A New Diastereodivergent Synthesis of 1,2-Disubstituted Homopropargylic Alcohols

Fabrice Chemla,*[a] Nicolas Bernard,[a] and Jean Normant[a]

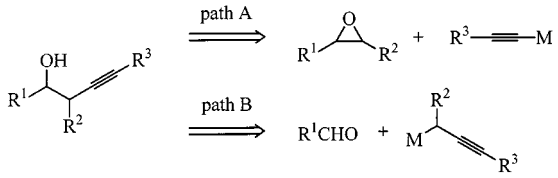
Dedicated to Professor R. W. Hoffmann, Marburg, on the occasion of his 65th birthday

Keywords: Propargylic oxiranes / Homopropargylic alcohols / Bromoallenes / Allenes

1,2-Disubstituted homopropargylic alcohols can be prepared in a diastereodivergent fashion starting from propargylic epoxides by BF_3-catalysed direct ring-opening or by double inversion through the intermediate formation of a bromoallenol moiety.

Introduction

1,2-Disubstituted homopropargylic alcohols constitute a class of compounds which has been widely used in organic synthesis. They are key intermediates in the synthesis of erythronolide B,[1] neomethynolide[2] and oudemansin C,[3] N-BOC ADDA,[4][5] and maytansinol[6] as well as in some approaches to milbemycins[7] and avermectins.[8] These types of compounds are generally prepared by two main pathways, the corresponding retrosynthetic analyses of which are depicted on Scheme 1.



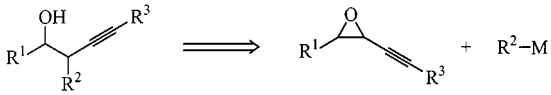
Scheme 1

Pathway A in Scheme 1 corresponds to the ring-opening of an oxirane by an alkynyl metal. This is the commonly used route,[9] but it suffers from evident drawbacks: the reaction has to be regioselective and is limited to the case of symmetrical[10][11] or monosubstituted oxiranes.[11][12] When the oxirane is substituted by a $-CH_2OR$[6] moiety, the reaction has also been found to be regioselective, but is restricted to this particular case.

Pathway B depicted in Scheme 1 involves the reaction of a propargylmetal with an aldehyde. This way has been well-studied[13] and requires a proper choice of the metal in order to obtain good regioselectivity (propargyl vs allenyl starting material) as well as a good stereoselectivity (*syn* vs *anti* starting material). When the metal is zinc, total control of the regioselectivity as well as a good control of the stereoselectivity by the allenylzinc intermediate was observed. Thus disubstituted *anti* homopropargylic alcohols have been obtained[14] by use of allenylzinc reagents, whereas allenyltin reagents lead to *syn* or *anti* homopropargylic alcohols, depending on the Lewis acid utilized.[15] The use of allenylboron,[16] chromium,[17] magnesium,[18] and titanium[19] reagents leads generally to a lower regioselectivity or stereoselectivity.

Some other syntheses of homopropargylic alcohols have been also described: the classical homoaldol reaction of chlorocrotylboronates with aldehydes furnishes homoallylic alcohols bearing a chlorine atom on the double bond; this type of molecule can undergo an elimination of hydrochloric acid to give homopropargylic alcohols.[20][21] Kocienski has developed an elegant methodology for the synthesis of homopropargylic alcohols by a Fritsch−Buttenberg−Wiechell-type rearrangement of lithiated enol carbamates.[22] This methodology has been used in the synthesis of avermectin.[8] Very recently, another approach by the base-catalysed ring opening of vinylidene oxetanes[23] has been described.

In our laboratory, we planned an alternative approach to the synthesis of homopropargylic alcohols (Scheme 2). The use of a propargylic oxirane should solve the problem of stereoselectivity, as usually the ring-opening of oxiranes is stereospecific, so the stereochemistry of the formed homopropargylic alcohol is directly related to the *cis* or *trans* stereochemistry of the starting propargylic oxirane. Moreover the two carbons of the oxirane should be differentiated from one another, the propargylic carbon being more electrophilic.



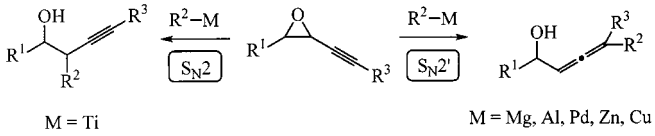
Scheme 2

However, this strategy raises an other problem, namely the possible participation of the triple bond. The ring opening of propargylic oxiranes has been studied already, and in most cases the reaction occurs by an S_N2' process (Scheme

[a] Laboratoire de Chimie des OrganoEléments, Université P. et M. Curie, Bte 183
4 place Jussieu, 75252 Paris Cedex 05, France
Fax: (internat.) +33 - 1/ 44 27 75 67
E-mail: fchemla@ccr.jussieu.fr

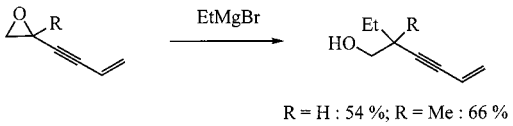
  1434−193X/99/0909−2067 $ 17.50+.50/0

3). This was observed with Grignard,[24] aluminium[25] and zinc reagents (under Pd° catalysis[26]), palladium,[27] and especially copper reagents.[24][28] In only two cases was the reaction described to follow an S_N2 pathway: Seebach and Krause have shown that titanium reagents were able to react with propargylic oxiranes without the participation of the triple bond and with retention of configuration at the propargylic carbon.[29] However, this method is limited to the use of aromatic, allyl and alkynyl reagents.



Scheme 3

However, Perveev[30] has observed that propargylic oxiranes bearing a double bond conjugated with the triple bond react with Grignard reagents in an S_N2 mode to give the corresponding enynol (Scheme 4).

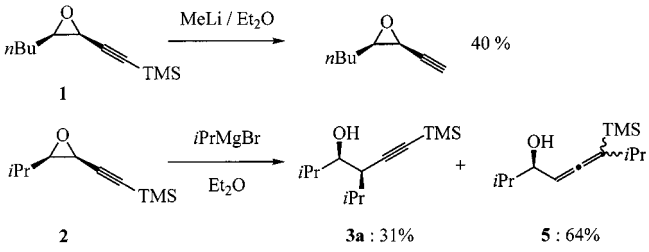


Scheme 4

Results and Discussion

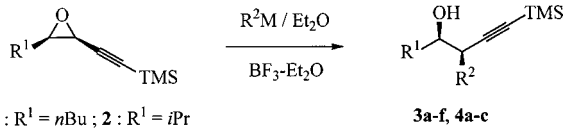
Ring-Opening of Propargylic Oxiranes with Organolithium and Grignard Reagents

This result from Perveev seemed to show that when the triple bond is deactivated (electronically or sterically), the reaction could occur on the desired propargylic position. We then decided to examine the reaction of organolithium and Grignard reagents with various propargylic oxiranes bearing a TMS moiety on the acetylenic position. These oxiranes were prepared by oxidation of the corresponding (*Z*)- or (*E*)-enynes by MCPBA or Oxone®/acetone, or by a method that we have recently described[31] involving the condensation of 3-chloro-1-trimethylsilyl zincioallene with aldehydes. Our first trials were conducted on the propargylic oxirane **1** (see Scheme 5). However, the reaction with MeLi in ether only led to the corresponding desilylated oxirane among a number of unidentified decomposition products. The reaction of oxirane **2** with *i*PrMgBr in ether was more encouraging as two products were obtained, the first one (**3a**) resulting from the desired S_N2 reaction (but in only 31% yield), and the other one (**5**) resulting from the S_N2' reaction in 64% yield. Product **3a** was obtained as a single diastereomer, but **5** was present as a mixture of two diastereomers in a 80:20 ratio, the relative configurations of which could not be determined. It should be noted that in the absence of the TMS group on the triple bond, a similar reaction was described to occur only by the S_N2' mode and with a similar stereoselectivity.[24]



Scheme 5

In order to activate the propargylic position, we then turned to a possible activation of the oxirane by a Lewis acid. BF_3-Et_2O is known to enhance the reactivity of oxiranes towards nucleophiles,[32] and to direct the reaction of alcohols in an inter-[33] or intramolecular[34] fashion at the propargylic position of propargylic oxiranes. We were pleased to see that in the presence of BF_3-Et_2O, organolithium and Grignard reagents are able to open propargylic epoxides only on the propargylic position and with a total stereoselectivity. Our results are summarized on Table 1.

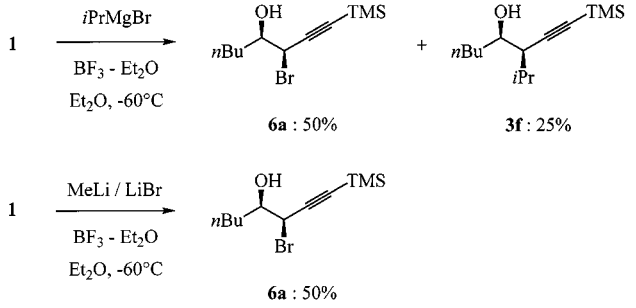


Entry	Oxirane	R^2M	Product	Yield (%)
1	**1**	MeLi	**3a**	90
2	**1**	*n*BuLi	**3b**	30
3	**1**	1-Cyclohexenyllithium	**3c**	31
4	**1**	EtMgCl	**3d**	75
5	**1**	BnMgCl	**3e**	65
6	**1**	*i*PrMgCl	**3f**	70
7	**2**	MeLi	**4a**	85
8	**2**	EtMgCl	**4b**	92
9	**2**	*i*PrMgCl	**4c**	91

Table 1. Preparation of *syn* homopropargylic alcohols from *cis* propargylic oxiranes

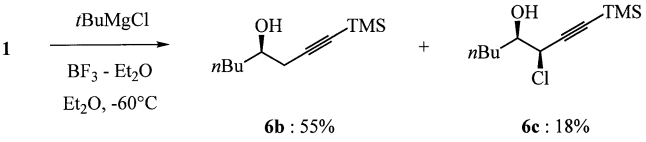
As can be seen in Table 1, the reaction is very efficient with Grignard reagents (entries 4–6, 8, 9), as well as with methyllithium (entries 1 and 7). The reaction of other organolithium reagents gave the corresponding homopropargylic alcohol, albeit in low yield (entries 2 and 3), along with considerable amounts of desilylated products and decomposition products. The mandatory use of salt-free alkyllithium reagents or of Grignard reagents derived from alkyl *chlorides* is shown in Scheme 6: the reaction of oxirane **1**

with MeLi, LiBr, or *i*PrMgBr gave the bromohydrin **6a** as the major product.



