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Ethynyloxirane anions: a new tool for natural product synthesis

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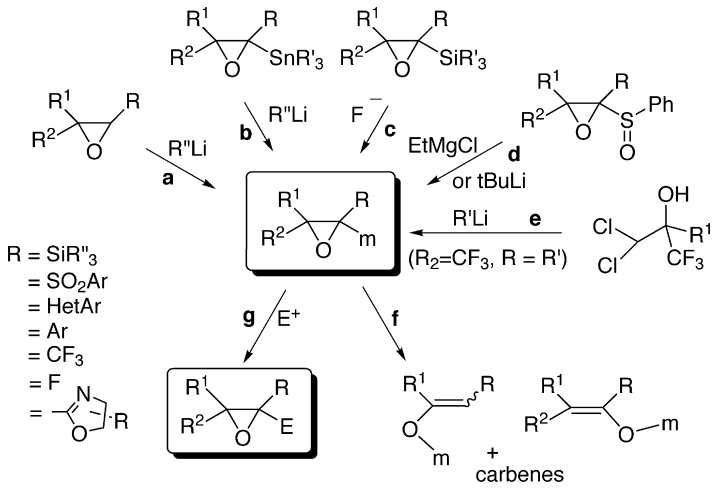
Abstract—Ethynyl oxiranes can be deprotonated with *n*BuLi in THF and trapped with various electrophiles, providing a stereoselective access to trisubstituted oxiranes. Alkyl iodides and aldehydes react readily with the ethynyloxiranyl anions but not sulfonyl derivatives. Mechanistic investigations highlighted the stabilizing role of the ethynyl group, the localization of the anion and the coordinating role of the oxirane oxygen atom during deprotonation.

1. Introduction

Although oxiranyl anions[1] are quite unstable species (Scheme 1, path f),[2] such intermediates have gained increasing interest in the last ten years.[3] Several routes have been reported for their preparation either directly from oxiranes[4–12] (Scheme 1, path a) or from already metalated or sulfinyl oxiranes[13–15] (Scheme 1, paths b–d). They can also be produced in situ from chlorhydrins (Scheme 1, path e).[16] If the starting or in situ generated oxirane carries electron-withdrawing[4–8,13] or coordinating[9] substituents or heteroaromatic,[10] aromatic or unsaturated groups,[11] the corresponding oxiranyl anion becomes stable enough to be trapped by electrophiles (Scheme 1, path g).[17] Nevertheless, applications of oxiranyl anions toward total synthesis of natural or bioactive products are still relatively scarce.[18]

The ethynyloxirane motif can however be found in various natural products as well as in man-made bioactive compounds. These natural products are secondary metabolites, which usually play a defensive role; they can be separated into two main classes of organisms. Plants produce a wide variety of substances containing an ethynyloxirane moiety; among them, a few are sulfonylated as shown in Scheme 2.[19] However, only a few algae (*Caulerpa*) also produce oxidized polyunsaturated



Scheme 1.

Keywords: ethynyl oxiranes; deprotonation; oxirane.
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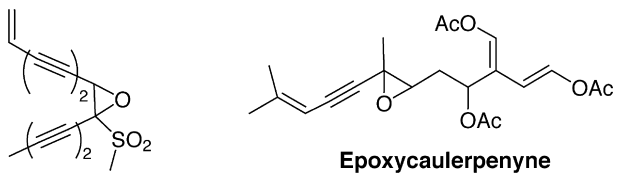


Scheme 2.

compounds (Scheme 2).[20] A few antibiotics produced by various microorganisms are known, oxirapentyn[21] and the so-called dienediyne family of antitumor antibiotics[22] (Scheme 3).

Ethynyloxiranes are also highly functionalized compounds, each carbon being functionalized. They are therefore very reactive and provide a rich chemistry, giving various synthetically useful intermediates.[23] They are also readily available in an enantio-enriched form from the corresponding epoxyalcohols.[24]

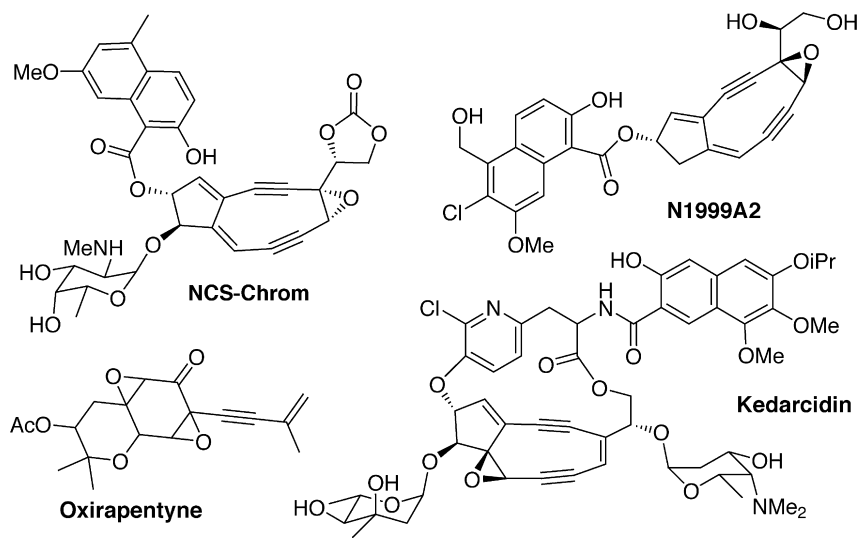
Interested in both aspects, we reasoned that it would be useful for synthesis to combine the availability of chiral epoxides with oxiranyl anion chemistry (Scheme 4). Such a strategy is especially appealing for the synthesis of the natural products mentioned above.

However, any application could be hampered by the nature of the anion derived from ethynyloxiranes. Due to their position, such oxiranyl anions are also propargylic and our goal was that stabilization would occur rendering oxiranyl anions stable enough to be trapped by electrophiles (Scheme 4). However, this stabilization is mainly due to delocalization. Indeed, propargyl carbanions are usually delocalized and they react at either end depending mainly on the nature of the metal associated with them. For these reasons, and since anions α to heteroatom are highly destabilized, ethynyloxiranyl anions could be isomerized and therefore also behave as epoxyallenyl anions. Alkylation of such anions could therefore lead to a mixture of products (Scheme 5).

