = 0.19). yield 72%. IR (neat) ν cm^{-1}: 3073-2935 (C-H); 1724 (C=O); 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 9.45 (d, 1H, J = 5.0 Hz), 7.65 and 7.41 (m, 10H), 3.72 (m, 2H), 3.32 (t, 1H, J = 5.0 Hz), 3.20 (m, 1H, J = 6.5; 5.0 Hz); 1.81 (m, 4H), 1.05 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 199.13, 135.60, 133.68, 129.76, 127.76, 62.90, 59.03, 58.03, 29.49, 26.70, 24.04, 19.24. $[\alpha]_D$ = +61.0° (c = 1.3, $CHCl_3$). Anal. for $C_{22}H_{28}O_3Si$, (calculated/found): %C 71.70 (71.41), %H 7.66 (7.65).

(2R,3S)-3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl)oxirane-2-carbaldehyde **15**.
Starting from 4.0 g (11.24 mmol) of epoxyalcohol **12** we have isolated 3.25 g (9.18 mmol) of epoxyaldehyde **15** by MPLC purification (method **C**) eluting with PE/Et_2O 7/3, (TLC, Rf = 0.26). Yield 82%. IR, NMR are identical to those of the above to those of compound **ent-15**. $[\alpha]_D$ = +48.3° (c = 1.6 $CHCl_3$).

(2S,3R)-3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl)oxirane-2-carbaldehyde **ent-15**.
Starting from 2.0 g (5.62 mmol) of epoxyalcohol **ent-12** we have isolated 1.66 g (4.69 mmol) of epoxyaldehyde **ent-15** by MPLC purification (method **C**) eluting with PE/Et_2O 7/3, (TLC, Rf = 0.33). yield 83%. IR (neat) ν cm^{-1}: 2960-2934 (C-H), 1729 (C=O), 1110 (C-O). ^1H NMR (200 MHz, $CDCl_3$) δ ppm: 9.03 (d, 1H, J = 6.0 Hz), 7.67 and 7.41 (m, 10H), 3.84 (2t, 2H, J = 6.0; 5.5 Hz), 3.42 (d, t, 1H, J = 5.5; 2.0 Hz), 3.21 (dd, 1H, J = 5.5; 2.0 Hz), 1.80 (bq, 2 H, J = 6.0; 5.5; 5.5 Hz), 1.07 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm: 198.3, 135.6, 133.4, 127.9, 60.5, 59.3, 54.8, 34.4, 26.9, 19.2. $[\alpha]_D$ = -47.2° (c = 1,4 $CHCl_3$). Anal. for $C_{21}H_{26}O_3Si$, (calculated/found): %C 71.15 (71.36), %H 7.39 (7.49).

(2R,3S)-3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl)oxirane-2-carbaldehyde **16**.
Starting from 4.77 g (12.89 mmol) of epoxyalcohol **13** we have isolated 3.52 g (9.57 mmol) of epoxyaldehyde **16** by MPLC purification (method **C**) eluting with PE/Et_2O 8/2, (TLC, Rf = 0.20). yield 84%. IR (film), ν cm^{-1}: 3073-2935 (C-H), 1729 (C=O), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 8.99 (d, 1H, J = 6.2 Hz), 7.67 and 7.41 (m, 10H), 3.73 (t, 2H, J = 5.5 Hz), 3.23 (m, 1H), 3.13 (dd, 1H, J = 6.2; 2.0 Hz), 1.73 (m, 4H), 1.07 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 198.4, 135.6, 133.7, 129.7, 127.7, 63.0, 59.2, 56.6, 28.6, 27.9, 26.9, 19.2. $[\alpha]_D$ = +37.6° (c = 2.2, $CHCl_3$). Anal. for $C_{22}H_{28}O_3Si$ (calculated/found): %C 71.70 (71.94), %H 7.66 (7.53).

(2S, 3R)-3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl)oxirane-2-carbaldehyde **ent-16**. Starting from 4.83 g (13.05 mmol) of epoxyalcohol **ent-13** we have isolated 3.99 g (10.84 mmol) of epoxyaldehyde **ent-16** by gravity liquid chromatography purification (method **A**) eluting with PE/Et_2O 7/3, (TLC, Rf = 0.32). yield 83%. IR, NMR are identical to those of the above to those of compound **13**. $[\alpha]_D$ = -38.6° (c = 2.15, $CHCl_3$).

