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Mukaiyama aldolisation reactions of α,β-epoxyaldehydes in aqueous media

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Abstract—The Mukaiyama aldolisation reaction in aqueous media of cis and trans α,β-epoxyaldehydes with *tert*-butyldimethylsilyl ketene acetal in the presence of Lewis's acids was studied. $Sc(OTf)_3$ gave the best results in terms of selectivity. The same reaction of cis and trans α,β-epoxyaldehydes with the enoxysilane of ethyl pyruvate resulted in epoxy substituted ulosonic derivatives issued from a double sequential condensation of the pyruvate on the epoxy derivatives.

1. Introduction

Use of water as a reaction solvent has received considerable attention in synthetic organic chemistry especially in relation to today's environmental concerns and the aim of reducing the use of harmful organic reagents. Numerous reactions have been performed in the last 10 years in this economical solvent, generally realised under mild conditions with respect to organic solvents. Recent developments include pericyclic reactions, transition metal catalyzed reactions, radical ones, oxidations and reductions, carbonyl additions.[1] Nucleophilic additions to carbonyl compounds, one of the major fields in organic synthesis make use of strong nucleophiles or weak ones in the presence of Lewis acid activators. While Lewis acid promoted reactions in organic solvents need strictly anhydrous conditions, during the last years rare earth metal triflates and some other metal salts have been found to catalyze aldol reactions in water systems.[2]

In the course of our ongoing research programme directed towards construction of 1,2,3 polyhydroxylated frames, useful synthons in the elaboration of ulosonic compounds and peptidonucleosides,[3] we developed a method based on the stereocontrolled addition on the α,β-epoxyaldehydes. In that respect, we have extensively studied the issue and the diastereoselectivity of the aldol reaction of various α,β-epoxyaldehydes[4a] with lithium enolates issued from acetates. The same general trends in terms of selectivity were observed under Mukaiyama conditions in organic solvents.[4b] On the other hand, we have reported a direct synthesis of bicyclic precursors of ulosonic esters[5a] and furanosidic fluorinated ulosonic analogues[5b] by reaction of cis and trans α,β-epoxyaldehydes, respectively, with ethyl 2-(trimethylsilyloxy)-2-propenoate in the presence of boron trifluoride diethyl etherate.

Terminal epoxides have recently been used in water reactions in order to derivatize sucrose by grafting a α,β(or α)-di (or mono)hydroxylated fatty chain.[6]

We wish to describe in this report, our first results on the aqueous Mukaiyama aldol reactions of α,β-epoxyaldehydes with enol silanes issued from *tert*-butyl acetate and ethyl pyruvate, an issue that has never been addressed before.

α,β-Epoxyaldehydes **4** and **5** were synthesized as reported previously[4a] while benzylated racemic cis epoxyaldehyde **6** was obtained by reaction with *m*-cpba.[7]

tert-Butyldimethylsilyl ketene acetal **7** was effectively obtained in high yield (93%) by reacting lithium *tert*-butyl acetate with *tert*-butyldimethyl silyl chloride in THF at 0 °C in the presence of HMPA.[4b]

Ethyl 2-(trimethylsilyloxy)-2-propenoate **13** was prepared in 70% yield from the corresponding pyruvate by treatment with trimethylsilylchloride and triethylamine in the presence of a catalytic amount of DMAP.[8]

Lewis acid catalysis of the aldolisation reaction in water

Keywords: Mukaiyama aldolisation reaction; Ulosonic esters; α,β-Epoxyaldehydes.
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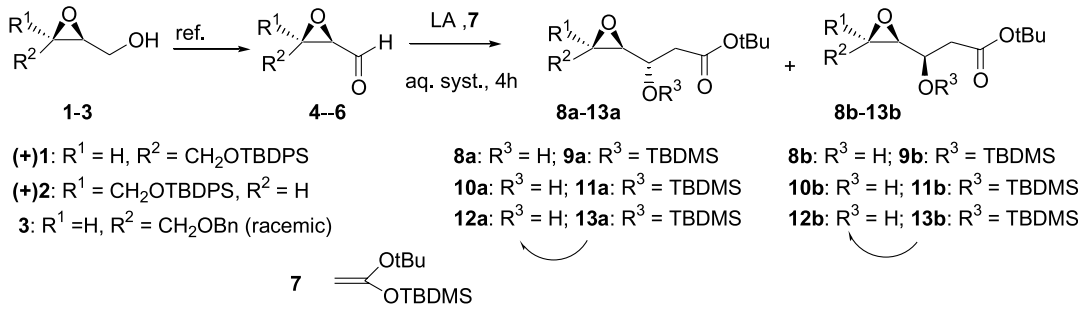


Scheme 1.

(Scheme 1), was first examined in the reaction of cis α,β-epoxyaldehyde **4** with ketene silyl acetal **7**. Different experimental conditions were evaluated (Table 1). Where lanthanide triflates were used in water, the reaction operated in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS). When the commercialized, scandium tris (dodecylsulfate) (STDS) or when a mixture THF/H_2O were used, SDS was not introduced.

A typical experimental procedure consisted in adding a surfactant solution containing the Lewis acid to the α,β-epoxyaldehyde, followed by the addition of ketene silyl acetal **7** and allowing the reaction to proceed for 4 h before quenching with saturated aq NaCl. The crude material was purified on silica gel and/or analyzed by analytical chromatography. In the latter case, yields were calculated from analytical data and by ^{1}H NMR spectroscopy.

While the reaction proceeded sluggishly in the presence of a catalytic amount of a lanthanide triflate, a certain amount of organic solvent (THF) and in the absence of any micellar system (Table 1, entry 1), it proceeded smoothly when SDS was used (Table 1, entries 2–5). In fact, the SDS/H_2O system led to the obtention of the aldol adducts in moderate yields. Europium and lanthanum triflates afforded same results in terms of yields (25 and 26%, respectively), and diastereoselectivity of the reaction (*anti*/*syn* 90/10 and 91/9, respectively). The aldolisation reaction in the presence of $Yb(OTf)_3$ led to a slightly better yield and diastereoselectivity, while the best results were obtained when operating in the presence of a catalytic amount of $Sc(OTf)_3$ in the H_2O/SDS micellar system (41% yield and 94:6 *anti*/*syn* diastereoface preference). In each case studied, about 15% of unreacted aldehyde was observed by ^{1}H NMR spectroscopy. Additional amount of ketene silylacetal **7** (2 equiv) did not lead to better results. On the other hand, prolonged reaction times (till 15 h) afforded degradation products that do not bear the epoxide ring and the yield of the aldol adducts highly decreased in each case. Finally, it is noteworthy, that when the aldolisation reaction in the presence of $Sc(OTf)_3$/SDS/H_2O system was stopped after 2 h (40% of unreacted aldehyde detected by analytical liquid chromatography), the same *anti* diastereoface preference was observed (*anti*/*syn* 94/6).