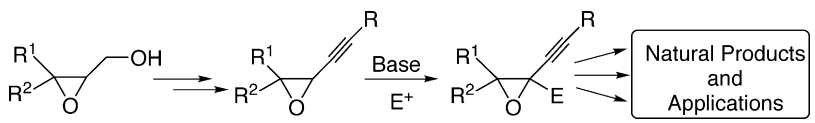
In this paper, we describe the deprotonation of ethynyl oxiranes and the use of this reaction as a tool for the stereoselective synthesis of trisubstituted ethynyl oxiranes.[25] We also shed some light about the actual process leading to the formation of these oxiranyl anions.

2. Results and discussion

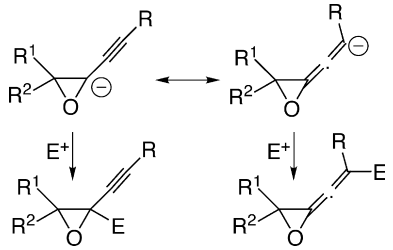
To study the deprotonation of ethynyl oxiranes and the quenching of the corresponding anions, we prepared several series of 2,3-epoxypent-4-yn-1-ols protected at their hydroxyl end and bearing various substituents at their acetylenic end. Theses compounds were readily obtained from the commercially available but-2-en-1,4-diol.[23e,g,24b,26]



Scheme 3.

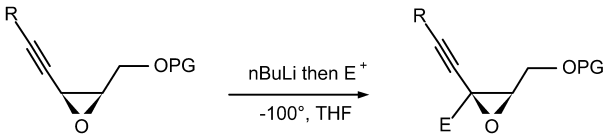


Scheme 4.



Scheme 5.

Table 1. Deprotonation of ethynyl oxiranes and anion trapping



	R	PG	Electrophile		Conversion (%)	Yields[a] (%)	Products	
1	$SiMe_3$	$SiMe_3$	**1a**	Me_3SiCl	100	94[b]	E=$SiMe_3$	**2a**
2	$SiMe_3$	$SiPh_2tBu$	**1b**	Me_3SiCl	100	96	E=$SiMe_3$	**2b**
3	$SiMe_3$	$SiPh_2tBu$	**1b**	MeI	100	81	E=Me	**3**
4	$SiMe_3$	$SiPh_2tBu$	**1b**	MeI[c]	79	39[d]	E=$SiMe_3$	**2b**

[a] Yields of isolated products.
[b] Isolated as the free alcohol.
[c] In the presence of HMPA 4 equiv.
[d] A product resulting from desilylation and methylation at the acetylenic position was also isolated (cf. text and Scheme 6).

2.1. Feasibility

As oxiranyl anions are unstable species even at low temperature,[2] we first looked for optimal conditions for their formation and trapping starting from various *cis*-2,3-epoxypent-4-yn-1-ols protected at both ends with silyl groups **1a–b**. With such derivatives, no intramolecular silyl migration[27] would occur for obvious stereochemical reasons.

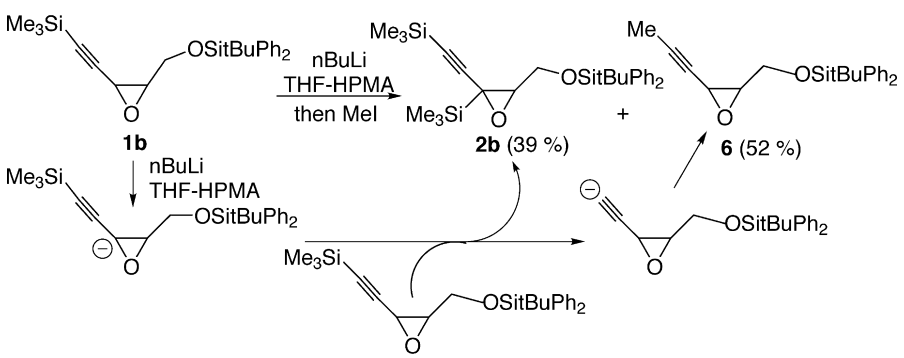
Dissolved in THF, these compounds were then submitted at various temperatures to various bases. To ensure an efficient quenching of the in situ formed anion, trimethylsilyl chloride (TMSCl) was first used as electrophile. Surprisingly enough, *n*-butyllithium proved to be very efficient although strong or complex bases are usually required.[4–5] At very low temperature (−100°C), this base gave quantitatively after a few minutes the expected anion as judged by the product isolated after addition of TMSCl and work-up in each case (Table 1, entries 1 and 2). Indeed, the structure of these new products **2a–b** evidenced the incorporation of a TMS group at the expected position. Their ^1H NMR spectrum clearly showed the presence of a new TMS group (0.07 ppm), the disappearance of the typical doublet corresponding to the proton at the three position and the simplification of the signal corresponding to H2 (from ddd to dd). The ^{13}C NMR spectrum corroborated these structures with again a new signal around-4.2 ppm typical for a TMS group and the switch of C3 from a tertiary to a quaternary carbon (44 ppm, d to 49 ppm, s).

With a less reactive electrophile, **1b** was still completely consumed in the same conditions and the formation of the expected product **3** was also observed. The yield was however lower but still very good (entry 3).

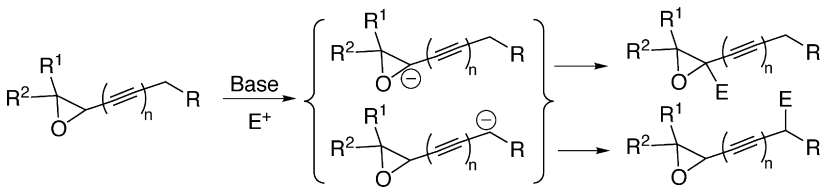
Surprisingly, when HMPA (4 equiv.) was added to the reaction mixture, the conversion was lower and none of the expected product was isolated. Instead two new products were formed, the NMR spectroscopic analysis of which revealed that both compounds were indeed alkylation products. The less polar product proved to have a trimethylsilyl group rather than the expected methyl group attached to the former oxiranyl anion position, it was therefore identical to **2b** (entry 4). In the more polar product **6**, the trimethylsilyl substituent of the triple bond was replaced by a methyl group. This result indicated that in the presence of HMPA, the oxiranyl anion became so reactive that reaction with itself predominated. It thus abstracted the trimethylsilyl substituent of the triple bond before reacting with the external electrophile. This intermolecular self-reaction led to an epoxyacetylide which was subsequently trapped by the added electrophile (Scheme 6).

2.2. Anion localization, stereochemistry and mechanism

It is worth noting that in the reactions described above, no allenic compound was detected as well as no degradation products. The conversion was always complete and the yield of trisubstituted oxiranes excellent. Even in the methylation reaction in the presence of HMPA, none of the rearrangement products was detected, indicating the



Scheme 6.