(2R,3S)-3-(3-((4-bromophenyl)methoxy) propyl)oxirane-2-carbaldehyde **17**. Starting from 4.77 g (15.85 mmol) of epoxyalcohol **14** we have isolated 3.7 g (12.37 mmol) of epoxyaldehyde **14** by gravity liquid chromatography purification (method **A**) eluting with PE/Et_2O: 4/6 (TLC, Rf = 0.31). yield 78%. IR (neat), ν cm^{-1}: 2935-2863 (C-H), 1726 (C=O), 1104 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 9.00 (d, 1H, J = 6.0 Hz), 7.46 and 7.18 (2d, 4H, J = 7.5 Hz), 4.44 (s, 2H), 3.50 (m, 2H), 3.26 (m, 1H), 3.14 (dd, 1H, J = 6.0; 2.0 Hz), 1.78 (m, 4H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 198.4, 137.3, 131.5, 129.3, 121.5, 72.3, 69.4, 59.2, 56.5, 28.3, 26.0. $[\alpha]_D$ = +54.1° (c = 1.9, $CHCl_3$). Anal. $C_{13}H_{15}O_3Br$, (calculated/found): %C 52.19 (52.47), %H 5.05 (5.16).

Aldolisations. The aldolic condensation reactions were realized following different procedures referenced A to D.

— Aldolisation 1 eq enolate/1 eq aldehyde: procedure A (-78°C). The 0.5 M lithium diisopropylamine (LDA) solution was prepared by adding dropwise n-butyllithium (1.6 M in hexane) to a stirred solution of diisopropylamine in diethyl ether at -78°C. After 30 min, one equivalent of *tert*-butylacetate was added dropwise and the mixture was stirred for 1 h. It was then transferred to a 0.5 M aldehyde solution in diethyl ether at -78°C. The aldol condensation average length is 2 h. The reaction was quenched by adding a saturated aqueous solution of NH_4Cl, the aqueous phase was extracted 3 times with Et_2O. The organic phases were gathered and dried over $MgSO_4$, filtered and concentrated. The residue purification condition will be given for each case.

— Aldolisation 2 eq of enolate/1 eq aldehyde: procedure B (-78°C) and C (-78°C to +25°C). The 2 equivalent lithiated enolate of *tert*-butylacetate 0.5 M solution in diethyl ether at -78°C prepared as stated above, was transferred onto a aldehyde 0.5 M solution in diethyl ether at -78°C. After one hour stirring the reaction temperature was either kept at -78°C or allow to raised or warmed to +25°C (procedure C), and this warming duration vary from 4 to 13 h.

Procedure D: 2.5 enolate equivalent with a condensation at temperature that as evolved from -78°C to -22°C for procedures A to C. The yields given are for the liquid chromatography isolated diastereoisomers. The diastereoisomeric ratio was measured by HPLC on the aldolisation reactions crude products.

aldehyde			procedure	epoxyesters		yield %
weight (g)	mmol	N°		*anti/syn*	N° (*anti/syn* : a/b)	
1.5	4.23	**ent-15**	A	73/27	**ent-18 (a/s)**	77
0.5	1.41	**ent-15**	B	75/25	**ent-18 (a/s)**	73
3.2	9.04	**15**	C	72/28	**18 (a/s)**	88
0.5	1.36	**ent-16**	B	76/24	**ent-19 (a/s)**	90
0.5	1.36	**ent-16**	C	75/25	**ent-19 (a/s)**	80
2.2	6.03	**16**	D	74/26	**19 (a/s)**	67
0.5	1.68	**17**	B	75/25	**20* (a/s)**	82
3.9	10.9	**5**	B	81/19	**7 (a/s)**	82
1	2.82	**5**	C	87/13	**7 (a/s)**	84
1	2.72	**6**	B	85/15	**8 (a/s)**	93
1	2.72	**6**	C	98/2	**8 (a/s)**	76

* These esters are separable by analytical HPLC but not by MPLC. The *anti/syn* ratio are both identical by analytical and ^1H NMR measurements.