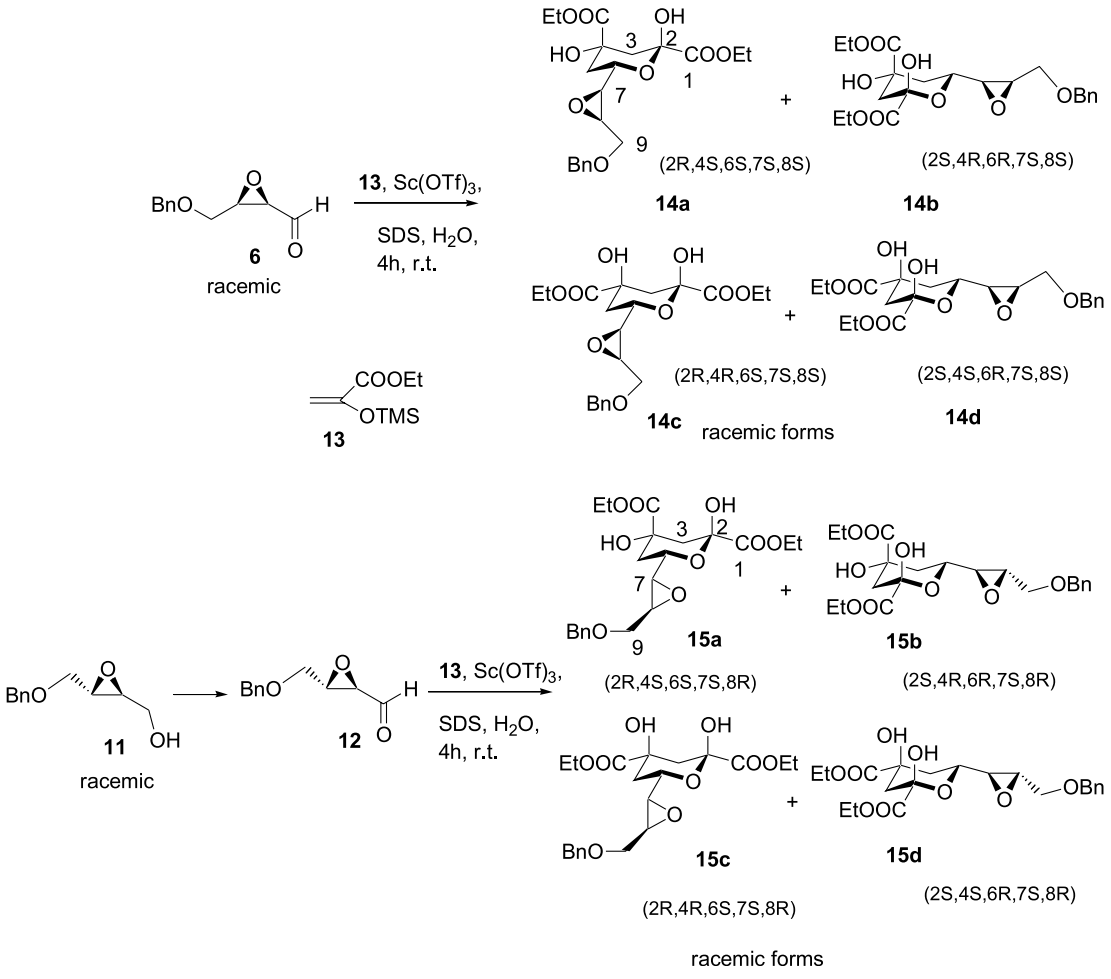
Some other systems have also been examined. Use of the Lewis acid-surfactant combined catalyst (LASC) scandium tris (dodecyl sulfate) STDS,[9] led to similar yields of aldol adducts as for $Sc(OTf)_3$ but to a lower diastereoselectivity (Table 1, entry 6). We also explore the possibility to enhance the reactivity of the reaction by adding a Brönsted acid. This has been recently reported in the case of aldol reactions in water between a benzaldehyde and silyl enolates in the presence of LASC catalysts.[10] Disappointingly, in the case of α,β-epoxyaldehyde **4**, reactions in the presence of a Brönsted acid (HCl, TsOH) and a lanthanide triflate or STDS were very sluggish (Table 1, entries 7–9), leading to degradation products and to invariably low yields of aldol adducts. Moreover, when the reaction mixture was quenched and examined in shorter periods (1 h), results showed essentially starting material and degradation products (absence of the epoxide ring by ^{1}H NMR spectroscopy).

Reaction was also tested with α,β-epoxyaldehydes **5**, **6**, by operating in the most favorable systems in terms of reactivity and selectivity. For trans epoxyaldehyde **5** reaction in the presence of $Sc(OTf)_3$ or $La(OTf)_3$ gave in

Table 1. Aqueous Mukaiyama aldol reaction of aldehydes **4–6** with **7** under different systems

Entry	Aldehyde	Lewis acid	System used	Yield%	*Anti*/*syn*
1	**4**	$Yb(OTf)_3$	H_2O/THF	<5	nd
2	**4**	$Eu(OTf)_3$	H_2O/SDS	25	90/10
3	**4**	$La(OTf)_3$	H_2O/SDS	46[a]	91/9
4	**4**	$Sc(OTf)_3$	H_2O/SDS	41[a]	94/6
5	**4**	$Yb(OTf)_3$	H_2O/SDS	33	94/6
6	**4**	STDS	H_2O	38	90/10
7	**4**	$La(OTf)_3$	H_2O/SDS/HCl	<5	nd
8	**4**	$La(OTf)_3$	H_2O/SDS/TsOH	<5	nd
9	**4**	STDS	H_2O/HCl	<5	nd
10	**5**	$Sc(OTf)_3$	H_2O/SDS	35[a]	73/27
11	**5**	$La(OTf)_3$	H_2O/SDS	33	67/33
12	**6**	$Sc(OTf)_3$	H_2O/SDS	40[a]	93/7
13	**6**	$La(OTf)_3$	H_2O/SDS	35	90/10

[a] After silica gel purification.



Scheme 2.

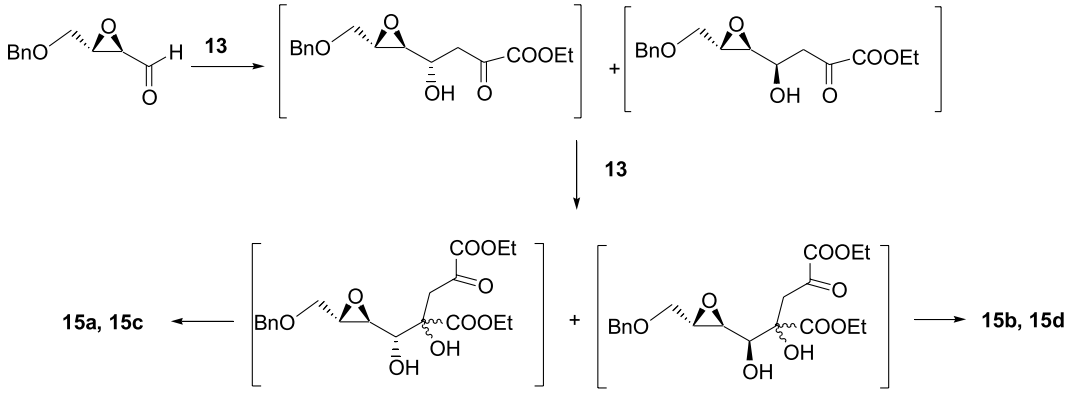
moderate yields the aldol compounds in a 3:1 diastereoisomeric ratio in favor of the *anti* derivative (Table 1, entries 10 and 11). Concerning the aldol reaction with cis benzylated epoxyaldehyde **6**, in order to better analyze the results, after determining by ^{1}H NMR spectroscopy the amount of non reacted aldehyde, the mixture was treated with SiO_2 supported *n*-Bu_4NF; the two separable hydroxy containing diastereoisomers were then analyzed. The $Sc(OTf)_3$/SDS/H_2O system afforded in 40% total yield the aldol adducts in a 93/7 *anti*/*syn* ratio, results similar to that obtained with aldehyde **4**.