Scheme 7.

gain in stability the ethynyl group provided to the oxiranyl anion.

In order to further check the role of the ethynyl substituents toward the localization of the anion, we prepared several derivatives and submitted them to the above mentioned conditions. With an alkyl group instead of trimethylsilyl group at the acetylenic end, 2 propagylic positions would indeed be available, one lying on the oxirane. Thus, the deprotonation and the trapping of such derivatives would provide a mixture of compounds the proportion of which would reflect the deprotonation extend and the relative stability of the corresponding anions (Scheme 7).

Due to its efficiency and its very fast reaction, TMSCl was again used as trapping agent in order to avoid any equilibration between the anions which could be formed. The results are collected in Table 2.

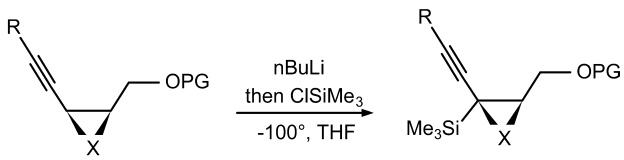
The epoxydiyne **4**[23e,g] exclusively provided the product **5** silylated at the propargylic oxirane position, clearly indicating the exclusive formation of the oxiranyl anion (entry 1). The yield was even slightly better than the one obtained from the corresponding TMS analog taken as a reference (entry 3). With a simple methyl group instead of TMS at the acetylenic end **6**, a mixture of products was produced among which the product **7** resulting from oxiranyl anion trapping was isolated with a low yield (entry 2). In this case, the mixture of products probably arose from a mixture of anions.

Although the results obtained from **4** seem to confirm the role of the oxirane, favoring deprotonation adjacent to it, the results from **6** led to a less conclusive answer. Furthermore, it was not clear what the exact role of the oxirane was. Two possibilities could be invoked: the well known higher acidity of three membered rings compared to alkanes, due to hybridization differences, or the Lewis basicity of the oxygen atom which may act as a ligand toward the added alkyllithium reagent.[6a]

To answer these questions, we prepared the cyclopropyl analog of **1a** and submitted this compound, **8**, to the same sequence. In our standard conditions, no silylation and therefore no deprotonation occurred while the corresponding oxirane reacted nicely (entry 4 vs 5). This result clearly indicates the importance of an adjacent oxygen atom as an acidifying factor for deprotonation and supports the coordinating role of the oxirane oxygen atom.

Since epimerization of oxiranyl anions has been observed in some cases,[6a,7c–d] we checked the stereochemical outcome of our process through two different experiments. The stereochemical integrity of the oxirane ring was first assessed by comparing the product obtained by trapping the oxiranyl anion with methyl iodide to a sample independently prepared by mcpba epoxidation of (*Z*)-3-methyl-5-trimethylsilylpent-2-en-4-yn-1-ol and *O*-silylation. Both products proved to be identical in all aspects, so the *cis* stereochemistry of the oxirane ring was preserved. This demonstrated the complete stereochemical stability of the oxiranyl anion in the reaction conditions. The reaction was then performed on enantiomerically pure materials. Optically pure **1a**[23e,g,26] was treated with *n*BuLi and then TMSCl as before, the silylated product **2a** was isolated as the free alcohol and proved to be chiral ($[\alpha]_D^{22}=+8.2$, $c=0.43$, CH_2Cl_2). It was then converted to its acetate and its enantiomeric purity was checked by ^1H NMR in the presence of chiral shift reagent ($Eu(hfc)_3$). A single set of signals was observed in conditions where the racemic compound displayed two sets. These results showed that neither isomerization nor racemization occurred in this reaction.

Table 2. Localization of the anion



	R	X	PG		Conversion (%)	Yields[a] (%)	Products
1	≡—nBu	O	$SiPh_2tBu$	**4**	100	98	**5**
2	Me	O	$SiPh_2tBu$	**6**	100	35[b]	**7**
3	$SiMe_3$	O	$SiPh_2tBu$	**1b**	100	96	**2b**
4	$SiMe_3$	O	$SiMe_3$	**1a**	100	94	**2a**
5	$SiMe_3$	CH_2	$SiMe_3$	**8**	0	0[c]	**9**

[a] Yields of isolated pure products.
[b] A series of unidentified products was also formed.
[c] The starting material was recovered.

2.3. Synthetic applications

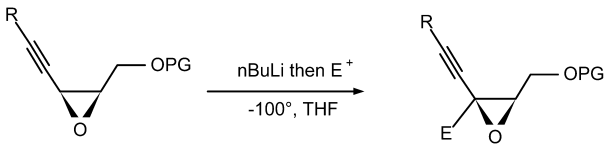
As mentioned above, the ethynyl oxirane moiety is distributed over various families of natural and bioactive products. Owing to their structures, two kinds of electrophiles seemed particularly appealing. Trapping ethynyloxirane anions with sulfonyl reagents would give a rapid access to precursors of the plant metabolites family (Scheme 2) and trapping with aldehydes would offer a good access to the epoxydienediyne family of antibiotics (Scheme 3). With these applications in mind, we thus explored the corresponding chemistry.

Direct sulfonylation of the ethynyl oxirane anion was first attempted. The ethynyl oxirane **1b** was used as starting material. After deprotonation in the usual conditions, mesyl chloride was added at very low temperature. Since no new product could be detected by TLC the temperature was gradually raised. However, only extensive degradation was observed and none of the expected product could be detected (Table 3, entry 1). More reactive methylsulfonyl derivatives did not help and again, degradation occurred (entries 2 and 3). These results suggested that the oxiranyl anion reacts with the mesyl derivative as a base rather than a nucleophile providing methylsulfolene, which then polymerized. To avoid such basic reaction, we performed the same reaction with phenylsulfonyl chloride, which does not have protons for an elimination reaction. Unfortunately, the expected product could only be detected in trace amount (entries 4 and 5). Sulfonylation of ethynyl oxirane anions does not seem possible.