Scheme 6

This bromide ion ring opening has been observed in the reaction of Grignard reagents with simple oxiranes.[35] With styrene oxide in the presence of BF_3-Et_2O, it has been observed[36] that alkylmagnesium chlorides give little of the chlorohydrin, whereas alkylmagnesium bromides lead to substantial amounts of the bromohydrin. In our hands, we never observed the formation of halohydrin when we used Grignard reagents derived from alkyl chlorides, except in the case of *t*BuMgCl (Scheme 7). The obtained reduction product **6b** can be attributed to the reaction of the oxirane with a hydride ion derived from the decomposition of $tBuBF_2$ as described previously.[37]

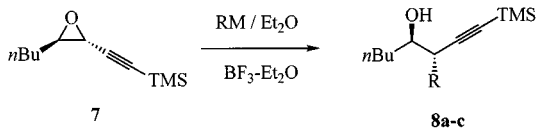


Scheme 7

The ring opening of *trans*-substituted propargylic oxiranes was also tried. We found that the reaction of oxirane **7** with organometallic reagents gives the corresponding *anti* homopropargylic alcohols **8a–c**, as reported on Table 2. These results suggest that the reaction is stereospecific. The stereochemistry of the products was proved unambiguously by protodesilylation of compounds **3a** and **8a** and comparison of the ^1H- and ^{13}C-NMR spectral data of the resulting propargylic alcohols with those reported in the litterature[20] for the *syn* diastereomer. Compound **8a** was then shown to be *anti*, so that the ring-opening of *trans* oxiranes leads to *anti* homopropargylic alcohols, whereas ring-opening of *cis* oxiranes gives *syn* alcohols.

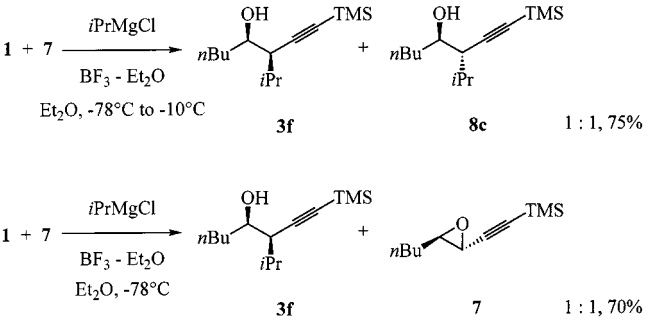
Kinetic Resolution of Propargylic Oxiranes

However, *trans* oxiranes were found to be less reactive than *cis* oxiranes, and in the former case the reaction has to be conducted at a higher temperature and yields are somewhat lower. This difference in the reactivity of *cis* and *trans* propargylic oxiranes has been exemplified in the following experiment: when a mixture of compounds **1** and **7** in a 1:1 ratio was allowed to react with *i*PrMgCl in ether in the presence of BF_3-Et_2O at −78 °C and the reaction mixture was allowed to warm up to −10 °C, a mixture of *syn* and *anti* homopropargylic alcohols **3f** and **8c** was obtained in a 1:1 ratio and a 75% overall yield. However, when the same reaction was performed at −78 °C, only the *syn* homopropargylic alcohol **3f** was then obtained in a 70% yield from the *cis* oxirane **1**, whereas the *trans* oxirane **7** was recovered unchanged (Scheme 8). This kinetic resolution is particularly interesting when it is not possible or time-consuming to prepare propargylic oxiranes in a well-defined stereochemically pure form.[31]



Entry	Oxirane	R^2M	Product	Yield (%)
1	**7**	MeLi	**8a**	60
2	**7**	EtMgCl	**8b**	62
3	**7**	*i*PrMgCl	**8c**	65

Table 2. Preparation of *anti* homopropargylic alcohols from *trans* propargylic oxiranes

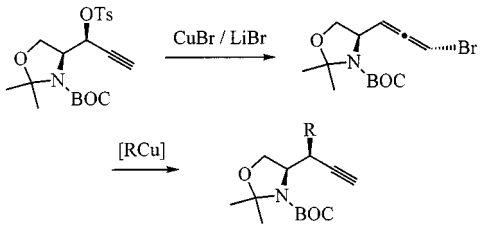


Scheme 8

However, this result shows the limits of this approach. Whereas *syn*-disubstituted homopropargylic alcohols are easy to prepare in good yields, the access to *anti*-disubstituted homopropargylic alcohols is more limited and yields are lower. We then turned to an alternate strategy: the use of bromoallenols.

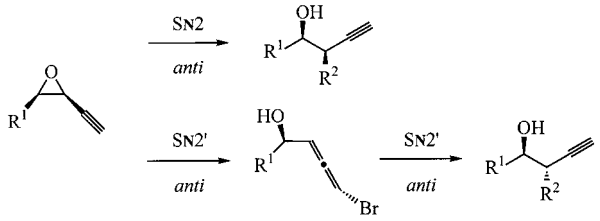
Recently, A. Mann and M. Taddei have described a very interesting methodology for the stereoselective preparation of acetylenic compounds.[5][38] Starting from a propargylic tosylate, they prepared the corresponding bromoallene by an S_N2' substitution with *anti* stereoselectivity; this bromoallene then undergoes a second S_N2' substitution with organocopper reagents, again with the *anti* stereoselectivity. The overall process then results in an S_N2 substitution with *retention* of the configuration at the propargylic position (Scheme 9).

We thought that this methodology should apply to propargylic oxiranes to give, after formation of the bromoallene through ring-opening with inversion and further substitution by organocopper reagents (also with inversion) the disubstituted homopropargylic alcohol corresponding to an



Scheme 9

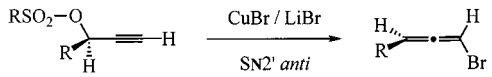
overall S_N2 process with retention of configuration, as described in Scheme 10.



Scheme 10

Preparation of Bromoallenols from Propargylic Oxiranes

Various methods have been described for the preparation of bromoallenes,[39] but to the best of our knowledge nothing is known about their preparation from propargylic epoxides. The commonly used method was described by Goré,[40] starting from a propargylic sulfonate (tosylate or mesylate), as depicted on Scheme 11. The reaction is known to occur with inversion of the configuration,[41] and has been used several times,[5,38,41,42] including in a total synthesis of natural products.[43]



Scheme 11

We applied such conditions (CuBr/LiBr in THF) in the case of the propargylic epoxide **9** (prepared from **1** by quantitative protodesilylation with KF in DMF/water). However, despite our many attempts with various reaction conditions (copper salt, bromide ion source, solvent, temperature), we observed only decomposition of the starting material. We then turned to another method described by Landor,[44] using propargylic alcohols as starting material, CuBr, and HBr as an activating agent. We were pleased to see that in the presence of ammonium bromide, propargylic oxiranes can be smoothly transformed into bromoallenols in good yields. Our results are reported in Table 3.

The reaction is stereospecific, as starting from two diastereomeric oxiranes, we obtained the two corresponding bromoallenols. Concerning its stereochemistry, we must emphazise that the reaction occurs with inversion of configuration (S_N2' *anti*), in contrast to the stereochemistry observed by Landor with propargylic alcohols. The stereoselectivity

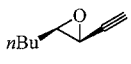
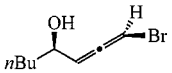
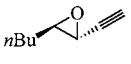
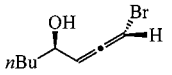
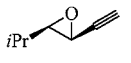
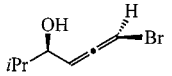
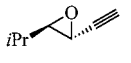
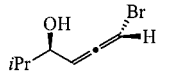
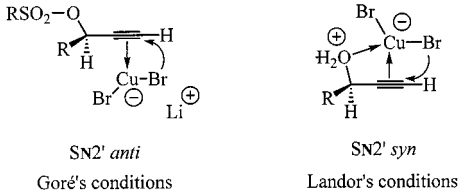
Entry	Starting oxirane		Bromoallenol		Yield (%)
1		**9**		**13**	70
2		**10**		**14**	65
3		**11**		**15**	55
4		**12**		**16**	73

Table 3. Reaction of bromoallenols from propargylic oxiranes

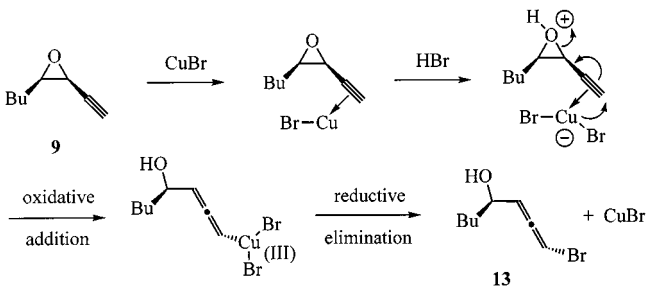
of the reaction was unambiguously proven by a subsequent reaction, namely an *anti* S_N2' substitution of the obtained bromoallenols (vide infra), and comparison of the obtained products with the corresponding homopropargylic alcohols already described in the first part of this report (vide supra).

The reason for the *syn* stereoselectivity in the Landor's case was attributed to a possible chelated intermediate, directing the oxidative addition of the copper species, as depicted on Scheme 12,[45] whereas no chelation occurs in the reaction of propargylic sulfonates with CuBr (Goré's conditions) so that the oxidative addition now occurs in an *anti* fashion,[41] as usual in the S_N2' substitutions with copper species.[46]



Scheme 12

In the case of our propargylic epoxides, the reaction conditions are those described by Landor, but the stereochemical course is the *anti* mode. This can be attributed to the absence of any possibility for chelation between the lone pairs of the oxygen atom (perpendicular to the oxirane plane) and the copper species already bound to the triple bond. The mechanism for this reaction can then be represented as depicted on the Scheme 13.