The Mukaiyama aldolisation reaction in aqueous media was also examined by reacting enol silane issued from ethyl pyruvate with cis α,β-epoxyaldehyde **6** (Scheme 2). The reaction is triggered by adding ethyl 2-(trimethylsilyloxy)-2-propenoate **13** in a mixture of SDS, $Sc(OTf)_3$, and aldehyde in water and allowed to proceed for 4 h before quenching. After two silica gel purifications of the complex reaction mixture, two fractions were isolated. Analytical chromatography of each fraction (C18 column $d=3$ mm, eluant H_2O/CH_3CN 65:35, flow rate 0.6 ml/mn, UV 220 nm) revealed the presence of two compounds. They have been identified by mass spectrometry and NMR as the modified ulosonic esters **14a**, **14b** and **14c**, **14d** obtained in 35% yield and in a ratio of 6:3:1:0.5.

The same reaction has also been performed with trans α, β-epoxyaldehyde **12** obtained in its racemic form in five steps and 56% total yield from the *cis*-buten-1,4-diol. Again, purification of the complex reaction mixture afforded two fractions revealing the presence of two compounds in each one. The products have been identified as before, as the modified ulosonic esters[11] **15a**, **15b**, and **15c**, **15d** obtained in 29% yield and in a ratio of 10:4:2:0.4.

Compounds **15a**–**15b** have been analyzed through extensive NMR analysis (^{1}H, 2D COSY, ^{13}C, ^{13}C DEPT, ^{1}H–^{13}C HMBC, and HSQC). Each compound shows large coupling constants between H_6 and H_{5ax} protons indicating a trans axial disposition of these two protons. A ^{4}J coupling constant appears between H_{3eq} and H_{5eq} protons. Chemical shifts for proton and carbon atoms for the couple (**a**,**b**) are almost identical indicating that axial/equatorial position of the substituents are the same. We may thus conclude that compounds **a**,**b** are in a chair conformation where the lateral epoxide ring is in equatorial position.

The ^{13}C chemical shift of the C2 carbon atom ($\delta=94.8$ ppm for **a** and **b**) is relevant of a pyranosidic ulosonic functionality while the C4 quaternary carbon atom resonates at $\delta=71.3$ ppm. Assuming that in ulosonic esters, the most favorable position of the C1 ester group is equatorial, the



Scheme 3.

relative configuration of the C4 quaternary carbon atoms is determined by the C3 proton chemical shifts. In fact, the chemical shifts of H3a, H3eq protons are inverted when changing the axial/equatorial position of the C2/C4 hydroxy groups (δ_{H3eq} greater than δ_{H3ax}), to an axial/axial disposition. This is in accordance with the findings in ulosonic acids[12] and with our previous work on modified methyl quinate compounds.[13] Nevertheless, we cannot still determine if compounds **a/b** are issued from the *anti*/*syn* aldolisation adducts.

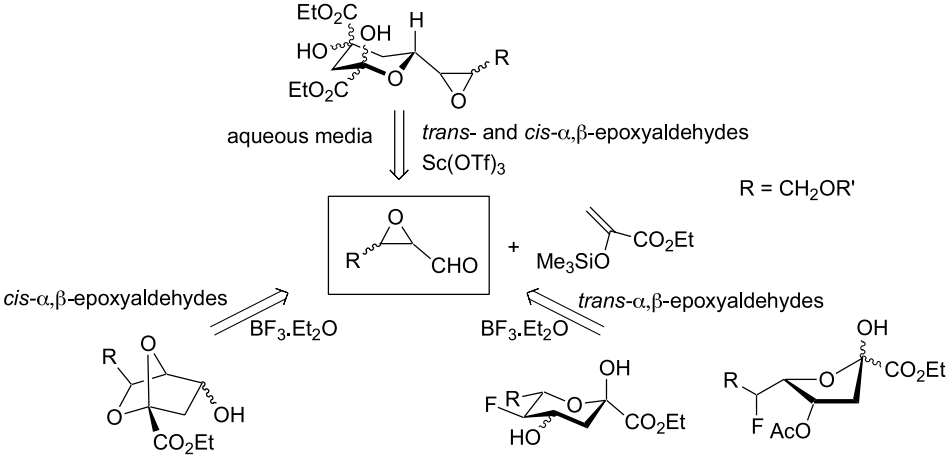
These modified ulosonic esters are issued from the sequential double condensation of the ethyl 2-(trimethylsilyloxy)-2-propenoate **13** on the aldehyde. Mukaiyama aldolisation reaction leads first to the two *anti*/*syn* adducts. A second reaction occurs between the carbonyl group and **13** leading to four diastereoisomeric intermediates that can then favorably cyclise affording the final adducts (Scheme 3).

Other reaction conditions have been used in order to isolate a monocondensation adduct (1 equiv of **13**, its portionwise addition, reaction time). The five-fold (0.2 equiv) portionwise addition of **13** (time interval 1 h) led to a complex reaction mixture possessing a weak peak in mass spectrometry ($m/z=328$ M+18), corresponding to the monocondensation adduct (that could not be isolated). The known propensity of pyruvate to autocondense is operating in the system studied here.[14]

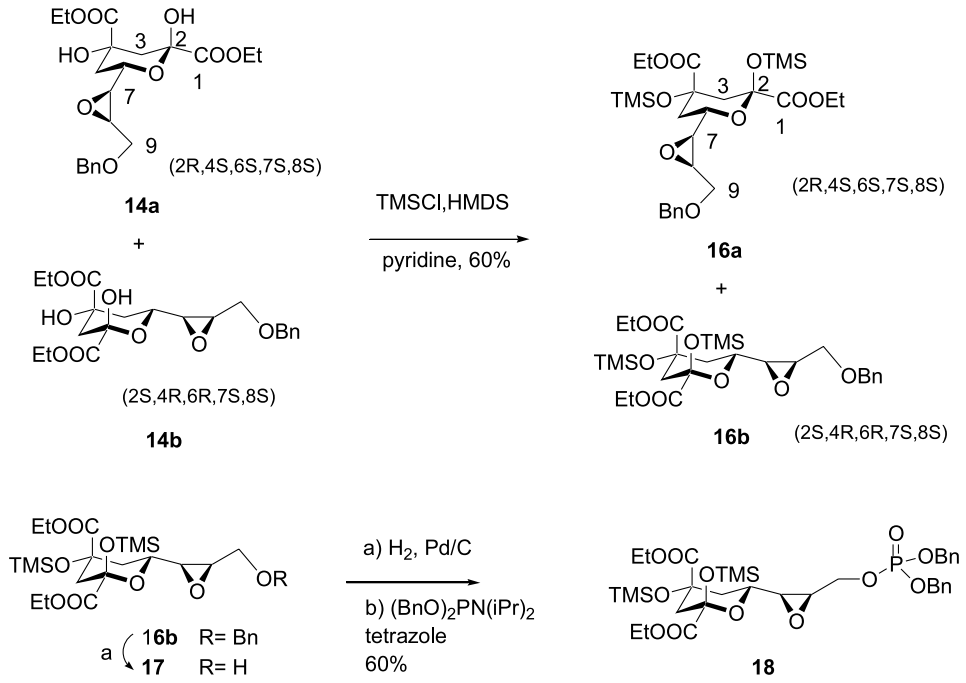
The aqueous Mukaiyama aldol reaction leads in this case to results completely different from the reaction in organic media (Scheme 4). In fact, we have shown earlier that in CH_2Cl_2 and when using $Et_2O\cdot BF_3$ (the only Lewis acid effectively operating), reaction with trans α,β-epoxyaldehydes yields essentially fluorinated ulosonic compounds,[5b] while cis α,β-epoxyaldehydes afford in a most efficient manner bicyclic compounds.[5a] Both adducts are issued from a monocondensation reaction of enolpyruvate with the corresponding aldehyde. This represents one of the rare examples where a Mukaiyama aldolisation reaction between same reactants, offers three different reaction pathways and final products depending on the geometry of the starting allylic alcohol (affording cis or trans α,β-epoxyaldehyde) and the reaction medium (organic, aqueous).