The reaction of ethynyloxirane anions with aldehydes was then explored with simple aldehydes (Table 4). Here again, the ethynyl oxirane **1b** was used as starting material. After deprotonation in the usual conditions, heptanal was added at very low temperature and 5 min later, two new products could be detected by TLC. After work-up and chromatography, these new compounds proved to be the expected diastereoisomeric products. Indeed, IR spectra clearly indicated the presence of a hydroxyl group while NMR spectra evidenced the presence of a CHOH motif with new signals at 3.81 and 3.46 ppm in the ^{1}H NMR spectrum and at 70.75 and 73.58 ppm in the ^{13}C NMR spectrum. The overall yield was excellent but the diastereoselectivity was quite low (entry 2). To look for the factors governing such diastereoselectivity and for comparison purposes, the same reaction was performed with a series of enolizable aldehydes more or less bulky around the carbonyl group. Ethanal was the simplest and the less bulky of these aldehydes; its reaction with **1b** anion gave a 50:50 mixture of adducts (entry 1). In this case, the overall yield was low owing to side-reactions, the facile enolization and polymerization of this aldehyde probably accounted for such poor results. The bulkier 2-methylpropanal gave the expected adducts with a better yield but still with a low diastereoselectivity (entry 3). The more rigid and bulkier cyclohexylcarbaldehyde furnished the corresponding alcohols with a similar yield but a slightly improved diastereoselectivity (entry 4). Running the reaction with tertiary and thus non-enolizable aldehydes was expected to provide better results. However, pivaldehyde gave results similar to secondary aldehydes with yield and diastereoselectivity only slightly higher than in the preceding cases (entry 5 vs 4 and 3). When the oxiranyl anion derived from **1b** was trapped with benzaldehyde, excellent yield and diastereoselectivity were observed (entry 6), only traces of one diastereoisomer were detected.

The ^{1}H NMR spectra of these diastereoisomers exhibited interesting features, which allowed for their stereochemical assignment. Indeed, the signal corresponding to the proton of the newly formed carbinol group was always at lower field in the less polar diastereoisomer. Interestingly, the adjacent alkyl group experienced the reverse situation. The adducts derived from acetaldehyde are typical, with a carbinol proton resonating at 3.92 ppm and a methyl group at 1.31 ppm for the less polar adduct, and at 3.68 and 1.93 ppm respectively for the more polar isomer.

Table 3. Trapping with sulfonyl derivatives



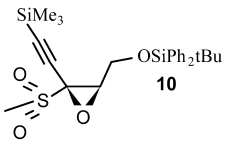
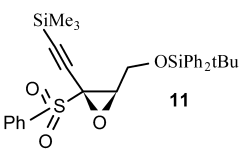
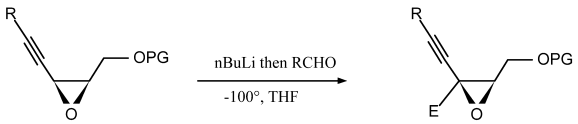
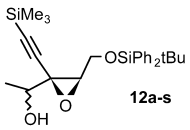
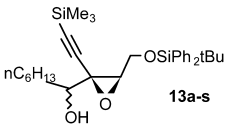
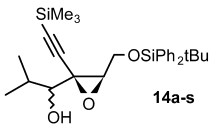
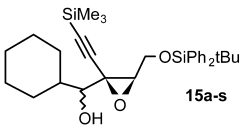
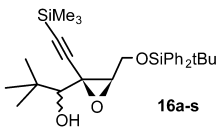
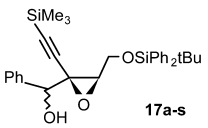
	R	PG		Electrophile	Yields	Products
1	$SiMe_3$	$SiPh_2tBu$	**1b**	CH_3SO_2Cl	0%	 **10**
2	$SiMe_3$	$SiPh_2tBu$	**1b**	CH_3SO_2F	0%	
3	$SiMe_3$	$SiPh_2tBu$	**1b**	CH_3SO_2OTf	0%	
4	$SiMe_3$	$SiPh_2tBu$	**1b**	$PhSO_2Cl$	Traces	 **11**
5	$SiMe_3$	$SiPh_2tBu$	**1b**	$PhSO_2Cl$	Traces	

Table 4. Trapping with aldehydes

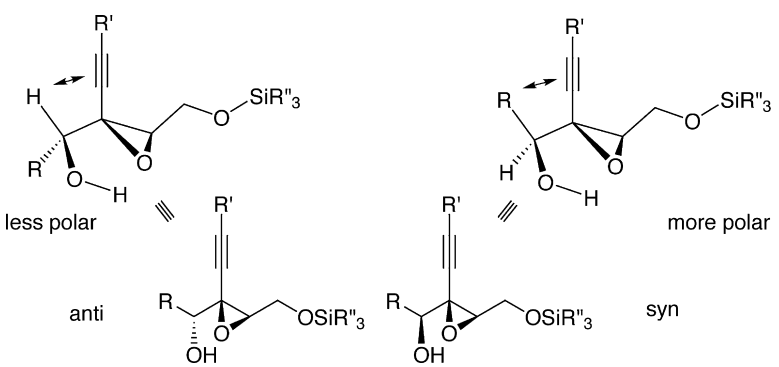


	R	PG	Aldehyde	Yield[a] (%)	Diastereomer[b]		Products
					−	+	
1	$SiMe_3$	$SiPh_2tBu$	CH_3CHO	25	50	50	 **12a-s**
2	$SiMe_3$	$SiPh_2tBu$	$nC_6H_{13}CHO$	90	43	57	 **13a-s**
3	$SiMe_3$	$SiPh_2tBu$	$(CH_3)_2CHCHO$	55	45	55	 **14a-s**
4	$SiMe_3$	$SiPh_2tBu$	$cC_6H_{13}CHO$	58	40	60	 **15a-s**
5	$SiMe_3$	$SiPh_2tBu$	$(CH_3)_3CCHO$	64	37	63	 **16a-s**
6	$SiMe_3$	$SiPh_2tBu$	C_6H_5CHO	91	5	95	 **17a-s**

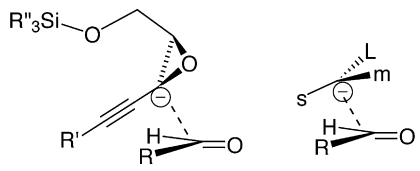
[a] The value corresponds to the combined yield of each separated pure diastereoisomer.
[b] − and + refer to the less and more polar diastereoisomer respectively; this ratio was determined from the ^1H NMR of the crude mixture.

These data are consistent with a major conformation in solution where the carbinol proton or the pendant alkyl group depending on the diastereoisomer experienced the magnetic anisotropy of the adjacent triple bond (Scheme 8). Therefore, the less polar diastereoisomer can be assigned as the *anti* adduct and the more polar diastereoisomer as the *syn* adduct.

Therefore, the actual major transition state of this alkylation reaction can be inferred from these results and assignments (Scheme 9, left). Interestingly enough, the proposed transition state is in perfect agreement with the model proposed by Bassindale et al.[28] for the addition of trisubstituted carbanions (Scheme 9, right).