(3S,4S,5R)-tert-butyl 3-(3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl))(2-oxiranyl))-3-hydroxypropanoate **7a**. Purification: Method **C**, eluant PE/EA/CH_2Cl_2: 6/0.8/3.2 (TLC, Rf_{7a} = 0.26, Rf_{7s} = 0.11). Starting from 1.0 g (2.82 mmol) of aldehyde **5**, we have isolated 0.93 g (1.97 mmol) of **7a** and 0.19 g (0.40 mmol) of **7s**, yield 84% (table entry 10). IR (neat), ν cm^{-1}: 3446 (O-H), 3074-2935 (CH), 1729 (C=O), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.68 and 7.42 (m, 10H), 3.84 (m, 2H), 3.78 (dddd, 1H, J = 8.3; 8.3; 3.5; 3.5 Hz, part X of ABX), 3.46 (d, 1H, J = 3.5 Hz), 3.20 (t d, 1H, J = 6.5; 4.3 Hz), 2.96 (dd, 1H, J = 8.3; 4.30 Hz), 2.62 (dd, 1H, J = 16.0; 3.5 Hz, part A of ABX), 2.59 (dd, 1H, J = 16.0; 8.3 Hz, part B of ABX), 1.89 (m, 2H), 1.47 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 171.73, 135.58, 133.33, 129.79, 127.77, 81.53, 66.20, 61.40, 57.92, 55.25, 40.16, 30.80, 28.12, 26.85, 19.15. $[\alpha]_D$ = -3.1° (c = 1.4, $CHCl_3$). MS, DCI/NH_3, (m/z, relative intensity): 488 (M+18, 100%), 471 (M+1, 2.7%).

(3R,4S,5R)-tert-butyl 3-(3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl))(2-oxiranyl))-3-hydroxypropanoate **7s**. IR (neat), ν cm^{-1}: 3454 (O-H), 3074-2934 (C-H), 1730 (C=O), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.67 and 7.41 (m, 10H), 3.82 (m, 3H, contains part X of ABX), 3.25 (ddd, 1H, J = 7.62; 4.58; 4.58 Hz), 3.00 (dd, 1H, J = 7.62; 4.58 Hz), 2.94 (d, 1H, J = 3.97 Hz), 2.51 (dd, 1H, J = 16.0; 7.6 Hz, part A of ABX), 2.46 (dd, 1H, J = 16.0; 4.88 Hz, part B of ABX), 1.90 (m, 1H), 1.76 (m, 1H), 1.45 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 170.68, 135.55, 133.51, 133.43, 129.76, 127.75, 81.57, 67.01, 61.39,

59.09, 54.88, 39.62, 31.24, 28.11, 26.86, 19.19. $[\alpha]_D$ = +16.3° (c = 1.1, $CHCl_3$). MS, DCI/NH_3, (m/z, relative intensity): 488 (M+18, 100%), 471 (M+1, 1,1%).

(3S,4S,5R)-tert-butyl 3-(3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl))(2-oxiranyl)-3-hydroxypropanoate **8a**. Purification: Method **C**, eluant PE/EA/CH_2Cl_2: 6/0.8/3.2 (CCM, Rf_{8a} = 0.22, Rf_{8s} = 0.09). Starting from 1 g (2.72 mmol) of aldehyde **6**, we have isolated 1.04 g (2.15 mmol) of **8a** and 0.19 g (0.39 mmol) of **8s**, yield 93%. IR (neat) ν cm^{-1}: 3441 (O-H); 3052 (C-H); 1730 (C=O), 1152-1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.68 and 7.38 (m, 10H), 3.72 (m, 1H, part X of ABX), 3.72 (m, 2H), 3.58 (d, 1H, J = 4.0 Hz), 3.01 (m, 1H), 2.91 (dd, 1H, J = 8.0; 4.0 Hz), 2.66 (dd, 1H, J = 16.5; 4.0 Hz, part A of ABX), 2.55 (dd, 1H, J = 16.5; 8.5 Hz, part B of ABX), 1.69 (m, 4H), 1.47 (s, 9H), 1.05 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 172.06, 135.60, 133.74, 133.69, 129.68, 127.70, 81.63, 65.91, 63.23, 58.18, 57.60, 40.02, 29.23, 24.02, 28.11, 26.89, 19.19. $[\alpha]_D$ = -8.6° (c = 1.5, $CHCl_3$). MS, DCI/NH_3, (m/z, relative intensity): 502 (M+18, 100%), 485 (M+1, 10.4%).