Some further functionnalisations have been performed on the **14a**,**b** compounds (Scheme 5). Silylation of the tertiary hydroxy functions was accomplished by reacting the mixture with TMSCl/HMDS in pyridine. The fully silylated compounds **16a** and **16b** were obtained individually after purification by silica gel chromatography in 60% total yield. Compound **16b** was then debenzylated and the primary alcohol **17** was phosphorylated in the presence of *N*,*N*-diisopropylamino-dibenzyl phosphoramidite followed by *m*-cpba oxidation, affording in 55% yield (two steps) the phosphorylated modified ulosonic ester **18**.

In summary, we have further extended the study on the



Scheme 4.



Scheme 5.

aldolisation reaction involving α,β-epoxyaldehydes. Rare earths functioning as Lewis acids in aqueous media can induce the aldolisation reaction of ketene silyl acetal. The issue and the diastereoselectivities observed concerning the aldol adducts remain the same in comparing with reactions operating in organic media (nucleophilic or Mukaiyama aldolisation reaction), while yields are lower. Rare earths can also perform the aqueous aldolisation reaction with the labile enoxysilane of ethylpyruvate, leading to new derivatives of ulosonic esters.

Further studies are in progress in order to optimize and extend the utility of the aqueous Mukaiyama aldol reaction involving α,β-epoxyalehydes.

2. Experimental

2.1. General remarks

The following solvents and reagents were dried prior to use: methylene chloride, dimethylformamide (from calcium hydride, stored over 4 Å molecular sieves), triethylamine (from calcium hydride, stored over potassium hydroxide pellets), THF (freshly distilled from sodium/benzophenone). Thin-layer chromatography (TLC) reaction monitoring was carried out with Macherey-Nagel ALUGRAM® SIL G/UV$_{254}$ (0.2 mm) plates visualized with 10% phosphomolybdic acid in ethanol or Dragendorff reagent as dipping solutions. Standard column chromatography was performed with SDS 70–200 μm silica gel. Medium-pressure liquid chromatography was performed with a Jobin-Yvon apparatus using Merck 15–40 μm or Amicon 6–35 μm silica gel. Analytical liquid chromatography was performed with a Spectroflow 400Kratos pump equipped with a UV 759A Applied Biosystems detector and a silica Novapack (15 cm) column (pressure 19 bars). NMR spectroscopic data were obtained with Bruker AC200, AC250, and AC400 instruments operating with ^{1}H spectra at 200, 250, and 400 MHz, respectively, ^{13}C spectra at 50, 63, and 100 MHz, respectively. Chemical shifts are quoted in parts per million (ppm) downfield from tetramethylsilane and coupling constants are in Hertz. Infrared (IR) spectra were recorded on a Perkin-Elmer FT-IR 1725X spectrometer. Mass spectrometry (MS) data were obtained on a NERMAG R10-10 spectrometer.

Synthesis of (2*S*,3*S*) and (2*S*,3*R*)-4-(*tert*-butyldiphenylsilyloxy)-2,3-epoxybutan-1-als **4** and **5** is accomplished in three (and five) steps, respectively, from *cis*-buten-1,4-diol, by using (+)DET as the chiral agent in the Sharpless asymmetric epoxidation reaction.[4a]

The general procedure for synthesis of racemic α,β-epoxyalcohols **3** and **11** has been previously reported.[7] The Döering method[15] has been used to obtain the corresponding aldehydes **6** and **12** as for compounds **4** and **5** starting from the corresponding epoxyalcohols.

2.1.1. (2*R*,3*R*) and (2*S*,3*S*)-4-(Benzyloxy)-2,3-epoxybutan-1-al 6. Aldehyde (1.58 g) was obtained through Döering oxidation of 2 g (10.3 mmol) of alcohol **3** (yield 80%).

^{1}H NMR (250 MHz, $CDCl_3$) δ 9.44 (d, 1H, $J_{1/2}$=4.8 Hz, H1), 7.36–7.28 (m, 5H, phenyl), 4.56 (s, 2H, PhCH_2O), 3.87 (dd, 1H, $J_{4a/3}$=3.5 Hz, $J_{4a/4b}$=11.5 Hz, H4a), 3.73 (dd, 1H, $J_{4b/3}$=4.5 Hz, $J_{4b/4a}$=11.5 Hz, H4b), 3.49 (m, 1H, H3), 3.40 (m, 1H, H2).

^{13}C NMR (50 MHz, $CDCl_3$) δ 197.8 (C1), 137.8 (Cq phenyl), 128.6, 127.8 (CH phenyl), 73.6 (CH_2OPh), 66.2 (C4), 58.0 and 57.4 (C2 and C3).

MS (DCI, NH_3): 210 (MNH_4^+, 100%). IR ($CHCl_3$) ν_{max} 3065–3033 (CH arom.), 2864 (CHO), 1723 (C=O), 1095 (C–O) cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.41; H, 6.29.

2.1.2. (2*R*,3*R*) and (2*S*,3*S*)-4-(Benzyloxy)-2,3-epoxybutan-1-ol 11. *m*-CPBA epoxidation of the starting allylic alcohol (3 g, 16.84 mmol) afforded 2.95 g (90% yield) of compound **11** after silica gel purification (petroleum ether/ether 3:7).

^1H NMR (250 MHz, $CDCl_3$) δ 7.35–7.28 (m, 5H, phenyl), 4.54 and 4.60 (AB syst, 2H, $J=11.9$ Hz PhCH_2O), 3.92 (dd, 1H, $J_{4a/3}=2.5$ Hz, $J_{4a/4b}=12.5$ Hz, H4a), 3.77 (dd, 1H, $J_{1a/2}=3.05$ Hz, $J_{1a/1b}=11.51$ Hz, H1a), 3.64 (dd, 1H, $J_{4b/4a}=12.73$ Hz, $J_{4b/3}=4.18$ Hz, H4b), 3.53 (dd, 1H, $J_{1b/2}=5.45$ Hz, $J_{1b/1a}=11.52$ Hz, H1b), 3.22–3.24 and 3.09–3.11 (2m, 2H, H2, and H3).

^{13}C NMR (50 MHz, $CDCl_3$) δ 137.8, 128.5, 127.9 (C arom., OBn), 73.4 (CH_2OBn), 69.7 (C4), 61.3 (C1), 55.7 and 54.2 (C2 and C3).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.28. Found: C, 67.99; H, 7.28.

2.1.3. (2*S*,3*R*) and (2*R*,3*S*)-4-(Benzyloxy)-2,3-epoxybutan-1-al 12. Aldehyde (1.50 g) was obtained through Döering oxidation of 2 g (10.3 mmol) of alcohol **11** (yield 75%).