Scheme 8.



Scheme 9.

3. Conclusion

In summary, we have shown that anions derived from ethynyloxiranes are stereochemically stable and can be trapped by various electrophiles, especially aldehydes. These oxiranyl anions can be easily generated using the convenient *n*butyllithium base. They are stabilized by the adjacent ethynyl substituent, nevertheless, we demonstrated that a kinetic acidification takes place due to coordination of *n*butyllithium to the oxirane oxygen atom.

Due to the availability of oxiranes, especially in an optically active form, this deprotonation–alkylation sequence provides an efficient and stereocontrolled access to trisubstituted functionalized oxiranes. Further synthetic applications are under development in our group.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200, AC-300 spectrometers. For ^{1}H NMR, TMS was used as internal standard, for ^{13}C NMR, solvent peak at 77.00 ($CDCl_3$) or 128.00 ppm (C_6D_6) were used. IR spectra were recorded on a Spectrafile IR™ Plus MIDAC spectrophotometer or a Perkin Elmer FTIR-1600. Mass Spectra were obtained from a Jeol D300 (70 eV) mass spectrometer or a Micromass AutoSpec or Trio-2000 mass spectrometers. Specific rotations were measured at 589 nm with an ADP 220 Bellingham–Stanley polarimeter or a Perkin–Elmer 241 polarimeter. Melting points were uncorrected. Column chromatographies were performed with Merck silica gel (0.040–0.063 mesh) while TLC-analysis used MERCK Art 5554 DC Alufolien Kieselgel 60 PF_{254} with detection by UV-absorption (254 nm). THF was distilled from Na/benzophenone; C_6H_6, CH_2Cl_2 were distilled from CaH_2. Yields were on isolated products.

4.2. Starting materials

The starting ethynyloxiranes **1a**, **1b** and **4**, were obtained as described in Ref. 23e,g. Compound **8** was obtained according to Refs. 26,29.

4.2.1. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxyhex-4-yne 6. To a solution under argon of *cis* 5-bromo-1-*tert*butyldiphenylsilyloxy-2,3-epoxyhex-4-yne (1.15 g, 2.77 mmol, 1 equiv.) in THF (28 mL) cooled at −100°C were added dropwise a commercial solution of *n*BuLi (1.6 M in hexane, 1.73 mL, 2.77 mmol, 1 equiv.). After 5 min, iodomethane (2 mL, 32 mmol, 11.6 equiv.) was added and the mixture was allowed to warm up to −40°C. HMPA (4 mL, 22 mmol, 7.95 equiv.) was then added. After 30 min at −40°C, water was added. After warming and extraction with dichloromethane, the organic phases were dried with magnesium sulfate. After filtration and solvent evaporation, the crude product was chromatographied over silica gel with hexanes–ethyl acetate (95–5) to give compound **6** (942 mg, 2.68 mmol) as a yellowish oil. Yield: 97%.

^{1}H NMR (300 MHz, C_6H_6) δ: 1.18 (9H, s), 1.25 (3H, d, J=1.8 Hz), 3.06 (1H, td, J=5.2, 4.0 Hz), 3.16 (1H, dq, J=4.0, 1.8 Hz), 4.06 (2H, d, J=5.2 Hz), 7.18–7.25 (6H, m), 7.77–7.85 (4H, m); ^{13}C NMR (75.5, C_6H_6) δ: 3.08 (q), 19.47 (s), 26.97 (q), 44.43 (d), 57.37 (d), 64.01 (t), 74.53 (s), 82.06 (s), 128.32 (d), 129.99 (d), 133.94 (s), 136.00 (d); IR (film) 2220, 1430, 1140, 1110, 820, 740 cm^{-1}. Anal. calcd for $C_{22}H_{26}O_2Si$: C, 75.38; H, 7.48. Found: C, 75.53; H, 7.62. (2*R*,3*R*)-**6**: $[\alpha]_D^{22}$=+5.1 (c=0.86, CH_2Cl_2, ee>99).

4.3. General procedure for deprotonation of ethynyloxiranes and trapping

To a solution under argon of ethynyloxirane (1 equiv.) in THF (10 mL/mmol) cooled at −100°C were successively added a commercial solution of *n*BuLi (1.6 M in hexane, 1 equiv.) and then the electrophile (1 equiv.). After 5 min, TLC usually indicated that the reaction was completed. Water was then added and the mixture was allowed to warm up. After extraction with dichloromethane, the organic phases were dried with magnesium sulfate. After filtration and solvent evaporation, yellowish oil was obtained and was subsequently purified by chromatography.

4.3.1. *cis* 2,3-Epoxy-3,5-bis(trimethylsilyl)pent-4-yn-1-ol, from 2a. The work-up is slightly different in order to directly obtain the more stable free alcohol. From 150 mg of **1a**, the crude oil obtained (189 mg) was directly taken up in methanol (0.6 mL, 1 mL/mmol) and a solution of citric acid (357 mg, 1.86 mmol, 0.3 equiv.) in methanol (1.9 mL, 1 mL/mmol) was added. After 30 min at room temperature, a 1–1 mixture of water-diethyl ether was added. After extraction with diethyl ether, drying with magnesium sulfate, solvent evaporation yielded an yellow oil, which was purified by chromatography (hexanes–ethyl acetate 60–40) to give the alcohol (141 mg, 0.58 mmol) as a yellowish oil; yield 94%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.06 (9H, s), 0.09 (9H, s), 2.57 (OH), 3.09 (1H, dd, J=6.1, 4.6 Hz), 3.80 (1H, dd, J=12.3, 6.1 Hz), 3.91 (1H, dd, J=12.3, 4.6 Hz); ^{13}C NMR (75.5, $CDCl_3$) δ: −4.28 (q), −0.26 (q), 49.16 (s), 60.89 (d), 63.22 (t), 92.71 (s), 102.29 (s); IR (film) 3400, 2140, 1250, 1045, 850, 835, 790, 760 cm^{-1}; MS *m/e* (intensity): 243 (M^++1, <1), 242 (M^+, 3), 241 (M^+−1, 6), 225 (3), 182 (81), 167 (100), 155 (42), 147 (96), 133 (38), 109 (44), 97 (28), 83 (34), 75 (92), 73 (100). Anal. calcd for $C_{11}H_{22}O_2Si$: C, 54.49; H, 9.15. Found: C, 54.52; H, 9.22. (2*R*,3*R*)-**2a**: $[\alpha]_D^{22}$=+8.2 (c=0.43, CH_2Cl_2, ee>99).