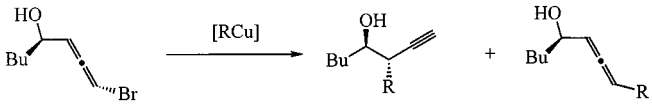


Scheme 13

S_N2' Reactions of Bromoallenols with Organometallics

Having in hand a stereospecific preparation of bromoallenols from propargylic oxiranes, we then turned to the next step, namely the S_N2' substitution reactions with organometallics. The substitution of bromoallenes by organometallics has been studied[47] by many research teams. Allenes have been obtained by an S_N2 substitution reaction with organolithium reagents[48] or sodium malonates[49] as well as with Grignard,[50] silver,[51] or zinc[51][52] reagents under palladium or nickel catalysis.[53] On the other hand, reaction with organocopper reagents is not so clear-cut, and the regioselectivity of the reaction seems to be relevant to the nature of the used organocopper reagent. Whereas lower-order cuprates (R_3Cu_2Li),[54] cyanocuprates (RCu(CN)Li),[38,54−56] or Vermeer-type[57] organocopper reagents ($RCu-MgBr_2-LiBr$)[55][58] are described to react with bromoallenes by an S_N2' reaction with the *anti* diastereoselectivity to give the acetylenic compound, Gilman cuprates (R_2CuLi),[59] copper reagents derived from Grignard reagents ($RCu-MgBr_2$) as well as Grignard reagents under Cu^I catalysis[55] are known to react by an S_N2 reaction to give the allenic product. Moreover, the regioselectivity also depends on the structure of the substrate: whereas bromoallenes react with cyanocuprates by an S_N2' reaction, TMS-substituted bromoallenes have been shown to undergo an S_N2 displacement to give the substituted allene.[60]

We then tried the substitution reaction on bromoallenol **13** derived from propargylic oxirane **9**. Unfortunately, all our attempts with various copper reagents gave us (in most cases) a mixture of the two possible regioisomers, the desired homopropargylic alcohol **3** as a minor compound, along with the (major) allenyl alcohol **17** (and not a reduction product as has been erroneously reported in our preliminary communication[61]). Our attempts are reported on Table 4.

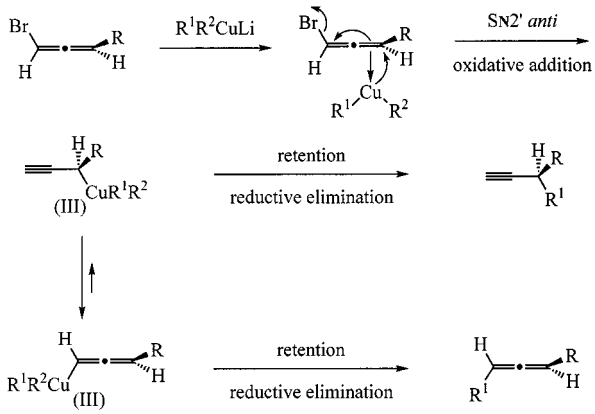


13 **8** **17**

Entry	[RCu]	S_N2' product	Yield (%)	S_N2 product	Yield (%)
1	MeCu(CN)Li	**8a**	35	**17a**	33
2	$Me_2Cu(CN)Li_2$	**8a**	0	**17a**	40
3	MeCu / LiBr	**8a**	30	**17a**	30
4	*i*PrMgBr / CuBr 5%	**8c**	<10	**17b**	40

Table 4. Reaction of bromoallenol **13** with organocopper reagents

The mechanism of the S_N2' reaction of bromoallenes by organocopper reagents has been depicted as shown in Scheme 14. Oxidative addition of the organocopper reagent on the bromoallenyl system occurs in an S_N2' fashion with inversion, leading to the propargylic Cu^{III} species. Reductive elimination with retention then gives the propargylic product.



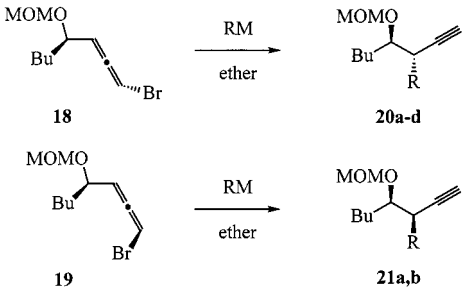
Scheme 14

However, if the propargylic Cu^{III} species has time enough to form the allenic Cu^{III} species in a metallotropic equilibrium, reductive elimination leads to the isomeric allenic compound. The obtention of the propargylic or allenic product is then directly related to the relative rates of the reductive elimination and the metallotropic shift. If the Cu^{III} species is very unstable (for example with cyanocuprates), reductive elimination occurs faster than the metallotropic shift, and the propargylic product is obtained; in contrast, if the Cu^{III} species is stabilized (by adding phosphanes or Me_2S for example), the metallotropic equilibrium occurs faster than the reductive elimination, leading to the allenic product.

In our case, the obtention of the allenic compound as a major product indicates that the Cu^{III} intermediate derived from the S_N2' substitution on bromoallenols is stabilized. We thought that this stabilization might perhaps be attributed to the presence of a free alcohol moiety, stabilizing the complex via its alcoholate. Thus protection of the alcohol should solve our problem. We chose the MOM group as a protecting group. Protection of the alcohol moiety as a MOM ether was easily achieved under standard conditions (MOMCl, iPr_2NEt), leading to protected bromoallenols **18** and **19** starting from bromoallenols **13** and **14**, respectively.

We were very pleased to see that our hypothesis was confirmed: the substitution reaction, with organocopper reagents, of the protected bromoallenols **18** and **19** occurred exclusively in an S_N2' fashion with almost all reagents we used. Our results are reported on Table 5.

The stereochemical assignment for the products was made by comparison of ^1H- and ^{13}C-NMR spectral data for compounds **20a**, **20b**, **21a**, and **21b** with those reported for compounds **8a**, **8c**, **3a**, and **3f**, respectively, after protection of the alcohol moiety as a MOM ether and desilylation procedure ($KF/DMF/H_2O$, room temperature, quantitative yield). As this S_N2' reaction is known to occur with inversion of the configuration, the stereoselectivity of the preceding step, namely the formation of bromoallenols was unambiguously confirmed to be also *anti*.



Entry	Reactant	RM	Alkyne	Yield (%)	d.e. (%)
1	**18**	MeCu(CN)Li	**20a**	95	>98
2	**18**	*i*PrMgBr - CuBr - Me_2S	**20b**	42	>98
3	**18**	*i*PrMgCl - CuBr - Me_2S	**20b**	43	>98
4	**18**	*i*PrMgBr - CuBr 5%	**20b**	85	>98
5	**18**	*i*PrMgBr	**20b**	90	>98
6	**18**	*n*BuCu(CN)Li	**20c**	95	>98
7	**18**	AllylMgBr - CuBr 5%	**20d**	53	60
8	**19**	MeCu(CN)Li	**21a**	91	>98
9	**19**	*i*PrMgBr	**21b**	83	>98

Table 5. Substitution reaction of protected bromoallenols with organometallic reagents

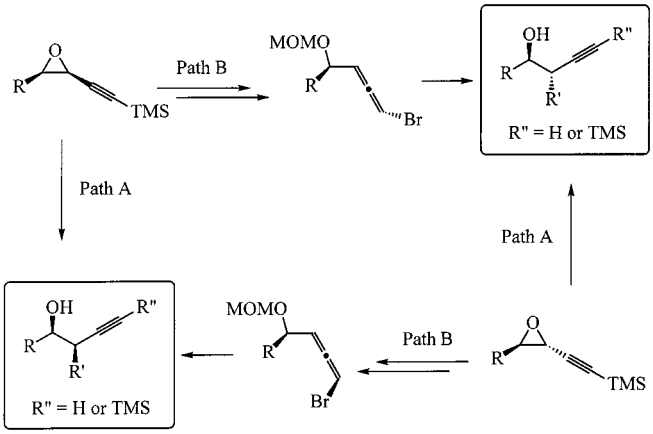
The regiochemistry of the substitution of protected bromoallenols was found to be excellent, except in the case when CuBr−Me_2S was used (entries 2 and 3). This copper salt is known to stabilize copper species efficiently; so it is not very surprising that in this case, the product derived from the S_N2 reaction (i.e. the allene) was also obtained in 29 and 28% yield.

The stereochemistry of the substitution reaction was also found to be excellent, except in the case when allylMgBr was used under copper catalysis (entry 7). We have no explanation for this phenomenon at the moment.

Finally we were very surprised that in the case of *i*PrMgBr, the presence of a copper salt was unnecessary. The substitution reaction occurs with an excellent regio- and stereocontrol (entries 5 and 9), giving the two diastereomers **20b** and **21b** starting from **18** and **19**, respectively. It has been described that bromoallenes react very slowly with Grignard reagents to give mixtures of products after a long reaction time.[53] In our case, the presence of the MOM group seems to activate the bromoallene moiety. From the best of our knowledge, only one example of substitution reaction of bromoallenes with Grignard reagents is described[62], leading to low regioselectivities. In our case, the regioselectivity is excellent, and again this can be attributed to the presence of the MOM moiety. However, the reaction is also stereospecific, and then the stereochemistry of the protected alcohol *does not* direct the substitution reaction. The protected bromoallenols react by an S_N2' reaction with *anti* stereoselectiviy. No explanation could yet be found for a this clean stereospecificity.

Conclusion

We have disclosed two highly regio- and stereoselective syntheses of 1,2-disubstituted homopropargylic alcohols starting from propargylic oxiranes. As can be seen in Scheme 15, the same *cis* propargylic oxirane can be used to prepare *syn* homopropargylic alcohols by direct ring-opening by organolithium and Grignard reagents under BF_3−Et_2O conditions (path A), or can lead to protected *anti* homopropargylic alcohols in three steps, namely a) stereoselective formation of the bromoallene, b) protection of the alcohol moiety and c) stereospecific substitution of the bromoallene. On the other hand, the same type of transformation can be applied to *trans* propargylic oxiranes to give, after direct ring-opening in the presence of BF_3−Et_2O, *anti* homopropargylic alcohols (path A) or protected *syn* homopropargylic alcohols by the same three-step method (path B).



Scheme 15

This work discloses a totally controlled diastereodivergent synthesis of 1,2-disubstituted homopropargylic alcohols starting from *cis* or *trans* propargylic oxiranes. It should be noted that as in these transformations, the homopropargylic center remains unchanged (this in shown by the stereospecificity of the reactions), this methodology can be easily applied to enantiomerically pure propargylic oxiranes[63] without any loss of the stereochemical information. Further results in this field will be reported in due course.