^1H NMR (250 MHz, $CDCl_3$) δ 9.05 (d, 1H, $J_{1/2}=6.26$ Hz, H1), 7.36–7.28 (m, 5H, phenyl), 4.58 (s, 2H, PhCH_2O), 3.85 (dd, 1H, $J_{4a/3}=2.62$ Hz, $J_{4a/4b}=11.67$ Hz, H4a), 3.58 (dd, 1H, $J_{4b/3}=4.96$ Hz, $J_{4b/4a}=11.66$ Hz, H4b), 3.48 (m, 1H, H3), 3.34 (dd, 1H, $J_{2/3}=1.97$ Hz, $J_{2/1}=6.23$ Hz, H2).

^{13}C NMR (50 MHz, $CDCl_3$) δ 197.7 (C1), 137.4 (Cq phenyl), 128.6, 128.1, 127.9 (CH phenyl), 73.6 (CH_2OPh), 66.2 (C4), 58.0 and 57.4 (C2 and C3).

IR ($CHCl_3$) ν_{max} 3068–3030 (CH arom.), 2869 (CHO), 1724 (C=O), 1090 (C–O) cm^{-1}.

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.91; H, 6.25.

2.1.4. Ethyl 2-(trimethylsilyloxy)-2-propenoate 13. To 200 ml of anhydrous toluene was added successively 24 ml of TMSCl (189.1 mmol, 1.3 equiv), 0.888 g of DMAP (7.27 mmol, 0.05 equiv) and 15.94 ml of ethyl pyruvate (145.46 mmol, 1 equiv). The solution was heated under reflux and 26.3 ml of Et_3N (189.1 mmol, 1.3 equiv) were added dropwise. After 2 h under reflux, the mixture was cooled, filtered rapidly then toluene evaporated off. The remaining crude product was distilled under reduced pressure (90 °C, 50 mbar) affording the desired product (19.2 g, 70% yield).

^1H NMR (250 MHz, $CDCl_3$) δ 5.52 (d, 1H, $J=1.10$ Hz, H3a), 4.88 (d, 1H, $J=1.04$ Hz, H3b), 4.22 (q, 2H, $J=7.18$ Hz, OCH_2CH$_3$), 1.31 (t, 3H, $J=7.18$ Hz, OCH$_2$CH_3), 0.23 (s, 9H, Si(CH_3)$_3$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 164.4 (C1), 147.1 (C2), 103.9 (C3), 61.1 (CH_2 ethyl), 14.1 (CH_3 ethyl), −0.5 (TMS).

IR (neat) ν_{max} 2963 (C=H), 1731 (C=O), 1627 (C=C) cm^{-1}. MS (DCI, NH_3): 206 (MNH_4^+, 100%).

2.2. Procedure for the aldolisation reaction with *tert*-butyl dimethylsilyl ketene acetal 7

A water solution (6 ml) containing the α,β-epoxyaldehyde (1.2 mmol), the Lewis acid (0.1 equiv), SDS (69.2 mg, 0.238 mmol, 0.2 equiv) and (or not) a Brönsted acid (0.1 equiv), was stirred for 10 min. Ketene silyl acetal **7** (0.553 g, 2.4 mmol, 2 equiv) was then added to the mixture, which was stirred vigorously (1250 rpm) for 4 h. The reaction was then quenched by adding 6 ml aq saturated NaCl. Extraction was operated with ethyl acetate (3× 10 ml). The organic phase was dried over $MgSO_4$ and solvent evaporated. Purification and identification of compounds **8–11** was done as previously reported.[4]

Reaction in the absence of a surfactant was performed as before in a THF–H_2O solution (6 ml, 2/1).

Reaction in the presence of STDS was done as before in the absence of SDS and in 12 ml of water.

Concerning the reaction with aldehyde **6**, the final reaction mixture was treated by TBAF on silica gel (1.7 g at about 1.25 mol of fluoride/g; 1.1 mmol) in anhydrous THF (15 ml). The reaction mixture was vigorously stirred for 7 h and filtered. Silica gel was washed several times with ethyl acetate and the combined organic phases concentrated. The crude product was purified by MPLC chromatography affording the known products **12a**, **12b**.[4a]

2.3. Procedure for the aldolisation reaction with ethyl 2-(trimethylsilyloxy)-2-propenoate 13

A water solution (40 ml) containing 1.5 g of α,β-epoxyaldehyde (7.81 mmol, 1 equiv), 0.445 g of SDS (1.54 mmol, 0.19 equiv), 0.385 g of scandium triflate (0.78 mmol, 0.1 equiv), was stirred for 10 min. Compound **13** (2.4 g, 12.7 mmol, 1.6 equiv) was then added and the mixture was vigorously stirred for 5 h, before quenching with potassium chloride (10 equiv) and diluting with ethyl acetate (45 ml). The organic phase obtained was extracted with H_2O (3×30 ml), dried over $MgSO_4$, filtered and the solvent evaporated.

2.3.1. Ethyl 2,4-dihydroxy-4-carbethoxy-6-(9-(benzyloxy)-7,8-*cis*-epoxy)-tetrahydropyran-2-carboxylate 14a–14d. The crude product was first purified by medium pressure silica gel chromatography (eluant petroleum ether/ether 55:45) affording 0.3 g of starting aldehyde. The remaining mixture was then purified by inverse phase chromatography (silica, Hyperprep C18, eluant H_2O/CH_3CN 70:30). Two fractions could be isolated containing compounds **14a**,**14b** (792 mg) and **14c**,**14d** (132 mg).

R_f: 0,4 (PE/AcOEt 5:5).

Analytical HPLC: C18, 3 mm column; eluant: H_2O/CH_3CN

65:35, flow rate = 0.6 ml/min, UV 220 nm. Retention time **14a/14b** = 4.26/2.62 min. **14c/14d** = 3.66/6.37 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ (**14a**,**14b**) 7.33–7.31 (m, 5H, phenyl), 4.61–4.51 (m, 2H, PhCH_2O), 4.29–4.20 (m, 4H, CH_2 ethyl), 4.09 (ddd, 1H, $J_{6/7}$ = 7.90 Hz, $J_{6/5ax}$ = 12.35 Hz, $J_{6/5eq}$ = 2.39 Hz, H_6), 3.76 (dd, 1H, $J_{9a/8}$ = 4.42 Hz, $J_{9a/9b}$ = 11.18 Hz, H9a), 3.63 (dd, 1H, $J_{9b/8}$ = 6.48 Hz, $J_{9b/9a}$ = 11.19 Hz, H9b), 3.29–3.24 (m, 1H, H_8), 3.08 (dd, 1H, $J_{7/6}$ = 7.77 Hz, $J_{7/8}$ = 4.52 Hz, H_7), 2.39 (dd, 1H, $J_{3eq/3ax}$ = 13.04 Hz, $^4J_{3eq/5eq}$ = 2.09 Hz, H3eq), 2.19 (td, 1H, $J_{5eq/3eq} = J_{5eq/6}$ = 2.10 Hz, $J_{5eq/5ax}$ = 12.90 Hz, H5eq), 2.16 (d, $J_{3ax/3eq}$ = 13.01 Hz, H3ax), 1.60 (t, 1H, $J_{5ax/5eq} = J_{5ax/6}$ = 12.68 Hz, H5ax), 1.31–1.24 (m, 6H, CH_3 ethyl).