(3R,4S 5R)-tert-butyl 3-(3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl))(2-oxiranyl-3-hydroxypropanoate **8s**. IR (neat) ν cm^{-1}: 3450 (O-H), 3073-2935 (C-H), 1730 (C=O), 1152-1109 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.66 and 7.40 (m, 10H), 3.86 (m, 1H, J = 8.0; 4.5 Hz, part X of ABX), 3.70 (m, 2H), 3.01 and 2.97 (m, 2H), 2.52 (dd, 1H, J = 16.0; 8.0 Hz, part A of ABX), 2.44 (dd, 1H, J = 16.0; 4.5 Hz, part B of ABX), 1.76 (m, 2H), 1.60 and 1.50 (m, 2H), 1.47 (s, 9H), 1.05 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 170.66, 135.57, 133.78, 129.66, 127.68, 81.64, 66.99, 63.25, 59.40, 57.10, 39.61, 29.77, 24,78, 28.13, 26.89, 19.22. $[\alpha]_D$ = +12.3° (c = 1.2, $CHCl_3$). MS, DCI/NH_3, (m/z, relative intensity): 502 (M+18, 100%).

(3S,4S,5S)-tert-butyl 3-(3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl))(2-oxiranyl))-3-hydroxypropanoate **18a**. Purification: Method **C**, eluant PE/EA/CH_2Cl_2: 5/1/4 (TLC, Rf = 0.39). IR and NMR are identical to those of its enantiomer compound *anti* **ent-18a**. $[\alpha]_D$ = -19.8° (c = 1.3, $CHCl_3$).

(3R,4S,5S)-tert-butyl 3-(3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl))(2-oxiranyl))-3-hydroxypropanoate **18s**. Purification: Method **C**, eluant PE/EA/CH_2Cl_2: 5/1/4 (TLC, Rf = 0.27). IR and NMR are identical to its enantiomer *syn* compound **ent-18s**. $[\alpha]_D$ = -12.8° (c = 1.4, $CHCl_3$).

(3R,4R, 5R)-tert-butyl 3-(3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl))(2-oxiranyl))-3-hydroxypropanoate **ent-18a**. Purification: Method **C**, eluant PE/EA/CH_2Cl_2: 5/1/4 (TLC, Rf = 0.39). Table entries 1, 2. IR (neat) ν cm^{-1}: 3464 (O-H), 3074-2935 (C-H), 1729 (C=O), 1590 (C=C), 1156-1110 (C-O).^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.66 and 7.40 (m, 10H), 3.99 (m 1H, J = 8.0; 4.8; 4.5; 4.0 Hz, part X of ABX), 3.80 (m, 2H), 3.15 (ddd, 1H, J = 7.5; 4.9; 2.2), 2.97 (d, 1H, J = 4.0 Hz), 2.85 (dd, 1H, J = 4.8; 2.2 Hz), 2.53 (dd, 1H, J = 16.0; 4.5 Hz, part A of ABX), 2.46 (dd, 1H, J = 16.0; 8.0 Hz, part B of ABX), 1.92 (m, 2H), 1.47 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 171.4, 135.6, 133.6, 129.7, 127.7, 81.5, 67.3, 60.8, 59.8, 54.2, 39.0, 34.9, 28.1, 26.9, 19.2. $[\alpha]_D$ = +20.8° (c = 2.0, $CHCl_3$). Anal. for $C_{27}H_{38}O_5Si$, (calculated/found): %C 68.90 (68.88), %H 8.14 (8.28). MS, DCI/NH_3, (m/z, relative intensity): 488 (M+18, 100%).

(3S, 4R, 5R)-tert-butyl 3-(3-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl))(2-oxiranyl)) -3-hydroxypropanoate **ent-18s**. Purification: Identical to compound **ent-18a** (TLC, Rf = 0.27). IR (neat) ν cm^{-1}: 3459 (O-H), 3074-3052 (C-H), 1728 (C=O), 1587 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.68 and 7.41 (m, 10H), 3.98 (ddd, 1H, J = 6.6; 5.5; 2.2 Hz), 3.80 (m, 2H), 3.15 (ddd, 1H, J = 5.9; 5.0; 2.0 Hz), 2.86 (dd, J = 4.5; 2.2 Hz), 2.76 (d, 1H, J = 5.5 Hz), 2.50 (d, 2H, J = 6.6 Hz), 1.78 (m, 2H), 1.47 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 170.9, 135.6, 133.6, 129.7, 127.7, 81.4, 67.5, 60.8, 60.5, 53.9, 39.9, 34.8, 28.1, 26.9, 19.2. $[\alpha]_D$ = +11.5° (c = 1.3, $CHCl_3$). Anal. for $C_{27}H_{38}O_5Si$, (calculated/found): %C 68.90 (68.97), %H 8.14 (8.31).