Experimental Section

General Remarks: All reactions were performed in oven-dried glassware under dry nitrogen. The reactions performed at low temperature were made in four-necked, round-bottomed flasks equipped with an internal thermometer and mechanical stirrer, and with liquid nitrogen as cryogenic liquid. − NMR: Bruker ARX 400 or AC 200. − IR: Perkin−Elmer 1420. − Organolithium and Grignard reagents were purchased from Aldrich Inc.

***cis*-2-Butyl-3-(trimethylsilylethynyl)oxirane (1)**: To a solution of (*Z*)-1-trimethylsilyloct-3-en-1-yne (0.4 mol) in CH_2Cl_2 (100 mL) at 0°C was added over a period of 30 min MCPBA (0.5 mol) in CH_2Cl_2 (0.5 L). The mixture was allowed to warm to room temp. The progress of the reaction was followed by GC. The reaction was

hydrolyzed with aqueous $NaHCO_3$, treated with aqueous Na_2SO_3, and washed with brine. The mixture was dried with magnesium sulfate, filtered, and concentrated in vacuo. The remaining MCPBA was removed by precipitation in pentane at −10°C. After removal of the solvent, the epoxide was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford 72.9 g (93%) of **1** as a colourless oil. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.40 (d, 1 H, *J* = 3.79 Hz), 3 (m, 1 H), 1.8−1.3 (m, 6 H), 0.94 (t, 3 H, *J* = 7.16 Hz), 0.18 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 100.90, 91.38, 58.68 and 45.69, 29.33, 28.29 and 22.90, 14.38, 0.32.

***cis*-2-Isopropyl-3-(trimethylsilylethynyl)oxirane (2):** (*Z*)-5-methyl-1-trimethylsilylhex-3-en-1-yne (11.31 g, 68 mmol) was dissolved in CH_3CN (960 mL) with acetone (48.2 mL) and 670 mL of a previously formed $4\cdot10^{-4}$ N solution of Na_2EDTA in water. Oxone (207.7 g) and $NaHCO_3$ (89.18 g) were added portionwise within 2 h. The pH of the solution must stay around 7. The mixture was stirred at room temp. overnight. After disappearance of the starting material, ether (300 mL) was added followed by water (300 mL). The layers were separated and the aqueous layer was extracted with ether (3 × 150 mL). The combined organic layers were washed with brine, dried with magnesium sulfate, filtered, and concentrated in vacuo to give the crude oxirane **2** (7.6 g, 61%) as a colourless oil. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.43 (d, 1 H, *J* = 4 Hz), 2.72 (dd, 1 H, *J* = 4 Hz, *J* = 9 Hz), 1.70 (m, 1 H), 1.14 and 1.04 (d, 3 H, *J* = 6.8 Hz), 0.17 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 100.71, 91.06, 64.08 and 45.69, 29.48, 20.08 and 18.20, 0.00. − IR (film, KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2860, 2170, 1465, 1350, 1245. − $C_{10}H_{18}OSi$: calcd. C 65.87, H 9.95; found C 65.74, H 10.01.

***trans*-2-Butyl-3-(trimethylsilylethynyl)oxirane (7):** (*E*)-1-trimethylsiloct-3-en-1-yne (6.42 g, 35.6 mmol) was dissolved in CH_3CN (500 mL) with acetone (25 mL) and 350 mL of a previously formed $4\cdot10^{-4}$ N solution of Na_2EDTA in water. Oxone (107.8 g) and $NaHCO_3$ (46.28 g) were added portionwise in 3 h. The pH of the solution must stay around 7. The mixture was stirred at room temp. for 5 h. After the disappearance of the starting material, ether (200 mL) was added followed by water (300 mL). The layers were separated and the aqueous layer was extracted with ether (3 × 100 mL). The combined organic layers were washed with brine, dried with magnesium sulfate, filtered, and concentrated in vacuo to give the crude oxirane **7** (4.95 g, 72%) as a colourless oil. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.10 (m, 2 H), 1.65−1.35 (m, 6 H), 0.93 (t, 3 H, *J* = 7.1 Hz), 0.19 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 102.46, 89.54, 61.25 and 45.91, 31.87, 28.15 and 22.84, 14.36, 0.32. − IR (film, KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2920, 2850, 2170, 1460, 1245.

General Procedure for the BF_3−Et_2O Assisted Ring-Opening of *cis* Propargylic Oxiranes 1 and 2: To a solution of oxirane (2 mmol) in dry Et_2O (10 mL) were added at −80°C BF_3−Et_2O (0.5 mL, 4 mmol) and the solution of the organometallic compound (6 mmol). The solution was vigorously stirred for 35 min at −70°C for **1** or 1 h at −70°C and 30 min at −50°C for **2**. After the disappearance of the starting material, two equivalents of MeOH and Et_3N were added. The temperature increased to −40°C. After stirring for 30 min the mixture was quenched with saturated aqueous NH_4Cl and the solution was allowed to warm to room temp. The mixture was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with 1 N HCl, brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford the corresponding *syn* homopropargylic alcohol as colourless oils.

(3*R,4*R**)-3-Methyl-1-trimethylsilyloct-1-yn-4-ol (3a):** From **1** (399 mg, 2 mmol) and salt-free methyllithium (9.1 mL of a 0.66 N solution in ether). Yield: 360 mg, 90%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.58 (m, 1 H), 2.60 (dt, 1 H, *J* = 7 Hz, *J* = 6.6 Hz), 1.6−1.25 (m, 6 H), 1.17 (d, 3 H, *J* = 7.1 Hz), 0.93 (t, 3 H, *J* = 7.2 Hz), 0.17 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 109.24, 86.84, 74.42, 34.22, 33.57, 28.31, 22.98, 15.99, 14.35, 0.47. − $C_{11}H_{24}OSi$: calcd. C 65.93, H 12.07; found C 65.99, H 11.97.

(3*R,4*R**)-3-Butyl-1-trimethylsilyloct-1-yn-4-ol (3b):** From **1** (399 mg, 2 mmol) and salt-free *n*-butyllithium (9.5 mL of a 0.62 N solution in ether). Yield: 145 mg, 29%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.57 (m, 1 H), 2.51 (m, 1 H), 1.7−1.2 (m, 12 H), 0.93 (2t, 6 H), 0.17 (s, 9 H).

(3*R,4*R**)-3-Cyclohex-1′-enyl-1-trimethylsilyloct-1-yn-4ol (3c):** From **1** (399 mg, 2 mmol) and salt-free cyclohexenyllithium (5.2 mL of a 1.15 N solution in ether). Yield: 195 mg, 35%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.71 (m, 1 H), 3.59 (m, 1 H), 3.02 (d, 1 H, *J* = 7.88 Hz), 2.2−1.3 (m, 14 H), 0.93 (t, 3 H, *J* = 6.9 Hz), 0.18 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 134.44, 127.29, 105.37, 89.60, 71.45, 49.41, 33.90, 28.27, 25.90, 25.77, 23.17, 23.06, 22.72, 14.43, 0.51. − IR (film, KBr): $\tilde{\nu}$ = 3440 cm^{-1}, 2925, 2160, 1445, 1245.

(3*R,4*R**)-3-Ethyl-1-trimethylsilyloct-1-yn-4-ol (3d):** From **1** (399 mg, 2 mmol) and ethylmagnesium chloride (3 mL of a 2 N solution in ether). Yield: 340 mg, 75%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.59 (m, 1 H), 2.46 (dt, 1 H, *J* = 5.17 Hz, *J* = 5.0 Hz), 1.75−1.3 (m, 8 H), 1.04 (t, 3 H), 0.93 (t, 3 H, *J* = 6.18 Hz), 0.16 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 107.76, 88.34, 73.50, 42.36, 33.84, 28.30, 23.49, 23.03, 14.40, 12.33, 0.54. − MS: *m/z* 227.03 (MH^+) ($M_{calc.}$ = 226.43). − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 2950, 2930, 2160, 1730, 1460, 1245. − $C_{13}H_{26}OSi$: calcd. C 68.96, H 11.57; found C 68.94, H 11.49.

(3*R,4*R**)-3-Benzyl-1-trimethylsilyloct-1-yn-4-ol (3e):** From **1** (399 mg, 2 mmol) and benzylmagnesium chloride (6 mL of a 1 N solution in ether). Yield: 375 mg, 65%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35−7.2 (m, 5 H), 3.60 (m, 1 H), 2.91 (dt, 1 H, *J* = 7.9 Hz, *J* = 9.5 Hz), 2.8−2.75 (m, 2 H), 1.8−1.3 (m, 6 H), 0.95 (t, 3 H, *J* = 7.34 Hz), 0.14 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 139.30, 129.40 and 128.06, 126.24, 106.79, 89.01, 72.84, 42.36, 36.48, 33.53, 27.84, 22.62, 14.02, 0.00. − MS: *m/z* 289.09 (MH^+) ($M_{calc.}$ = 288.50). − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 3050, 3020, 2950, 2920, 2850, 2160, 1450, 1245.

(3*R,4*R**)-3-Isopropyl-1-trimethylsilyloct-1-yn-4-ol (3f):** From **1** (399 mg, 2 mmol) and isopropylmagnesium chloride (3 mL of a 2 N solution in ether). Yield: 335 mg, 70%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.61 (m, 1 H), 2.37 (dd, 1 H, *J* = 5.5 Hz, *J* = 7.6 Hz), 1.98 (qd, 1 H), 1.8−1.7 and 1.6−1.35 (m, 6 H), 1.00 (2 d, 6 H, *J* = 6.62 Hz), 0.94 (t, 3 H, *J* = 6.99 Hz), 0.17 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100MHz): δ = 106.02, 89.31, 71.83, 47.78, 34.66, 28.19, 23.05, 27.69, 21.87, 18.70, 14.44, 0.57. − MS: *m/z* 241.04 (MH^+) ($M_{calc.}$ = 240.46).