δ (**14c** or **14d**) 7.34–7.31 (m, 5H, phenyl), 4.61 and 4.52 (2d, 2H, J = 11.71 Hz, PhCH_2O), 4.29–4.25 (m, 4H, CH_2 ethyl), 4.03 (ddd, 1H, $J_{6/7}$ = 7.79 Hz, $J_{6/5ax}$ = 11.37 Hz, $J_{6/5eq}$ = 2.72 Hz, H_6), 3.90 (dd, 1H, $J_{9a/8}$ = 3.39 Hz, $J_{9a/9b}$ = 11.74 Hz, H9a), 3.55 (dd, 1H, $J_{9b/8}$ = 6.82 Hz, $J_{9b/9a}$ = 11.74 Hz, H9b), 3.28–3.21 (m, 1H, H_8), 3.04 (dd, 1H, $J_{7/6}$ = 7.76 Hz, $J_{7/8}$ = 4.20 Hz, H_7), 2.47 (d, 1H, $J_{3ax/3eq}$ = 14.08 Hz, H3ax), 2.05–1.90 (m, 3H, H3eq, H5eq, H5ax), 1.31–1.24 (m, 6H, CH_3 ethyl).

δ (**14d**,**14c**) 7.34–7.31 (m, 5H, phenyl), 4.46 and 4.58 (2d, 2H, J = 11.71 Hz, PhCH_2O), 4.29–4.20 (m, 4H, CH_2 ethyl), 4.14 (ddd, 1H, $J_{6/7}$ = 7.38 Hz, $J_{6/5ax}$ = 12.25 Hz, $J_{6/5eq}$ = 2.37 Hz, H_6), 3.67 (dd, 1H, $J_{9a/8}$ = 5.91 Hz, $J_{9a/9b}$ = 11.07 Hz, H9a), 3.63 (dd, 1H, $J_{9b/8}$ = 6.82 Hz, $J_{9b/9a}$ = 11.09 Hz, H9b), 3.28–3.21 (m, 1H, H_8), 3.09 (dd, 1H, $J_{7/6}$ = 7.36 Hz, $J_{7/8}$ = 4.48 Hz, H_7), 2.46 (d, 1H, $J_{3ax/3eq}$ = 14.09 Hz, H3ax), 2.05–1.90 (m, 2H, H3eq and H5ax), 1.70 (td, 1H, $J_{5eq/5ax}$ = 13.4 Hz, $J_{5eq/6} = {}^4J_{5eq/3eq}$ = 2.32 Hz, H5eq), 1.31–1.24 (m, 3H, CH_3 ethyl).

^{13}C NMR (63 MHz, $CDCl_3$) δ (**14a**,**14b**) 173.9, 173.7, 168.0, 169.2 (CO_2Et), 137.8 (Cq phenyl), 128.5, 128.2, 127.9, 127.8, 127.7 (CH phenyl), 94.7 (C2), 73.3 and 73.1 (O*C*H_2Ph), 70.8 and 72.1 (C4), 69.6 and 68.4 (C6), 68.2 and 68.0 (C9), 62.8, 62.7, and 62.1 (CH_2 ethyl), 57.3 and 56.8 (C8), 55.7 and 54.5 (C7), 40.7, 40.5, and 36.7, 35.0 (C5 and C3), 14.0 and 13.9 (CH_3 ethyl).

δ (**14c** and **14b**) 173.7, 173.6, 168.8, and 169.7 (CO_2Et), 137.9 and 137.6 (Cq phenyl), 128.5, 128.4, 128.0, 127.9, 127.8, 127.7 (CH phenyl), 94.8 (C2), 73.4 and 73.2 (O*C*H_2Ph), 72.2 and 72.0 (C4), 68.1 and 68.0 (C9), 66.2 and 64.7 (C6), 62.6, 62.5 and 62.4 (CH_2 ethyl), 57.3, 56.7 (C8), 55.9 and 54.5 (C7), 37.2, 36.9, 35.2 (C5 and C3), 14.1, 14.0 (CH_3 ethyl).

MS (DCI, NH_3): 442 (M+18). IR (neat) ν_{max} 3431 (OH), 3060 (CH arom.), 2983 (CH), 1738 (C=O) cm^{-1}.

Anal. Calcd for $C_{21}H_{28}O_9$: C, 59.43; H, 6.60. Found: C, 59.64; H, 6.48.

2.3.2. Ethyl 2,4-dihydroxy-4-carbethoxy-6-(9-(benzyloxy)-7,8-*trans*-epoxy)-tetrahydropyran-2-carboxylate 15a–15d. The crude product was first purified by medium pressure silica gel chromatography (eluant petroleum ether/ethyl acetate 6:4) affording 0.25 g of starting aldehyde. The remaining mixture was then purified by inverse phase chromatography (silica, hyperprep C18, eluant H_2O/CH_3CN 55:45). Two fractions could be isolated containing compounds **15a**, **15b** (0.73 g), and **15c**, **15d** (0.125 g).

R_f: 0,28 (PE/AcOEt 5:5).

Analytical HPLC: C18, 3 mm column, eluant: H_2O/CH_3CN 65:35, flow rate = 0.6 ml/min, UV 220 nm. Retention time **15a/15b** = 6.72/3.77 min. **15c/15d** = 4.14/2.69 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ (**15a** or **15b**) 7.31–7.30 (m, 5H, phenyl), 4.56 and 4.51 (2d, 2H, J = 12.00 Hz, PhCH_2O), 4.24–4.18 (m, 4H, CH_2 ethyl), 4.11 (ddd, 1H, $J_{6/7}$ = 5.48 Hz, $J_{6/5ax}$ = 12.15 Hz, $J_{6/5eq}$ = 2.37 Hz, H6), 3.73 (dd, 1H, $J_{9a/8}$ = 2.97 Hz, $J_{9a/9b}$ = 11.71 Hz, H9a), 3.48 (dd, 1H, $J_{9b/8}$ = 5.33 Hz, $J_{9b/9a}$ = 11.56 Hz, H9b), 3.20 (ddd, 1H, $J_{8/9a} = J_{8/7}$ = 2.71 Hz, $J_{8/9b}$ = 5.19 Hz, H_8), 3.03 (dd, 1H, $J_{7/6}$ = 5.48 Hz, $J_{7/8}$ = 2.23 Hz, H7), 2.39 (dd, 1H, $J_{3eq/3ax}$ = 13.2 Hz, $^4J_{3eq/5eq}$ = 2.22 Hz, H3eq), 2.27 (td, 1H, $J_{5eq/6} = {}^4J_{5eq/3eq}$ = 2.22 Hz, $J_{5eq/5ax}$ = 12.88 Hz, H5eq), 2.15 (d, 1H, $J_{3ax/3eq}$ = 13.19 Hz, H3ax), 1.65 (t, 1H, $J_{5ax/5eq} = J_{5ax/6}$ = 12.59 Hz, H5ax), 1.30–1.24 (m, 6H, CH_3 ethyl).

δ (**15b** or **15a**) 7.31–7.30 (m, 5H, phenyl), 4.56 and 4.51 (d, 2H, J = 12.00 Hz, PhCH_2O), 4.24–4.18 (m, 4H, CH_2 ethyl), 4.14 (ddd, 1H, $J_{6/7}$ = 4.64 Hz, $J_{6/5ax}$ = 12.15 Hz, $J_{6/5eq}$ = 2.51 Hz, H_6), 3.76 (dd, 1H, $J_{9a/8}$ = 2.81 Hz, $J_{9a/9b}$ = 11.55 Hz, H9a), 3.43 (dd, 1H, $J_{9b/8}$ = 5.63 Hz, $J_{9b/9a}$ = 11.55 Hz, H9b), 3.16 (ddd, 1H, $J_{8/9b}$ = 5.26 Hz, $J_{8/9a} = J_{8/7}$ = 2.67 Hz, H_8), 2.99 (dd, 1H, $J_{7/6}$ = 4.37 Hz, $J_{7/8}$ = 2.15 Hz, H_7), 2.38 (dd, 1H, $J_{3eq/3ax}$ = 13.19 Hz, $^4J_{3eq/5eq}$ = 2.30 Hz, H3eq), 2.27 (td, 1H, $J_{5eq/6} = {}^4J_{5eq/3eq}$ = 2.22 Hz, $J_{5eq/5ax}$ = 12.88 Hz, H5eq), 2.16 (d, 1H, $J_{3ax/3eq}$ = 13.19 Hz, H3ax), 1.61 (dd, 1H, $J_{5ax/6}$ = 12.15 Hz, $J_{5ax/5eq}$ = 12.88 Hz, H5ax), 1.30–1.24 (m, 3H, CH_3 ethyl).