(3S,4S,5S)-tert-butyl 3-(3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl))(2-oxiranyl))-3-hydroxypropanoate **19a**. Purification: Method **C**, eluant PE/EA/CH_2Cl_2: 5/1/4 (TLC, Rf = 0.35). IR (neat), ν cm^{-1}: 3463 (O-H), 3074-2935 (C-H), 1729 (C=O), 1150-1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.67 and 7.42 (m, 10H), 3.92 (m, 1H, J = 7.8; 4.9; 4.5; 4.0 Hz), 3.70 (m, 2H), 3.00 (d, 1H, J = 4.0 Hz), 2.90 (m, 1H), 2.78 (dd, 1H, J = 4.9; 2.0 Hz), 2.51 (dd, 1H, J = 16.0; 4.5 Hz, part A of ABX), 2.44 (dd, 1H, J = 16.0; 7.8 Hz, part B of ABX), 1.66 (m, 4H), 1.47 (s, 9H), 1.05 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 171.43, 135.38, 133.85,

129.62, 127.67, 81.57, 67.31, 63.25, 59.76, 56.38, 39.02, 28.89, 28.16, 28.11, 26.87, 19.23. $[\alpha]_D$ = -15.0° (c = 3.2, $CHCl_3$). Anal. for $C_{28}H_{40}O_5Si$, (calculated/found): %C 70.12 (69.36), %H 8.12 (8.31).

(3R,4S,5S)-tert-butyl 3-(3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl))(2-oxiranyl)) -3-hydroxypropanoate **19s**. Purification: Method **C**, eluant PE/EA/CH_2Cl_2: 5/1/4 (TLC, Rf = 0.24). IR: (neat), ν cm^{-1}: 3451 (O-H), 3074-2936 (C-H), 1729 (C-O), 1156-1110 (C-O). ^1H NMR: (250 MHz, $CDCl_3$) δ ppm: 7.66 and 7.40 (m, 10H), 3.92 (m, 1H), 3.69 (m, 2H), 2.95 (m, 1H), 2.78 (m, 2H), 2.48 (m, 2H), 1.67 (m, 4H), 1.47 (s, 9H), 1.05 (s, 9H). ^{13}C NMR: (63 MHz, $CDCl_3$) δ ppm: 170.93, 135.57, 132.82, 129.64, 127.67, 81.48, 67.58, 63.25, 60.51, 56.01, 39.80, 28.86, 28.11, 26.87, 19.22. $[\alpha]_D$ = -6.8° (c = 4.3, $CHCl_3$). Anal. for $C_{28}H_{40}O_5Si$, (calculated/found): %C 70.12 (69.73), %H 8.12 (8.62).

(3R,4R,5R)-tert-butyl 3-(3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl)(2-oxiranyl)) -3-hydroxypropanoate **ent-19a**. Purification: idem compound **19a**. IR and NMR are identical to those of its enantiomer compound **19a**. $[\alpha]_D$ = +15.4° (c = 2.4, $CHCl_3$).

(3R,4S,5S)-tert-butyl 3-(3-(3-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)propyl))(2-oxiranyl)) -3-hydroxypropanoate **ent-19s**. Purification: same as compound **19s**. IR and NMR are identical to those of its enantiomer compound **19s** above. $[\alpha]_D$ = +7.3° (c = 2.1, $CHCl_3$).

(3S,4S,5S)-tert-butyl 3-(3-(3-((4-bromophenyl)methoxy)propyl))(2-oxiranyl))-3-hydroxypro-panoate **20a** and *(3R,4S,5S)-tert-butyl 3-(3-(3-((4-bromophenyl)methoxy)propyl))(2-oxiranyl))-3-hydroxypropanoate* **20s**. Purification: Method **C**, eluant PE/EA/CH_2Cl_2: 4/2/4 (CCM, Rf = 0.28). Starting from 0.5 g (1.68 mmol) of epoxyaldehyde **17**, 0.57 g (1.37 mmol) of the diastereoisomeric mixture **20a/20s** was isolated, yield = 82%. IR (neat), ν cm^{-1}: 3452 (O-H), 2978-2932 (C-H), 1726 (C=O), 1104 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.45 and 7.19 (d, 4H, J = 7.5 Hz), 4.44 (s, 2H), 3.94 (m, 1H, minor compound, part X of ABX), 3.91 (m, 1H, major compound, part X of ABX), 3.10 (d, 1H, J = 3.6 Hz), 3.00 (m, 1H), 2.80 (m, 1H), 2.50 (m, 2H, part AB of syst ABX), 1.76 (m, 4H), 1.45 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 171.4, 137.5 131.5, 129.3, 121.4, 81.6, 72.2, 69.8, 67.4, 60.4, 55.9, 59.7, 56.34, 39.8, 39.1, 28.5, 26.2, 28.1. Anal. for $C_{19}H_{27}O_5Br$, (calculated/found): %C 54.94 (54.84), %H 6.55 (6.59).