(3*R,4*R**)-3,5-Dimethyl-1-trimethylsilylhex-1-yn-4-ol (4a):** From **2** (364 mg, 2 mmol) and salt-free methyllithium (9.1 mL of a 0.66 N solution in ether). Yield: 340 mg, 85%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.32 (t, 1 H, *J* = 5.84 Hz), 2.65 (m, 1 H), 1.92 (qd, 1 H), 1.8 (s, 1 H), 1.18 (d, 3 H, *J* = 7 Hz), 0.98 and 0.92 (d, 3 H, *J* = 6.8 Hz), 0.17 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 109.48, 86.38, 78.89, 31.36, 30.24, 19.53, 17.33, 15.15, 0.22.

(3*R,4*R**)-3-Ethyl-5-methyl-1-trimethylsilylhex-1-yn-4-ol (4b):** From **2** (364 mg, 2 mmol) and ethylmagnesium chloride (3 mL of a 2 N solution in ether). Yield: 390 mg, 92%. − ^{1}H NMR ($CDCl_3$,

400 MHz): δ = 3.37 (dd, 1 H, *J* = 4.96 Hz, *J* = 11.48 Hz), 2.47 (m, 1 H), 2.02 (m, 1 H), 1.68 (d, 1 H, *J* = 4.68 Hz), 1.60 (m, 1 H), 1.44 (m, 1 H), 1.05 (t, 3 H, *J* = 7.32 Hz), 0.96 and 0.95 (d, 6 H, *J* = 5.52 Hz), 0.16 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 108.15, 88.04, 77.88, 39.36, 30.40, 22.63, 19.86, 16.45, 11.86, 0.24.

(3*R,4*R**)-3-Isopropyl-5-methyl-1-trimethylsilylhex-1-yn-4-ol (4c):** From **2** (364 mg, 2 mmol) and isopropylmagnesium chloride (3 mL of a 2 N solution in ether). Yield: 410 mg, 91%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.32 (m, 1 H), 2.44 (dd, 1 H, *J* = 3.44 Hz, *J* = 9.2 Hz), 2.19−2.05 (m, 2 H), 1.40 (d, 1 H, *J* = 5.64 Hz), 1.04 and 1.01 (d, 6 H, *J* = 6.76 Hz), 0.97 and 0.91 (d, 6 H, *J* = 6.72 Hz), 0.17 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 105.57, 89.09, 75.87, 44.18, 30.92, 26.87, 22.42, 20.77, 17.1, 14.86, 0.54.

(3*R,4*R**)-3-Bromo-1-trimethylsilyloct-1-yn-4-ol (6a)**: From **1** (399 mg, 2 mmol) and isopropylmagnesium bromide (3 mL of a 2 N solution in ether). Yield: 280 mg, 50%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.48 (d, 1 H, *J* = 6.32 Hz), 3.73 (m, 1 H), 2.16 (d, 1 H, *J* = 6.52 Hz), 1.85−1.30 (m, 6 H), 0.94 (t, 3 H, *J* = 7.16 Hz), 0.20 (s, 3 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 100.48, 95.18, 74.49, 45.59, 33.47, 27.88, 22.81, 14.25, −0.5.

2,7-Dimethyl-6-trimetylsilylocta-4,5-dien-3-ol (5): To a solution of **2** (363 mg, 2 mmol) in dry Et_2O (10 mL), was added isopropylmagnesium chloride (8 mmol, 5 mL of a 1.6 N solution in ether) at −80°C. The solution was vigorously stirred for 10 min at −80°C and was allowed to warm to room temp. in 30 min. After 5 h at room temp., the mixture was quenched with 1 N aqueous HCl. The mixture was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with 1 N HCl, brine, dried with magnesium sulfate, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford **4c** (140 mg, 31%), then **5** (289 mg, 64%) as a mixture of two diastereomers (80:20 from ^{1}H-NMR analysis). − ^{1}H NMR ($CDCl_3$, 400 MHz): Major diastereomer: δ = 5.02 (dd, 1 H, *J* = 1.53 Hz, *J* = 6.61 Hz), 3.88 (dd, 1 H, *J* = 6.6 Hz, *J* = 6.64 Hz), 2.26 (m, 1 H), 1.74 (m, 1 H), 1.05 (d, 6 H, *J* = 6.62 Hz), 0.98 (d, 6 H, *J* = 7.12 Hz), 0.14 (s, 9 H). − Minor diastereomer: δ = 5.06 (dd, 1 H, *J* = 2.03 Hz, *J* = 6.1 Hz), 3.88 (dd, 1 H, *J* = 6.6 Hz, *J* = 6.64 Hz), 2.26 (m, 1 H), 1.74 (m, 1 H), 1.05 (d, 6 H, *J* = 6.62 Hz), 0.96 (d, 6 H, *J* = 7.12 Hz), 0.14 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 203.8 and 203.58, 107.51, 91.43, 91.07, 76.71 and 75.88, 35.40, 29.78, 24.8, 24.7, 19.32, 19.22, 0.

Reaction of 1 with *tert*-Butylmagnesium Chloride: To a solution of **1** (392 mg, 2 mmol) in dry Et_2O (10 mL) were added BF_3−Et_2O (0.5 mL, 4 mmol) and *tert*-butylmagnesium chloride (6 mmol, 4.2 mL of a 1.43 N solution in ether) at −80°C. The solution was vigorously stirred for 2 h at −70°C and then allowed to warm to −20°C. The reaction was followed by GC. After the disappearance of the starting material, two equivalents of MeOH and Et_3N were added to the solution. After 10 min at −30°C the mixture was quenched with saturated aqueous NH_4Cl and the solution was allowed to warm to room temp. The mixture was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with 1 N HCl, brine, dried with magnesium sulfate, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford **6b** (256 mg, 55%) and **6c** (71 mg, 18%) as a colourless oils.

1-Trimethylsilyloct-1-yn-4-ol (6b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.74 (m, 1 H), 2.47 (ABX syst., dd, 1 H, *J* = 4.6 Hz, *J* = 16.8 Hz), 2.36 (ABX syst., dd, 1 H, *J* = 7.04 Hz, *J* = 16.8 Hz), 1.97 (d, 1 H, *J* = 4.04 Hz), 1.57−1.26 (m, 6 H), 0.93 (t, 3 H, *J* = 6.7 Hz), 0.17 (s, 3 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 103.7, 87.98, 70.26, 36.3, 29.27, 28.12, 22.98, 14.38, 0.46.

(3*R,4*R**)-3-Chloro-1-trimethylsilyloct-1-yn-4-ol (6c)**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.76 (d, 1 H, *J* = 6.16 Hz), 3.76 (m, 1 H), 2.33 (d, 1 H, *J* = 4 Hz), 1.80−1.35 (m, 6 H), 0.92 (t, 3 H, *J* = 7.04 Hz), 0.20 (s, 3 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 100.74, 93.4, 75.08, 55.32, 33.02, 27.96, 22.87, 14.29, 0.05.

Protodesilylation of Compound 3a: To a solution of **3a** (135 mg, 0.65 mmol) in freshly distilled DMF (1 mL) were added KF (35 mg, 0.91 mmol) and water (2 drops). The mixture was stirred at room temp. for 1 h until the colour turned to dark red. The solution was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with brine, dried with magnesium sulfate, filtered, and concentrated in vacuo to afford 91 mg (83%) of (3*R**,4*R**)-3-methyloct-1-yn-4-ol as a yellow oil. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.58 (m, 1 H), 2.60 (m, 1 H), 2.13 (d, 1 H, *J* = 2.48 Hz), 1.8−1.25 (m, 6 H), 1.20 (d, 3 H, *J* = 7.04 Hz), 0.93 (t, 3 H, *J* = 6.8 Hz). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 86.53, 74.13, 70.21, 33.35, 32.79, 28.06, 22.70, 15.91, 14.08.

General Procedure for the BF_3−Et_2O Assisted Ring-Opening of *trans* Propargylic Oxirane 7: To a solution of **7** (400 mg, 2 mmol) in 10 mL of dry ether were added BF_3−Et_2O (0.5 mL, 4 mmol) and the solution of the organometallic compound (6 mmol) at −80°C. The solution was vigorously stirred for 45 min at −80°C, and then allowed to warm to −20°C for 2 h. After the disappearance of the starting material, the mixture was cooled to −80°C and MeOH (2 equiv.) and Et_3N (2 equiv.) were added. The temperature increased to −40°C. After 10 min at this temperature the mixture was quenched with saturated aqueous NH_4Cl and the solution was allowed to warm to room temp. The mixture was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with 1 N HCl, brine, dried with magnesium sulfate, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford the corresponding homopropargylic alcohol.

(3*S,4*R**)-3-Methyl-1-trimethylsilyloct-1-yn-4-ol (8a):** From **7** (399 mg, 2 mmol) and salt free methyllithium (9.1 mL of a 0.66 N solution in ether). Yield: 240 mg, 60%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.39 (m, 1 H), 2.55 (m, 1 H), 1.83 (d, *J* = 6.84 Hz, 1 H), 1.6−1.30 (m, 6 H), 1.20 (d, 3 H, *J* = 7.04 Hz), 0.92 (t, 3 H, *J* = 7.2 Hz), 0.16 (s, 9 H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 108.77, 87.86, 74.59, 35.12, 34.59, 28.33, 23.06, 17.79, 14.42, 0.55. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 2950, 2930, 2860, 2180, 1450, 1245. − $C_{11}H_{24}OSi$: calcd. C 65.93, H 12.07; found C 66.08, H 11.93.

(3*S,4*R**)-3-Ethyl-1-trimethylsilyloct-1-yn-4-ol (8b):** From **7** (399 mg, 2 mmol) and ethylmagnesium chloride (3 mL of a 2 N solution in ether). Yield: 280 mg, 62%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.47 (m, 1 H), 2.38 (m, 1 H), 1.75 (d, *J* = 7.64 Hz, 1 H), 1.65−1.30 (m, 8 H), 1.03 (t, 3 H, *J* = 7.48 Hz), 0.92 (t, 3 H, *J* = 6.92 Hz), 0.17 (s, 9 H). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 106.74, 89.11, 73.01, 42.43, 35.61, 28.37, 25.19, 23.05, 14.41 and 12.47, 0.56. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 2950, 2920, 2860, 2160, 1455, 1245. − calcd. $C_{13}H_{26}OSi$: C 68.96, H 11.57; found C 69.02, H 11.51.