δ (**15c** or **15d**) 7.31–7.23 (m, 5H, phenyl), 4.56 and 4.51 (2d, 2H, J = 11.60 Hz, PhCH_2O), 4.27–4.18 (m, 5H, CH_2 ethyl and H6), 3.74 (dd, 1H, $J_{9a/8}$ = 2.79 Hz, $J_{9a/9b}$ = 11.67 Hz, H9a), 3.43 (dd, 1H, $J_{9b/8}$ = 5.60 Hz, $J_{9b/9a}$ = 11.68 Hz, H9b), 3.13 (ddd, 1H, $J_{8/9a} = J_{8/7}$ = 2.65 Hz, $J_{8/9b}$ = 5.10 Hz, H_8), 3.02 (dd, 1H, $J_{7/6}$ = 4.72 Hz, $J_{7/8}$ = 2.18 Hz, H_7), 2.45 (d, 1H, $J_{3eq/3ax}$ = 14.06 Hz, H3ax), 1.98–1.90 (m, 2H, H3eq and H5ax), 1.73 (dt, 1H, $J_{5ax/5eq}$ = 13.4 Hz, $J_{5eq/6} = {}^4J_{5eq/3eq}$ = 2.37 Hz, H5eq), 1.31–1.27 (m, 6H, CH_3 ethyl).

^{13}C NMR (100 MHz, $CDCl_3$) δ (**15a** or **15b**) 173.5 and 169.3 (CO_2Et), 137.9 (Cq phenyl), 128.6 and 127.9 (CH phenyl), 94.8 (C2), 73.4 (OCH_2Bn), 71.3 (C4), 69.6 (C9), 69.4 (C6), 62.9 (CH_2 ethyl), 62.1 (CH_2 ethyl), 56.9 (C8), 54.3 (C7), 40.6 (C5), 35.3 (C3), 14.1 (CH_3 ethyl).

δ (**15b** or **15a**) 173.5 and 169.3 (CO_2Et), 137.9 (Cq phenyl), 128.6 and 127.9 (CH phenyl), 94.7 (C2), 73.4 (OCH_2Bn), 71.3 (C4), 69.7 (C9), 68.5 (C6), 62.9 (CH_2 ethyl), 62.1 (CH_2 ethyl), 56.6 (C8), 55.1 (C7), 40.6 (C5), 35.3 (C3), 14.1 (CH_3 ethyl).

δ (**15c** or **15d**) 173.9 and 168.6 (CO_2Et), 137.8 (Cq phenyl), 128.4, 128.0, 127.9, 127.8 (CH phenyl), 94.9 (C2), 73.2 (OCH_2Bn), 72.2 (C4), 69.5 (C9), 66.1 (C6), 62.6 (CH_2

ethyl), 62.4 (CH_2 ethyl), 56.4 (C8), 55.3 (C7), 37.3 and 34.8 (C_5+C_3), 14.1 and 19.2 (CH_3 ethyl).

δ (**15d** or **15c**) 173.9 and 168.6 (CO_2Et), 137.8 (Cq phenyl), 128.4, 128.0, 127.9, 127.8 (CH phenyl), 94.9 (C2), 73.5 (OCH_2Bn), 72.1 (C4), 69.5 (C9), 66.3 (C6), 62.7 (CH_2 ethyl), 62.4 (CH_2 ethyl), 57.3 (C8), 53.5 (C7), 36.9 and 34.7 (C_5+C_3), 14.1 and 19.2 (CH_3 ethyl).

MS (DCI, NH_3): 442 (M+18). IR (neat) ν_{max} 3431 (OH), 3065 (CH arom.), 2984 (CH), 1732 (C=O) cm^{-1}.

Anal. Calcd for $C_{21}H_{28}O_9$: C, 59.43; H, 6.60. Found: C, 59.24; H, 6.69.

2.3.3. Ethyl 2,4-di-trimethylsilyloxy-4-carbethoxy-6-(9-(benzyloxy)-7,8-*cis*-epoxy)-tetrahydropyran-2-carboxylate 16a,16b. To a solution of compounds **14a**, **14b** (0.171 g, 0.4 mmol) in pyridine (1 ml), was added under stirring and nitrogen TMSCl (0.186 ml, 1.45 mmol, 3.6 equiv) and HMDS (0.223 ml, 1.05 mmol, 1 equiv), the reaction mixture was stirred at rt for 8 h before adding methylene chloride (2 ml) and an aq solution of NH_4Cl 20% (2 ml). The aqueous phase was extracted with ether (3× 5 ml) and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified on silica gel (eluant petroleum ether/ether 6:4) affording **16a** (65 mg) and **16b** (53 mg) along with 25 mg of starting material (yield 60%).

R_f: **16a**:0,44 (PE/Et_2O 6:4); **16b**:0,32 (PE/Et_2O 6:4).

^{1}H NMR (250 MHz, $CDCl_3$) δ (**16a**) 7.37–7.26 (m, 5H, CH arom.), 4.66 and 4.56 (2d, 2H, $J=11.9$ Hz, $PhCH_2O$), 4.22–4.06 (m, 5H, CH_2 ethyl and H6), 3.96 (dd, 1H, $J_{9a/9b}=11.6$ Hz, $J_{9a/8}=2.7$ Hz, H9a), 3.56 (dd, 1H, $J_{9b/9a}=11.6$ Hz, $J_{9b/8}=7.3$ Hz, H9b), 3.29 (m, 1H, H8), 3.07 (dd, 1H, $J_{7/8}=4.2$ Hz, $J_{7/6}=7.1$ Hz, H7), 2.13 (dd, 1H, $J=14.2$, 1.8 Hz, H3eq), 2.01–1.92 (m, 3H, H3ax, H5eq, and H5ax), 1.32–1.26 (m, 6H, CH_3 ethyl), 0.11 (s, 18H, OTMS).

δ (**16b**) 7.36–7.27 (m, 5H, CH arom.), 4.60 and 4.54 (2d, 2H, $J=11.7$ Hz, $PhCH_2O$), 4.25–4.05 (m, 5H, CH_2 ethyl, and H6), 3.67 and 3.65 (2 s, 2H, H9a, and H9b), 3.27 (m, 1H, H8), 3.17 (dd, 1H, $J_{7/8}=4.5$ Hz, $J_{7/6}=7.9$ Hz, H7), 2.15 (dd, 1H, $J_{3eq/3ax}=14.3$ Hz, $^4J_{3eq/5eq}=2.0$ Hz, H3eq), 2.07 (d, 1H, $J_{3ax/3eq}=14.3$ Hz, H3ax), 1.89 (dd, 1H, $J_{5ax/5eq}=13.6$ Hz, $J_{5ax/6}=11.8$ Hz, H5ax), 1.76 (td, 1H, $J_{5eq/6}=^4J_{5eq/3eq}=2.1$ Hz, $J_{5eq/5ax}=13.6$ Hz, H5eq), 1.34–1.23 (m, 6H, CH_3 ethyl), 0.17 (s, 9H, OTMS), 0.12 (s, 9H, OTMS).