4.3.2. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-3,5-bis(trimethylsilyl)pent-4-yne 2b. From 150 mg of **1b**, the desired compound **2b** (169 mg, 0.35 mmol) was obtained after purification as a yellowish oil, yield: 96%. ^{1}H NMR

(300 MHz, $CDCl_3$) δ: 0.07 (9H, s), 0.13 (9H, s), 1.08 (9H, s), 3.13 (1H, dd, J=5.5, 4.7 Hz), 3.93 (1H, dd, J=11.4, 5.5 Hz), 4.02 (1H, dd, J=11.4, 4.7 Hz), 7.34–7.47 (6H, m), 7.66–7.73 (4H, m); ^{13}C NMR (75.5, $CDCl_3$) δ: −4.16 (q), −0.23 (q), 19.29 (s), 26.80 (q), 48.96 (s), 61.05 (d), 64.68 (t), 92.27 (s), 102.51 (s), 127.67 (d), 129.64 (s), 135.55 (d); IR (film) 2150, 1580, 1425, 1250, 1110, 1090, 845, 760 cm^{-1}. Anal. calcd for $C_{27}H_{40}O_2Si_3$: C, 67.44; H, 8.38. Found: C, 67.13; H, 8.24. (2*R*,3*R*)-**2b**: $[\alpha]_D^{22}$=+4.5 (c=0.54, CH_2Cl_2, ee>99).

4.3.3. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-3-methyl-5-trimethylsilylpent-4-yne 3. See Ref. 23h.

4.3.4. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-3-trimethyl silylundeca-4,6-diyne 5. From 150 mg of **4**, the desired compound **5** (173 mg, 0.36 mmol) was obtained after purification as a yellowish oil, yield: 98%. ^{1}H NMR (300 MHz, C_6H_6) δ: 0.05 (9H, s), 0.65 (3H, t, J=7.1 Hz), 1.05–1.20 (4H, m), 1.19 (9H, s), 1.84 (2H, t, J=6.8 Hz), 3.23 (1H, t, J=5.2 Hz), 4.19 (2H, d, J=5.2 Hz), 7.20–7.33 (6H, m), 7.77–7.87 (4H, m); ^{13}C NMR (75.5, C_6H_6) δ: −4.11 (q), 13.47 (q), 18.98 (t), 19.50 (s), 21.99 (t), 27.04 (q), 30.26 (t), 49.15 (s), 61.79 (d), 65.91 (t), 65.92 (t), 72.22 (s), 74.16 (s), 81.12 (s), 128.12 (d), 129.30 (s), 133.70 (d), 136.03 (d); IR (film) 2240, 1430, 1250, 1110, 1080, 840, 820, 740 cm^{-1}; MS *m/e* (intensity): 432 (M^+−57, 15), 358 (6), 271 (25), 163 (33), 135 (31), 133 (25), 85 (29), 83 (48), 73 (100). Anal. calcd for $C_{30}H_{40}O_2Si_2$: C, 73.71; H, 8.25. Found: C, 73.52; H, 8.22. (2*R*,3*R*)-**5**: $[\alpha]_D^{22}$=−1.8 (c=0.22, CH_2Cl_2, ee>99).

4.3.5. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-3-trimethyl silylhex-4-yne 7. From 150 mg of **6**, the desired compound **7** (59 mg, 0.15 mmol) was obtained after purification as a yellowish oil, yield: 35%. ^{1}H NMR (300 MHz, C_6H_6) δ: 0.11 (9H, s), 1.19 (9H, s), 1.32 (3H, s), 3.28 (1H, t, J=5.1 Hz), 4.25 (2H, d, J=5.1 Hz), 7.17–7.25 (6H, m), 7.79–7.88 (4H, m); ^{13}C NMR (75.5, C_6H_6) δ: −4.02 (q), 3.36 (q), 19.50 (s), 27.03 (q), 48.99 (s), 60.94 (d), 65.26 (t), 76.95 (s), 82.61 (s), 127.99 (d), 129.34 (d), 133.82 (s), 136.04 (d); IR (film) 1470, 1425, 1245, 1110, 1095, 1060, 840, 740 cm^{-1}; (2*R*,3*R*)-**7**: $[\alpha]_D^{22}$=−2.7 (c=0.12, CH_2Cl_2, ee>99).

4.3.6. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-3-(1-hydroxy ethyl)-5-trimethylsilylpent-4-yne. From 500 mg of **1b**, diastereoisomers **12a** (69 mg, 0.15 mmol) and **12s** (69 mg, 0.15 mmol) were obtained after purification as yellowish oils, yield: 25%.

Compound **12a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.05 (9H, s), 1.05 (9H, s), 1.31 (3H, d, J=6.3 Hz), 1.98 (1H, br.s), 3.41 (1H, dd, J=5.7, 4.8 Hz), 3.85 (1H, dd, J=11.6, 5.7 Hz), 3.92 (1H, q, J=6.3 Hz), 3.96 (1H, dd, J=11.6, 4.8 Hz), 7.31–7.45 (6H, m), 7.64–7.70 (4H, m); ^{13}C NMR (50.3, $CDCl_3$) δ: −0.42 (q), 18.69 (q), 19.32 (s), 26.81 (q), 58.75 (s), 59.55 (d), 63.62 (t), 67.20 (d), 93.20 (s), 99.28 (s), 127.75 (d), 129.78 (d), 133.26 (s) 135.58 (d); IR (film): 3490, 2170, 1470, 1428, 1250, 1113, 1040, 845, 761, 741, 702; MS (FAB): 453, 436, 395, 376, 351, 241, 221, 197, 135. Anal. calcd for $C_{26}H_{36}O_3Si_2$ C, 69.98; H, 8.02. Found: C, 70.02; H, 8.11

Compound **12s**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.04 (9H, s), 1.04 (9H, s), 1.32 (3H, d, J=6.4 Hz), 1.73 (1H, d, J=7.7 Hz), 3.35 (1H, dd, J=5.5, 4.9 Hz), 3.68 (1H, q, J=6.5 Hz), 3.83 (1H, dd, J=11.6, 5.5 Hz), 3.94 (1H, dd, J=11.6, 4.9 Hz), 7.29–7.43 (6H, m), 7.60–7.68 (4H, m); ^{13}C NMR (50.3, $CDCl_3$) δ: −0.31 (q), 19.34 (s), 19.60 (q), 26.87 (q), 59.26 (s), 61.49 (d), 63.61 (t), 69.17 (d), 93.27 (s), 98.90 (s), 127.81 (d), 129.84 (d), 133.27 (s) 135.63 (d); IR (film): 3470, 2170, 1472, 1430, 1250, 1113, 1043, 844, 761, 741, 702; MS (FAB): 453, 436, 395, 376, 351, 241, 221, 197, 135.