(3*S,4*R**)-3-Isopropyl-1-trimethylsilyloct-1-yn-4-ol (8c):** From **7** (399 mg, 2 mmol) and isopropylmagnesium chloride (3 mL of a 2 N solution in ether). Yield: 310 mg, 65%. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.59 (m, 1 H), 2.23 (dd, 1 H, *J* = 4.48 Hz, *J* = 6.8 Hz), 1.85 (qd, 1 H), 1.78 (d, 1 H, *J* = 8.12 Hz), 1.6−1.3 (m,

6 H), 1.01 (dd, 6 H, J = 6.72 Hz, J = 11.6 Hz), 0.93 (t, 3 H, J = 6.84 Hz), 0.18 (s, 9 H). – ^{13}C NMR ($CDCl_3$/TMS, 50 MHz): δ = 105.23, 90.2, 70.75, 47.68, 35.81, 29.1, 28, 22.79, 21.48, 19.83, 14.14, 0.28.

Kinetic Resolution of Propargylic Oxiranes 1 and 7: To a solution of **1** (400 mg, 2 mmol) and **7** (400 mg, 2 mmol) in 15 mL of dry ether were added BF_3–Et_2O (1 mL, 8 mmol) and isopropylmagnesium chloride (6 mL of a 2 N solution in ether). at −80°C. The solution was vigorously stirred for 45 min at −80°C, then MeOH (2 equiv.) and Et_3N (2 equiv.) were added. The temperature increased to −40°C. After 10 min at this temperature the mixture was quenched with saturated aqueous NH_4Cl and the solution was allowed to warm to room temp. The mixture was extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with 1 N HCl, brine, dried with magnesium sulfate, filtered, and concentrated in vacuo. The residue was filtered on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford the unchanged propargylic oxirane **7** (300 mg, 75%), then the homopropargylic alcohol **3f** (360 mg, 75%).

***cis*-2-Butyl-3-ethynyloxirane (9):** To a solution of **1** (4.9 g, 25 mmol) in freshly distilled DMF (50 mL) were added KF (1.45 g, 25 mmol) and water (2 mL). The mixture was stirred at room temp. until the completion of the reaction (ca. 2 h). The mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with aqueous $Na_2S_2O_3$, brine, dried with magnesium sulfate, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford **9** (2.85 g, 92%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.43 (dd, 1 H, J = 1.83 Hz), 3.05 (m, 1 H), 2.36 (d, 1 H, J = 1.83 Hz), 1.75–1.40 (m, 6 H), 0.95 (t, 9 H, J = 7.25 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 77.32, 73.95, 58.35, 45.17, 29.35, 28.41, 22.90, 14.41.

***trans*-2-Butyl-3-ethynyloxirane (10):** To a solution of **7** (3 g, 15.2 mmol) in freshly distilled DMF (25 mL) were added KF (1.3 g, 23 mmol) and water (2 mL). The mixture was stirred at room temp. until completion of the reaction (ca. 4 h). The mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with brine, dried with magnesium sulfate, and filtered. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford **10** (1.77 g, 94%) as a colourless oil. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.11 (m, 2 H), 2.32 (d, 1 H, J = 1.5 Hz), 1.65–1.35 (m, 6 H), 0.93 (t, 3 H, J = 7.1 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 81.02, 72.11, 60.81, 45.28, 31.77, 28.09, 22.81, 14.34.

***cis*-2-Isopropyl-3-ethynyloxirane (11):** To a solution of **2** (7.6 g, 41.8 mmol) in freshly distilled DMF (200 mL) were added KF (2.7 g, 46 mmol) and water (40 mL). The mixture was stirred at room temp. until the completion of the reaction (ca. 4 h). The mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried with magnesium sulfate, filtered, and concentrated in vacuo. The solvents were removed by distillation under atmospheric pressure. The product was distilled under low pressure to afford **11** (3.86 g, 84%) as a pale yellow oil. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.44 (dd, 1 H, J = 1.8 Hz, J = 4.2 Hz), 2.72 (dd, 1 H, J = 4.4 Hz, J = 9.1 Hz), 2.35 (d, 1 H, J = 1.8 Hz), 1.70 (m, 1 H), 1.15 and 1.05 (d, 3 H, J = 6.8 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 78.96, 73.40, 63.40, 44.94, 29.13, 19.77, 18.08. – IR (film, KBr): $\tilde{\nu}$ = 3290 cm^{-1}, 2960, 2920, 2860, 2110, 1465, 1380, 1355, 1245.

General Procedure for the Preparation of Allenyl Bromides 13, 14, 15, and 16 from Propargylic Oxiranes: To a solution of propargylic oxirane (2 mmol) in Et_2O (1 mL) were added a mixture of HBr (240 μL of an aqueous 48% solution, 1.5 mmol), CuBr (286 mg, 2 mmol), NH_4Br (100 mg, 1 mmol), and Cu° at −20°C. The mixture was stirred at −5°C, the reaction was monitored by GC. The solution was quenched after 15 min with an aqueous solution of NH_4Cl/NH_3, extracted twice with Et_2O (2 × 20 mL), the combined organic layers were washed with aqueous NH_4Cl/NH_3, brine, dried with Na_2SO_4, and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford the allenyl bromide.

(2*S,4*R**)-1-Bromoocta-1,2-dien-4-ol (13):** From **9** (250 mg, 2 mmol). Yield: 285 mg, 70%. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.11 (dd, 1 H, J = 1.6 Hz, J = 5.6 Hz), 5.49 (t, 1 H, J = 5.76 Hz), 4.31 (m, 1 H), 1.60 (m, 2 H), 1.50–1.20 (m, 4 H), 0.93 (t, 3 H, J = 7 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 200.66, 104.69, 74.50, 69.39, 37.05, 27.76, 22.92, 14.30. – $C_8H_{13}OBr$: calcd. C 46.85, H 6.39; found C 46.79, H 6.42.

(2*R,4*R**)-1-Bromoocta-1,2-dien-4-ol (14):** From **10** (250 mg, 2 mmol). Yield: 290 mg, 71%. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.11 (dd, 1 H, J = 1.84 Hz, J = 5.98 Hz), 5.47 (t, 1 H, J = 5.8 Hz), 4.32 (m, 1 H), 1.75–1.30 (m, 6 H), 0.94 (t, 3 H, J = 6.84 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 200.84, 104.57, 76.07, 69.40, 36.93, 27.62, 22.71, 14.24. – $C_8H_{13}OBr$: calcd. C 46.85, H 6.39; found C 46.76, H 6.46.

(2*S,4*R**)-1-Bromo-5-methylhexa-1,2-dien-4-ol (15):** From **11** (220 mg, 2 mmol). Yield: 270 mg, 70%. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.10 (dd, 1 H, J = 2.00 Hz, J = 5.66 Hz), 5.46 (t, 1 H, J = 5.8 Hz), 4.07 (dt, 1 H, J = 1.75 Hz, J = 5.76 Hz), 1.79 (m, 1 H), 0.97 (d, 6 H, J = 6.81 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 50 MHz): δ = 201.3, 103.21, 74.85, 74.12, 34.45, 18.47, 17.92. – IR (film, KBr): $\tilde{\nu}$ = 3380 cm^{-1}, 2950, 1955, 1465, 1380, 1185.

(2*R,4*R**)-1-Bromo-5-methylhexa-1,2-dien-4-ol (16):** From **12** (220 mg, 2 mmol). Yield: 280 mg, 73%. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.12 (dd, 1 H, J = 1.52 Hz, J = 5.48 Hz), 5.45 (t, 1 H, J = 5.92 Hz), 4.10 (ddd, 1 H, J = 1.52 Hz, J = 5.68 Hz, J = 6.12 H), 1.83 (m, 1 H), 1.00 and 0.98 (d, 3 H, J = 4.36 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 201.37, 103.13, 74.60, 74.54, 34.52, 18.36, 18.10.

Reaction of Allenyl Bromide 13 with Methylcopper: Methyllithium (4.4 mmol, 2.5 mL of a 2 M solution in ether) was added to a slurry of CuCN (395 mg, 4.4 mmol) in dry Et_2O (20 mL). The mixture was allowed to warm to −10°C for 30 min. The mixture was then cooled to −80°C and **13** (235 mg, 1.1 mmol) in Et_2O (10 mL) was dropwise added. The solution was stirred for 15 min at −70°C and then allowed to warm to room temp. for 1 h. The mixture was quenched with an aqueous solution of NH_4Cl/NH_3, extracted twice with Et_2O (3 × 20 mL), the combined organic layers were washed with NH_4Cl/NH_3, brine, dried with magnesium sulfate, and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (90:10) as eluent to afford **8** and **17a** (108 mg, 77%) as a unseparable mixture.

(3*S,4*R**)-3-Methyloct-1-yn-4-ol (8):** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.45 (m, 1 H), 2.54 (m, 1 H), 2.12 (d, 1 H, J = 2.44 Hz), 1.7–1.2 (m, 6 H), 1.22 (d, 3 H, J = 7.04 Hz), 0.90 (t, 3 H, J = 7.3 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 85.31, 74.16, 71.02, 34.93, 32.97, 28.03, 22.75, 17.56, 14.15.

5-Hydroxynona-2,3-diene (17a): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.25 (m, 1 H), 5.17 (m, 1 H), 4.13 (m, 1 H), 1.70 (dd, 3 H, J = 3.3 Hz, J = 6.9 Hz), 1.6–1.3 (m, 6 H), 0.92 (t, 3 H, J = 6.6 Hz).

– ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 203.11, 95.24, 88.7, 70.25, 37.26, 27.67, 27.00, 22.75, 14.50.

6-Hydroxy-2-methyldeca-3,4-diene (17b): Isopropylmagnesium chloride (6.6 mmol, 3.3 mL of a 2 M solution in ether) was added at −80°C to a mixture of CuBr (10 mg, 0.33 mmol.) and **13** (233 mg, 1.1 mmol) in Et_2O (20 mL). The mixture was stirred for 2 h at −80°C and then allowed to warm to 0°C for 90 min. The mixture was quenched with an aqueous solution of NH_4Cl/NH_3, extracted twice with Et_2O (3 × 20 mL), the combined organic layers were washed with NH_4Cl/NH_3, brine, dried with magnesium sulfate, and the solvent removed in vacuo to afford **17b** (74 mg, 40%) as a yellow oil. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.33 (m, 1 H), 5.27 (m, 1 H), 4.13 (m, 1 H), 2.33 (m, 1 H), 1.6−1.3 (m, 6 H), 1.02 (d, 6 H, *J* = 6.6 Hz), 0.92 (t, 3 H, *J* = 6.8 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 202, 101.87, 97.76, 71.56, 38.15, 28.87, 28.63, 23.55, 23.41, 15.0.