^{13}C NMR (63 MHz, $CDCl_3$) δ (**16a**) 173.6 and 170.1 (CO_2Et), 137.9 (Cq phenyl), 128.4, 127.8, 127.7 (CH phenyl), 95.8 (C2), 74.0 (C4), 73.2 (OCH_2Ph), 68.7 (C9), 64.0 (C6), 61.8 (CH_2 ethyl), 61.5 (CH_2 ethyl), 56.9 (C8), 56.4 (C7), 40.9, and 37.6 (C_5 and C_3), 14.1 (CH_3 ethyl), 1.8 and 1.4 (OTMS).

δ (**16b**) 173.4 and 170.6 (CO_2Et), 137.7 (Cq phenyl), 128.5, 127.9, 127.8 (CH phenyl), 96.3 (C2), 73.9 (C4), 73.5 (OCH_2Ph), 68.4 (C9), 66.4 (C6), 61.8 (CH_2 ethyl), 61.6 (CH_2 ethyl), 57.3 (C8), 54.2 (C7), 40.1 and 37.0 (C_5 and C_3), 14.1 (CH_3 ethyl), 1.9 and 1.3 (OTMS).

MS (DCI, NH_3): 586 (M+18).

Anal. Calcd for $C_{27}H_{44}O_9Si_2$: C, 57.04; H, 7.73. Found: C, 57.28; H, 7.92.

2.3.4. Ethyl 2,4-di-trimethylsilyloxy-4-carbethoxy-6-(9-(dibenzylphosphate)-7,8-*cis*-epoxy)-tetrahydropyran-2-carboxylate 18. Compound **16b** (45 mg, 0.079 mmol) was hydrogenolyzed in the presence of 8 mg of Pd/C 10% in freshly distilled ethyl acetate (4 ml). After 24 h under stirring, the mixture was filtered off and concentrated affording 37 mg (97% yield) of the epoxyalcohol **17**, used without purification.

R_f: 0,2 (PE/Et_2O 5:5).

^{1}H NMR (250 MHz, $CDCl_3$) δ 4.33 (ddd, 1H, $J_{6/7}=7.0$ Hz, $J_{6/5ax}=11.7$ Hz, $J_{6/5eq}=2.2$ Hz, H6), 4.25–4.12 (m, 4H, CH_2 ethyl), 3.81 (m, 2H, H9a, and H9b), 3.24 (m, 2H, H8, and H7), 2.17 (dd, 1H, $J_{3eq/3ax}=14.3$ Hz, $^4J_{3eq/5eq}=2.1$ Hz, H3eq), 1.95 (d, 1H, $J_{3ax/3eq}=14.3$ Hz, H3ax), 1.89 (dd, 1H, $J_{5ax/5eq}=13.6$ Hz, $J_{5ax/6}=11.8$ Hz, H5ax), 1.74 (td, 1H, $J_{5eq/6}=^4J_{5eq/3eq}=2.2$ Hz, $J_{5eq/5ax}=13.5$ Hz, H5eq), 1.34–1.26 (m, 6H, CH_3 ethyl), 0.17 (s, 9H, OTMS), 0.13 (s, 9H, OTMS).

^{13}C NMR (63 MHz, $CDCl_3$) δ 173.4 and 170.5 (CO_2Et), 96.1 (C2), 73.9 (C4), 65.9 (C6), 61.9 (CH_2 ethyl), 61.6 (CH_2 ethyl), 60.9 (C9), 57.9, 56.2 (C7 and C8), 40.2, 36.9 (C_5 and C_3), 14.1, 14.0 (CH_3 ethyl), 1.9 and 1.2 (OTMS).

MS (DCI, NH3): 496 (MNH_4^+). IR (neat) ν_{max} 3465 (OH); 2960 (CH); 1741 (C=O) cm^{-1}.

To a solution of epoxyalcohol **17** (37 mg, 0.077 mmol) in methylene chloride (1.3 ml) containing tetrazole (6 mg, 0.0857 mmol, 1.11 equiv), was added dropwise *N*,*N*-diisopropyl dibenzyl phosphoramidite (28 mg, 0.081 mmol, 1.05 equiv). The mixture was stirred for 3 h at rt then cooled to −40 °C before adding *m*-cpba (77.3 mg, 0.317 mmol, 4 equiv). The temperature was then allowed to reach 0 °C and stirring was continued for 45 min. The reaction was then quenched with a 10% $Na_2S_2O_3$ aq solution (3 ml). After 15 min, it was diluted with methylene chloride (15 ml). The organic phase obtained was washed successively with 10% $Na_2S_2O_3$ (5 ml), saturated aq $NaHCO_3$ (5 ml), saturated aq NaCl (5 ml), dried over $MgSO_4$, filtered and concentrated. The crude product was purified on silica gel (eluant petroleum ether/CH_2Cl_2/AcOEt 5:8:2) affording 35 mg (60% yield) of the desired compound **18**.

R_f: 0,16 (PE/Et_2O 5:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 10H, Ph), 4.25 (ddd, 1H, $J_{6/7}=7.0$ Hz, $J_{6/5ax}=11.7$ Hz, $J_{6/5eq}=2.2$ Hz, H6), 4.20–4.05 (m, 6H, CH_2 ethyl, CH_2O), 3.23 (m, 1H, H8), 3.14 (dd, 1H, $J_{7/8}=4.5$, $J_{7/6}=7.1$ Hz, H7), 2.17 (dd, 1H, $J_{3eq/3ax}=14.3$ Hz, $^4J_{3eq/5eq}=2.1$ Hz, H3eq), 1.92 (d, 1H, $J_{3ax/3eq}=14.3$ Hz, H3ax), 1.84 (dd, 1H, $J_{5ax/5eq}=13.6$ Hz, $J_{5ax/6}=11.8$ Hz, H5ax), 1.64 (td, 1H, $J_{5eq/6}=^4J_{5eq/3eq}=2.2$ Hz, $J_{5eq/5ax}=13.5$ Hz, H5eq), 1.26–1.20 (m, 6H, CH_3 ethyl), 0.12 (s, 9H, OTMS), 0.11 (s, 9H, OTMS).

^{13}C NMR (63 MHz, $CDCl_3$) δ 173.2 and 170.3 (CO_2Et), 135.7, 135.6 (Cq phenyl), 128.6, 128.4, 128.0, 127.4 (CH phenyl), 96.2 (C2), 73.8 (C4), 69.5 (d, $^2J_{C/P}=5.5$ Hz, CH_2OPh), 66.3 (d, $^2J_{C9/P}=5.5$ Hz, C9), 65.6 (C6), 61.9 (CH_2 ethyl), 61.6 (CH_2 ethyl), 57.8 (C7), 54.4 (d, $^3J_{C8/P}=8.1$ Hz, C8), 40.0 and 37.0 (C_5 and C_3), 14.0 (CH_3 ethyl), 1.9 and 1.2 (OTMS).

^{31}P NMR (81 MHz, $CDCl_3$) δ −0.77.

MS (DCI, NH3): 756 (MNH_4^+). IR (neat) ν_{max} 2961 (CH alcane), 1743 (C=O), 1251 (P=O), 1020 (P–O) cm^{-1}.

Anal. Calcd for $C_{34}H_{51}O_{12}PSi_2$: C, 55.26; H, 6.91. Found: C, 55.14; H, 6.72.

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