(3S,5S)-1-(2-(5-(2-(2,2-dimethyl-1,1-diphenyl-1-silapropoxy)ethyl)-3,3-dimethyl(2,4-dioxo-lanyl))ethoxy)-2,2-dimethyl-1,1-diphenyl-1-silapropane **36**. A solution of γ,δ-epoxy-β-hydroxyester **7a** (601 mg, 1.28 mmol) in THF (15 ml) under argon and stirring was treated with RedAl (0.79 mL, 2.7 mmol). The mixture was stirred for 1 h, two more equivalents were additionned and stirring was maintained for another 3 h. The mixture was then diluted with ether (10 mL) and hydrolyzed by dropwise addition of water (10 mL) then acidified to pH = 3. The organic phases were washed with water (2 mL) saturated $NaHCO_3$ (2 mL and saturated NaCl (2 mL). The combined aqueous phases were acidified and submitted to continuous extraction with ether for 12 h. All organic phases were then combined dried over $MgSO_4$ and solvent evaporated. The crude product was used in the next step. A solution of triol (165 mg, 0.41 mmol) in anhydrous DMF (2 mL) was treated under stirring and argon with imidazole (118 mg, 1.75 mmol) and tert-butyldiphenylsilylchloride (113 μL, 0.41 mmol). The mixture was stirred for 12 h, then hydrolyzed with 1 mL of saturated NH_4Cl solution and extracted with ether (3 x 10 mL). The organic phases were dried over $MgSO_4$ and solvent evaporated. HPLC purification of the crude product (eluant petroleum ether : ethyl acetate 7:3 afford 249 mg of compound **35** (yield 95%). ^1H NMR (200 MHz, $CDCl_3$) δ ppm: 7.70-7.65 (m, 8H), 7.42-7.38 (m, 12H), 4.21-3.90 (M, 2H), 3.92-3.77 (M, 4H), 3.40 (BR, 1H), 3.35 (BR, 1H), 1.92-1.62 (M, 6H), 1.05 (S, 9H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.6, 129.7, 127.7, 70.9, 63.15, 35.1, 27.0, 19.2. Anal. for $C_{39}H_{52}O_4Si_2$, (calculated/found): %C 74.3 (74.7), %H 7.9 (7.8).

To a solution of compound **35** (173 mg, 0.27 mmol) in 2,2-dimethoxypropane (2 mL) under argon, was added camphor sulphonic acid (1.5 mg). The mixture was stirred for 1 h, hydrolyzed with saturated $NaHCO_3$ solution (1 mL) extracted with ether (2 x 10 mL), dried over $MgSO_4$ and solvent evaporated to afford 140 mg (yield 100%) of compound **36** (tlc, eluant petroleum ether : ether 8:2). ^1H NMR (200 MHz, $CDCl_3$) δ ppm: 7.71 (M, 8H), 7.42-7.35 (M, 12H), 4.15-4.02 (DD, J = 2.5, 11.0 HZ, 2H), 3.92-3.67 (M, 4H), 1.76-1.62 (M, 4H), 1.54-1.45 (DDD, J = 2.1; 2.5; 12.5 HZ, 2H), 1.47 (S, 3H), 1.41 (S, 3H), 1.36-1.22 (DDD, J = 10.6; 11.0; 12.5 Hz, 2H), 1.05 (S, 18H). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 135.6, 133.6, 129.7, 127.7, 98.7, 60.3, 59.8, 45.5, 39.3, 30.3, 27.0, 19.9, 19.3. Anal. for $C_{42}H_{56}O_4Si_2$, (calculated/found): %C 74.1 (74.0), %H 8.2 (8.1).

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