4.3.7. *cis* 1-*tert*-Butyldiphenylsilyloxy-2,3-epoxy-3-trimethylsilylethynyldecan-4-ol. From 500 mg of **1b**, diastereoisomers **13a** (247 mg, 0.47 mmol) and **13s** (328 mg, 0.63 mmol) were obtained after purification as yellowish oils, yield: 90%.

Compound **13a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.10 (9H, s), 0.90 (3H, t, J=6.5 Hz), 1.10 (9H, s), 1.25–1.6 (9H, m), 1.75–1.85 (1H, m), 1.96 (OH, br.s), 3.45 (1H, dd, J=5.5, 4.9 Hz), 3.81 (1H, dd, J=7.7, 7.1 Hz), 3.90 (1H, dd, J=11.5, 5.5 Hz), 3.99 (1H, dd, J=11.5, 4.9 Hz), 7.35–7.50 (6H, m), 7.68–7.75 (4H, m); ^{13}C NMR (75.5, $CDCl_3$) δ: −0.45 (q), 14.06 (q), 19.27 (s), 22.59 (t), 25.02 (t), 26.76 (q), 29.19 (t), 31.63 (t), 32.92 (t), 57.99 (s), 59.65 (d), 63.54 (t), 70.75 (d), 93.12 (s), 99.45 (s), 127.70 (d), 129.72 (d), 133.21 (s),135.53 (d); IR (film): 3472, 2170, 1470, 1471, 1428, 1251, 1113, 844; MS (FAB+Na): 545, 351, 241, 221, 199, 176, 135, 115. Anal. calcd for $C_{31}H_{46}O_3Si_2$: C, 71.21; H, 8.87. Found: C, 71.29; H, 8.95.

Compound **13s**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.10 (9H, s), 0.91 (3H, t, J=6.5 Hz), 1.08 (9H, s), 1.25–1.55 (8H, m), 1.58–1.70 (1H, m), 1.76–1.86 (2H, m), 3.34 (1H, dd, J=5.3, 5.1 Hz), 3.45 (1H, br.t, J=6.5 Hz), 3.89 (1H, dd, J=11.5, 5.5 Hz), 3.98 (1H, dd, J=11.5, 5.1 Hz), 7.37–7.48 (6H, m), 7.68–7.72 (4H, m); ^{13}C NMR (75.5, $CDCl_3$) δ: −0.42 (q), 14.04 (q), 19.26 (s), 22.57 (t), 25.14 (t), 26.76 (q), 29.16 (t), 31.59 (t), 33.73 (t), 58.86 (s), 61.73 (d), 63.40 (t), 73.58 (d), 93.17 (s), 98.67 (s), 127.70 (d), 129.73 (d), 133.17 (s), 135.52 (d); IR (film): 3451, 2171, 1472, 1428, 1250, 1113, 844; MS (FAB+Na): 545, 351, 239, 221, 197, 154, 135.

4.3.8. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-5-methyl-3-trimethylsilylethynylhexan-4-ol. From 500 mg of **1b**, diastereoisomers **14a** (155 mg, 0.3 mmol) and **14s** (187 mg, 0.37 mmol) were obtained after purification as yellowish oils, yield: 55%.

Compound **14a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.06 (9H, s), 0.92 (3H, d, J=6.8 Hz), 1.04 (9H, s), 1.05 (3H, d, J=6.9 Hz), 1.84 (1H, br.d, J=2.8 Hz), 2.05–2.16 (1H, m), 3.44 (1H, dd, J=5.4, 5.3 Hz), 3.65 (1H, dd, J=3.2, 2.8 Hz), 3.87 (1H, dd, J=11.4, 5.4 Hz), 3.95 (1H, dd, J=11.4, 5.3 Hz), 7.30–7.44 (6H, m), 7.62–7.69 (4H, m); ^{13}C NMR (50.3, $CDCl_3$) δ: −0.30 (q), 16.07 (q), 19.34 (s), 19.97 (q), 26.87 (q), 30.68 (d), 57.45 (s), 59.73 (d), 63.60 (t), 74.72 (d), 93.07 (s), 99.89 (s), 127.84 (d), 129.85 (d), 133.29 (s) 135.65 (d); IR (film): 3490, 2170, 1472, 1428, 1251, 1113, 1011, 844, 761, 741, 702; MS (FAB): 503, 481, 463, 424,

403, 351, 331, 241, 221, 199, 163, 135. Anal. calcd for $C_{28}H_{40}O_3Si_2$: C, 69.95; H, 8.39. Found: C, 70.05; H, 8.39.

Compound **14s**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.10 (9H, s), 0.98 (3H, d, J=6.8 Hz), 1.03 (3H, d, J=6.8 Hz), 1.07 (9H, s), 1.97 (1H, d, J=6.5 Hz), 1.97–2.12 (1H, m), 3.02 (1H, dd, J=6.7, 6.5 Hz), 3.28 (1H, dd, J=5.3, 5.1 Hz), 3.88 (1H, dd, J=11.4, 5.1 Hz), 3.97 (1H, dd, J=11.4, 5.1 Hz), 7.33–7.47 (6H, m), 7.65–7.71 (4H, m); ^{13}C NMR (50.3, $CDCl_3$) δ: −0.27 (q), 18.14 (q), 19.20 (q), 19.33 (s), 26.82 (q), 31.88 (d), 58.48 (s), 62.48 (d), 63.37 (t), 79.54 (d), 92.99 (s), 98.65 (s), 127.81 (d), 129.85 (d), 133.19 (s) 135.60 (d); IR (film): 3470, 2170, 1472, 1428, 1250, 1113, 1043, 844, 761, 741, 702; MS (FAB): 503, 463, 423, 403, 351, 331, 241, 221, 199, 176, 163, 135.

4.3.9. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-3-(hydroxycyclohexylmethyl)-5-trimethylsilylpent-4-yne. From 500 mg of **1b**, diastereoisomers **15a** (148 mg, 0.28 mmol) and **15s** (222 mg, 0.43 mmol) were obtained after purification as yellowish oils, yield: 58%.