(2*S,4*R**)-1-Bromo-4-(methoxymethoxy)octa-1,2-diene (18):** To a stirred solution of **13** (413 mg, 2 mmol) in *i*Pr_2NEt (2 mL) was added dropwise methoxymethyl chloride (293 mg, 3.6 mmol) at 5°C. The solution was allowed to warm to room temp. and was stirred for 5 h. After disappearance of the starting material, the resulting dark orange solution was hydrolyzed with 1 N HCl and extracted with ether (3 × 20 mL). The combined organic layers were washed with 1 N HCl, brine, dried with magnesium sulfate, filtered, and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (95:5) as eluent to afford **13** (91%, 453 mg) as a colourless oil. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.02 (d, 1 H, *J* = 5.6 Hz), 5.29 (dd, 1 H, *J* = 5.6 Hz, *J* = 7.4 Hz), 4.77 (d, 1 H, *J* = 7.4 Hz), 4.60 (d, 1 H, *J* = 6.8 Hz), 4.19 (dt, 1 H, *J* = 7.2 Hz, *J* = 6.7 Hz), 3.40 (s, 3 H), 1.70−1.30 (m, 6 H), 0.92 (t, 3 H, *J* = 6.9 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 202.42, 100.97, 94.51, 73.66, 73.03, 55.74, 35.21, 27.57, 22.57, 14.09. – IR (film, KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2925, 2870, 2105, 1725, 1455. – $C_{10}H_{17}O_2Br$: calcd, C 48.21, H 6.88; found C 48.31, H 6.78.

(2*R,4*R**)-1-Bromo-4-(methoxymethoxy)octa-1,2-diene (19):** To a stirred solution of **14** (860 mg, 4.2 mmol) in *i*Pr_2NEt (6 mL) under nitrogen was added dropwise methoxymethyl chloride (1 mL, 7.6 mmol) at 0°C. The solution was allowed to warm to room temp. and was stirred for 12 h. After disappearance of the starting material, the mixture was hydrolyzed with 1 N HCl and extracted with ether (3 × 20 mL). The combined organic layers were washed with 1 N HCl, brine, dried with magnesium sulfate, filtered, and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (95:5) as eluent to afford **19** (940 mg, 90%) as a colourless oil. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.06 (dd, 1 H, *J* = 1.04 Hz, *J* = 5.68 Hz), 5.30 (dd, 1 H, *J* = 5.8 Hz, *J* = 6.96 Hz), 4.75 (d, 1 H, *J* = 6.84 Hz), 4.60 (d, 1 H, *J* = 6.84 Hz), 4.23 (dt, 1 H, *J* = 6.16 Hz, *J* = 6.92 Hz), 3.40 (s, 3 H), 1.75−1.35 (m, 6 H), 0.93 (t, 3 H, *J* = 6.84 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 201.75, 101.57, 94.48, 73.52, 73.45, 55.63, 35.32, 27.46, 23.54, 14.07. – IR (film, KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2920, 2860, 2180, 1465, 1375, 1245. – $C_{10}H_{17}O_2Br$: calcd. C 48.21, H 6.88; found C 48.29, H 6.97.

(3*S,4*R**)-3-Methyl-4-(methoxymethoxy)oct-1-yne (20a):** Methyllithium (5 mmol, 3.33 mL of a 1.5 M solution in ether) was added to a suspension of CuCN (455 mg, 5 mmol) in Et_2O (10 mL). The mixture was allowed to warm to −35°C for 1 h. The mixture was then cooled to −80°C and **18** (250 mg, 1 mmol) in Et_2O (10 mL) was added dropwise. The solution was stirred for 1 h at −70°C and then allowed to warm to −55°C for 2 h. The mixture was quenched with an aqueous solution of NH_4Cl/NH_3, extracted twice with Et_2O (2 × 20 mL), the combined organic layers were washed with brine, dried with magnesium sulfate, and the solvent removed in vacuo to afford **20a** (175 mg, 95%) as a pale yellow oil. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.70 (s, 2 H), 3.53 (m, 1 H), 3.41, (s, 3 H), 2.76 (m, 1 H), 2.09 (d, 1 H, *J* = 2.48 Hz), 1.75−1.30 (m, 6 H), 1.22 (d, 3 H, *J* = 7.04 Hz), 0.92 (t, 3 H, *J* = 6.88 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 96.69, 86.39, 80.44, 70.06, 56.2, 31.49, 30.25, 28.36, 23.13, 16.42, 14.44. – IR (film, KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 2920, 2870, 2810, 2100, 1460, 1370, 1205. – $C_{11}H_{20}O_2$: calcd. C 71.69, H 10.94; found C 71.78, H 11.01.

(3*S,4*R**)-3-Isopropyl-4-(methoxymethoxy)oct-1-yne (20b):** To a solution of **18** (250 mg, 1 mmol) in Et_2O (10 mL) was added dropwise at −80°C isopropylmagnesium bromide (3 mmol, 1.8 mL of a 1.7 M solution in ether). The solution was allowed to warm slowly to 0°C. After 1 h at this temperature, the reaction was carried on at room temp. for 2 h. After disappearance of the starting material, the mixture was hydrolyzed with 1 N HCl and extracted with ether (3 × 20 mL). The combined organic layers were washed with 1 N HCl, brine, dried with $MgSO_4$, filtered, and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (95:5) as eluent to afford **20b** (191 mg, 90%) as a pale yellow oil. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.75 (d, 1 H, *J* = 7.08 Hz), 4.72 (d, 1 H, *J* = 7.08 Hz), 3.68 (dt, 1 H, *J* = 5.52 Hz, *J* = 11.4 Hz), 3.42 (s, 3 H), 2.28 (m, 1 H), 2.13 (d, 1 H, *J* = 2.52 Hz), 1.90 (m, 1 H), 1.70−1.20 (m, 6 H), 1.07 (d, 3 H, *J* = 6.7 Hz), 0.93 (t, 3 H, *J* = 7.12 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 96.33, 83.91, 77.45, 71.73, 56.19, 43.85, 32.48, 28.43, 27.71, 23.20, 21.65, 20.55, 14.41. – IR (film, KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 2950, 2920, 2860, 2810, 2105, 1465, 1380.

(3*S,4*R**)-3-Butyl-4-(methoxymethoxy)oct-1-yne (20c):** *n*-Butyllithium (5 mmol, 3.3 mL of a 1.6 N solution in hexane) was added to a mixture of CuCN (448 mg, 5 mmol) in Et_2O (15 mL). The mixture was allowed to warm to −35°C for 1 h. The mixture was then cooled to −80°C and **18** (248 mg, 1 mmol) in Et_2O (10 mL) was added dropwise. The solution was stirred for 1 h at −80°C. The mixture was quenched with an aqueous solution of NH_4Cl/NH_3, extracted twice with Et_2O (2 × 20 mL), the combined organic layers were washed with brine, dried with magnesium sulfate, and the solvent removed in vacuo to afford **20c** (215 mg, 95%) as a pale yellow oil. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.71 (d, 1 H, *J* = 7.08 Hz), 4.69 (d, 1 H, *J* = 7.08 Hz), 3.57 (m, 1 H), 3.39 (s, 3 H), 2.59 (m, 1 H), 2.10 (d, 1 H, *J* = 2.48 Hz), 1.80−1.25 (m, 12 H), 0.93 (m, 6 H). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 96.29, 84.99, 79.53, 70.53, 55.81, 36.16, 31.53, 30.03, 29.93, 28.16, 22.79, 22.63, 14.09. – IR (film, KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 2950, 2930, 2860, 2100, 1465, 1395, 1365.

(3*R,4*R**)-3-Methyl-4-(methoxymethoxy)oct-1-yne (21a):** methyllithium (60 mmol, 28.6 mL of a 2 M solution in ether) was added to a suspension of CuCN (4.64 g, 60 mmol) in Et_2O (50 mL). The mixture was allowed to warm to −35°C for 1 h. The mixture was then cooled to −80°C and **19** (3 g, 12 mmol) in Et_2O (20 mL) was added dropwise. The solution was stirred for 1 h at −70°C and then allowed to warm to −55°C for 2 h. The mixture was quenched with an aqueous solution of NH_4Cl/NH_3, extracted twice with Et_2O (2 × 20 mL), the combined organic layers were washed with brine, dried with magnesium sulfate, and the solvent removed in vacuo to afford **21a** (2 g, 91%) as a yellow oil. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.70 (s, 2 H), 3.46 (m, 1 H), 3.42 (s, 3 H), 2.78 (m, 1 H), 2.08 (d, 1 H, *J* = 2.48 Hz), 1.75−1.30 (m, 6 H), 1.19 (d, 3 H, *J* = 7.08 Hz), 0.92 (t, 3 H, *J* = 7.2 Hz). – ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 96.70, 86.62, 80.76, 69.93, 56.15, 31.19, 30.67, 27.89, 23.12, 17.28, 14.43. – IR (film, KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 2950, 2930, 2820, 2110, 1450, 1370, 1145.

(3*R,4*R**)-3-Isopropyl-4-(methoxymethoxy)oct-1-yne (21b):** To a solution of **19** (248 mg, 1 mmol) in Et_2O (10 mL) was added dropwise at −80°C isopropylmagnesium bromide (3 mmol, 1.9 mL of a 1.6 M solution in ether). After 1 h the solution was allowed to warm slowly to −10°C for 4 h. After disappearance of the starting material, the mixture was hydrolyzed with 1 N HCl and extracted with ether (3 × 20 mL). The combined organic layers were washed with 1 N HCl, brine, dried with $MgSO_4$, filtered, and the solvent removed in vacuo. The residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (95:5) as eluent to afford **21b** (177 mg, 83%) as a pale yellow oil. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.69 (AB system, 2 H, *J* = 7 Hz), 3.63 (m, 1 H), 3.42 (s, 3 H), 2.50 (m, 1 H), 2.09 (d, 1 H, *J* = 2.48 Hz), 1.93 (m, 1 H), 1.70−1.30 (m, 6 H), 1.03 and 1.00 (d, 3 H, *J* = 6.64 Hz), 0.93 (t, 3 H, *J* = 7.2 Hz). − ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ = 96.39, 83.55, 77.54, 71.96, 56.21, 43.90, 31.53, 27.95, 27.14, 23.85, 21.72, 19.71, 14.36. − IR (film, KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 2950, 2920, 2860, 2100, 1460, 1380, 1360, 1220. − calcd. $C_{11}H_{20}O_2$: C 75.53, H 11.39; found C 75.61, H 11.46.