Compound **15a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.11 (9H, s), 1.07 (9H, s), 1.15–1.40 (5H, m), 1.65–1.85 (5H, m), 1.90 (1H, d, J=6.2 Hz), 2.06 (1H, br.d, J=12.5 Hz), 3.01 (1H, dd, J=6.2, 7.9 Hz), 3.24 (1H, t, J=5.3 Hz), 3.91 (2H, d, J=5.3 Hz), 7.25–7.51 (6H, m), 7.65–7.74 (4H, m); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: −0.34 (q), 19.26 (s), 25.76 (t), 26.02 (t), 26.36 (t), 26.69 (s), 28.62 (t), 29.15 (t), 41.48 (d), 58.49 (s), 62.53 (d), 63.20 (t), 79.05 (d), 92.98 (s), 98.55 (s), 127.74 (d), 129.77 (d), 133.13 (s), 135.51 (d); IR (film): 3456, 2175, 1470, 1428, 1250, 1190, 1110, 1050, 850; MS (FAB+NaI): 543, 505, 241, 221, 199, 197, 172, 135, 115. Anal. calcd for $C_{31}H_{44}O_3Si_2$ C, 71.49; H, 8.52. Found: C, 71.41; H, 8.42.

Compound **15s**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.10 (9H, s), 1.06 (9H, s), 1.12–1.34 (5H, m), 1.60–1.87 (6H, m), 3.45 (1H, dd, J=5.5, 5.3 Hz), 3.67 (1H, d, J=3.3 Hz), 3.89 (1H, dd, J=11.4, 5.3 Hz), 3.96 (1H, dd, J=11.3, 5.5 Hz), 7.32–7.49 (6H, m), 7.65–7.72 (4H, m); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: −0.27 (q), 19.34 (s), 25.83 (t), 26.09 (t), 26.42 (t), 26.76 (s), 28.67 (t), 29.24 (t), 41.56 (d), 58.80 (s), 62.59 (d), 63.29 (t), 79.10 (d), 93.20 (s), 98.35 (s), 127.79 (d), 129.83 (d), 134.60 (s), 135.58 (d); IR (film): 3470, 2170, 1472, 1428, 1250, 1115, 1043, 844, 761.

4.3.10. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-5,5-dimethyl-3-trimethylsilylethynylhexan-4-ol. From 500 mg of **1b**, diastereoisomers **16a** (143 mg, 0.29 mmol) and **16s** (244 mg, 0.49 mmol) were obtained after purification as yellowish oils, yield: 64%.

Compound **16a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.10 (9H, s), 1.07 (9H, s), 1.08 (9H, s), 3.45 (1H, t, J=5.3 Hz), 3.59 (1H, s), 3.93 (1H, dd, J=11.0, 5.3 Hz), 4.01 (1H, dd, J=11.0, 5.3 Hz), 7.40–7.50 (6H, m), 7.75–7.80 (4H, m); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: −0.6 (q), 19.26 (s), 26.76 (q), 26.9 (q), 35.0 (s), 55.6 (s), 60.2 (d), 63.2 (t), 73.4 (d), 93.8 (s), 101.2 (s), 127.7 (d), 129.7 (d), 133.1 (s),135.5 (d); IR (film): 3490, 2170, 1470, 1425, 1250, 1112, 1011, 844, 761, 741, 702; MS (FAB+Na): 517, 477, 421, 351, 331, 241, 221, 199, 135. Anal. Calcd for $C_{29}H_{42}O_3Si_2$ C, 70.30; H, 8.68. Found: C, 70.52; H, 8.72.

Compound **16s**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.14 (9H, s), 1.06 (9H, s), 1.10 (9H, s), 3.33 (1H, t, J=5.2 Hz), 3.37 (1H, s), 3.92 (1H, dd, J=11.0, 5.2 Hz), 4.01 (1H, dd, J=11.0, 5.2 Hz), 7.40–7.50 (6H, m), 7.74–7.80 (4H, m); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: −0.5 (q), 19.24 (s), 26.74 (q), 26.92 (q), 36.10 (s), 56.71 (s), 62.05 (d), 63.02 (t), 75.77 (d), 93.12 (s), 99.24 (s), 127.71 (d), 129.73 (d), 133.12 (s),135.51 (d); IR (film): 3490, 2165, 1470, 1425, 1250, 1115, 1010, 850, 760; MS (FAB+Na): 517, 477, 437, 421, 351, 331, 241, 221, 199, 154, 135.

4.3.11. *cis* 1-*tert*Butyldiphenylsilyloxy-2,3-epoxy-3-(hydroxyphenylmethyl)-5-trimethylsilyl pent-4-yne. From 500 mg of **1b**, diastereoisomers **17a** (29 mg, 0.06 mmol) and **17s** (544 mg, 1.06 mmol) were obtained after purification as yellowish oils, yield: 91%.

Compound **17a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.00 (9H, s), 1.04 (9H, s), 2.45 (1H, d, J=2.0 Hz), 3.66 (1H, t, J=5.2 Hz), 3.89 (2H, d, J=5.2 Hz), 4.91 (1H, d, J=2.0 Hz), 7.32–7.47 (11H, m), 7.58–7.68 (4H, m); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: −0.50 (q), 19.33 (s), 26.82 (q), 58.68 (s), 59.50 (d), 63.33 (t), 73.16 (d), 94.35 (s), 99.22 (s), 127.51 (d), 127.80 (d), 128.27 (d), 128.47 (d), 129.80 (d), 133.29 (s), 135.62 (d), 138.50 (s); IR (film): 3456, 2174, 1472, 1428, 1251, 1188, 1113, 1050, 848, 701; MS (FAB): 515, 498, 437, 351, 331, 241, 221, 199, 163, 135. Anal. calcd for $C_{31}H_{38}O_3Si_2$ C, 72.33; H, 7.74. Found: C, 72.51; H, 7.85.

Compound **17s**. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.00 (9H, s), 1.08 (9H, s), 2.67 (1H, d, J=6.2 Hz), 3.52 (1H, dd, J=5.3, 5.1 Hz), 3.90 (1H, dd, J=11.7, 5.3 Hz), 4.02 (1H, dd, J=11.7, 5.1 Hz), 4.59 (1H, d, J=6.2 Hz), 7.31–7.49 (11H, m), 7.63–7.72 (4H, m); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: −0.56 (q), 19.38 (s), 26.87 (q), 59.40 (s), 61.72 (d), 63.38 (t), 75.81 (d), 94.39 (s), 98.56 (s), 126.98 (d), 127.54 (d), 127.84 (d), 128.27 (d), 129.85 (d), 133.27 (s), 135.65 (d), 139.31 (s).

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References

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