Acknowledgments

Thanks are due to Pr. Alexandre Alexakis for many helpful discussions, and to Monique Baudry for the preparation of starting materials. CNRS (URA 476) is gratefully acknowledged for financial support, as well as Ministère de la Recherche for a grant (N.B.).

[1] E. J. Corey, E. J. Trybulski, L. S. Melvin, K. C. Nicolaou, J. A. Secrist, R. Lett, P. W. Sheldrake, J. R. Falck, D. J. Brunelle, M. F. Haslanger, S. Kim, S. Yoo, *J. Am. Chem. Soc.* **1978**, *100*, 4618.
[2] J. Inanaga, Y. Kawanami, M. Yamaguchi, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1521.
[3] H. Akita, H. Matsukura, T. Oishi, *Tetrahedron Lett.* **1986**, *27*, 5397
[4] J. S. Panek, T. Hu, *J. Org. Chem.* **1997**, *62*, 4914
[5] F. D′Aniello, A. Mann, M. Taddei, *J. Org. Chem.* **1996**, *61*, 4870; F. D′Aniello, A. Mann, A. Schoenfelder, M. Taddei, *Tetrahedron.* **1997**, *53*, 1447.
[6] T. Skrydstrup, M. Bénéchie, F. Khuong-Huu, *Tetrahedron Lett.* **1990**, *49*, 7145; M. Bénéchie, F. Khuong-Huu, *J. Org. Chem.* **1996**, *61*, 7133; M. Bénéchie, F. Khuong-Huu, *Synlett* **1992**, 266.
[7] R. Baker, R. H. O. Boyes, D. M. P. Broom, M. J. O′Mahony, C. J. Swain, *J. Chem. Soc., Perkin Trans. 1* **1987**, 1613; R. Baker, J. C. Head, C. J. Swain, *J. Chem. Soc., Perkin Trans. 1* **1988**, 85.
[8] J. P. Ferezou, M. Julia, Y. Li, L. W. Liu, A. Pancrazi, *Bull. Soc. Chim. Fr.* **1995**, *132*, 428.
[9] P. J. Garratt, "Alkylation of Alkynyl Carbanions", in: *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, *3*, 271.
[10] See for example: M. A. Adams, A. J. Duggan, J. Smolanoff, J. Meinwald *J. Am. Chem. Soc.* **1979**, *101*, 5364.
[11] M. Yamaguchi, I. Hirao *Tetrahedron Lett.* **1983**, *24*, 391.
[12] C. Semeyn, R. H. Blaauw, H. Hiemstra, W. N. Speckamp *J. Org. Chem.* **1997**, *62*, 3426.
[13] R. Epzstein, "The Formation and Transformations of Allenic and α-acetylenic Carbanions", in: *Comprehensive Carbanion Chemistry* (Eds.: E. Buncel, T. Durst), Elsevier, Amsterdam, **1984**; *B*, 107−175; H. Yamamoto, "Propargyl and Allenyl Organometallics", in: *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, London, **1991**; *2*, 81−98.
[14] G. Zweifel, G. Hahn, *J. Org. Chem.* **1984**, *49*, 4565; T. Harada, T. Katsuhira, A. Osada, K. Iwazaki, K. Maejima, A. Oku, *J. Am. Chem. Soc.* **1996**, *118*, 11377.
[15] J. A. Marshall, X. Wang, *J. Org. Chem.* **1990**, *55*, 6246; J. A. Marshall, X. Wang, *J. Org. Chem.* **1991**, *56*, 3211; J. A. Marshall, X. Wang, *J. Org. Chem.* **1992**, *57*, 1242; J. A. Marshall, J. Perkins, *J. Org. Chem.* **1994**, *59*, 3509.
[16] E. Favre, M. Gaudemar *J. Organomet. Chem.* **1975**, *92*, 17.
[17] P. Place, C. Vernière, J. Goré, *Tetrahedron* **1981**, *37*, 1359.
[18] M. Karila, M.-L. Capmau, W. Chodkiewicz, *C. R. Acad. Sci., Ser. C* **1969**, *269*, 342.
[19] M. Ishiguro, N. Ikeda, H. Yamamoto, *J. Org. Chem.* **1982**, *47*, 2225.
[20] R. W. Hoffmann, V. Giesen, M. Fuest, *Liebigs Ann. Chem.* **1993**, 629.
[21] M. Matsumoto, K. Kuroda, *Tetrahedon Lett.* **1980**, *21*, 4021; P. Pianetti, P. Rollin, J. R. Pougny, *Tetrahedron Lett.* **1986**, *27*, 5853.
[22] P. Kocienski, N. Dixon, *Synlett* **1989**, 52.
[23] L. M. Dollinger, A. R. Howell, *J. Org. Chem.* **1998**, *63*, 6782.
[24] A. Alexakis, I. Marek, J.-F. Normant, *Tetrahedron Lett.* **1989**, *30*, 2387; A. Alexakis, I. Marek, J.-F. Normant, *Tetrahedron* **1991**, *47*, 1677.
[25] B. M. Trost, J. M. Tour, *J. Org. Chem.* **1989**, *54*, 484.
[26] H. Kleijn, J. Meijer, G. C. Overbeek, P. Vermeer, *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 97.
[27] I. Minami, M. Yuhara, H. Watanabe, J. Tsuji *J. Organomet. Chem.* **1987**, *334*, 225; M. E. Piotti, H. Alper, *J. Org. Chem.* **1997**, *62*, 8484.
[28] P. R. Ortiz de Montellano, *J. Chem. Soc., Chem. Commun.* **1973**, 709; P. Vermeer, J. Meijer, C. de Graaf, H. Schreurs, *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 46; A. Doutheau, J. Sartoretti, J. Goré, *Tetrahedron* **1983**, *39*, 3059; C. A. Oehlschlager, E. Czyzewska, *Tetrahedron Lett.* **1983**, *24*, 5587; J. A. Marshall, K. Pinney *J. Org. Chem.* **1993**, *58*, 7180.
[29] N. Krause, D. Seebach, *Chem. Ber.* **1988**, *121*, 1315.
[30] F. Y. Perveev, N. I. Kudryashova, *Zhur. Obshch. Khim.* **1953**, *23*, 348; *Chem. Abstr.* **1954**, *48*, 2566d.
[31] F. Chemla, N. Bernard, J. Normant, *Tetrahedron Lett.* **1999**, *40*, 75.
[32] M. Yamaguchi, I. Hirao, *Tetrahedron Lett.* **1983**, *24*, 391; M. J. Eis, J. E. Wrobel, B. Ganem, *J. Am. Chem. Soc.* **1984**, *106*, 3693.
[33] A. A. Petrov, *Zhur. Obshch. Khim.* **1954**, *24*, 803.
[34] C. Mukai, Y. Sugimoto, Y. Ikeda, M. Hanaoka, *Tetrahedron Lett.* **1994**, *35*, 2183.
[35] R. W. Herr, C. R. Johnson, *J. Am. Chem. Soc.* **1970**, *92*, 4979.
[36] H. Imogaï, M. Larchevèque, *Tetrahedron: Asymmetry* **1997**, *8*, 965.
[37] A. Alexakis, D. Jachiet, J.F. Normant, *Tetrahedron* **1986**, *42*, 5607.
[38] F. D′Aniello, A. Mann, M. Taddei, C.-G. Wermuth, *Tetrahedron Lett.* **1994**, *35*, 7775.
[39] For general references, see: P. D. Landor, "Synthesis of allenes", in: *The Chemistry of the Allenes* (Ed.: S. R. Landor), Academic Press, London, **1982**, 83−88; H. F. Schuster, G. M. Coppola, *Allenes in Organic Synthesis*, John Wiley&Sons, New York, **1984**, 272−280.
[40] M. Montury, J. Goré, *Synth. Commun.* **1980**, *10*, 873.
[41] C. J. Elsevier, J. Meijer, G. Tadema, P. M. Stehouwer, H. J. T. Bos, P. Vermeer, *J. Org. Chem.* **1982**, *47*, 2194; C. J. Elsevier, P. Vermeer, A. Gedanken, W. Runge, *J. Org. Chem.* **1985**, *50*, 364.
[42] C. J. Elsevier, H. J. T. Bos, P. Vermeer, *J. Org. Chem.* **1984**, *49*, 379; A. M. Caporusso, C. Polizzi, J. Lardicci, *J. Org. Chem.* **1987**, *52*, 3920; J. D. Bunyak, H. P. Borate, G. W. Lamb, D. D. Khasnis, C. Husting, H. Isom, U. Siriwardane, *J. Org. Chem.* **1993**, *58*, 1325.
[43] K. S. Feldman, C. C. Mechem, L. Nader, *J. Am. Chem. Soc.* **1982**, *104*, 4011; T. A. Grese, K. D. Hutchinson, L. E. Overman, *J. Org. Chem.* **1993**, *58*, 2468.
[44] S. R. Landor, A. N. Patel, P. F. Whiter, P. M. Greaves, *J. Chem. Soc.* **1966**, 1223; S. R. Landor, B. Demetriou, R. J. Evans, R. Grzeskowiak, P. Davey, *J. Chem. Soc.* **1972**, 1995.
[45] However, this *syn* stereoselectivity was also reported to be not general: C. Elsevier, P. Vermeer, *J. Org. Chem.* **1984**, *49*, 1649.
[46] E. J. Corey, N. W. Boaz, *Tetrahedron Lett.* **1984**, *25*, 3055.
[47] For general references, see: S.R. Landor, "Reactions of allenes", in: *The Chemistry of the Allenes* (Ed.: S. R. Landor), Academic Press, London, **1982**, 241−244; H. F. Schuster, G. M. Coppola, *Allenes in Organic Synthesis*; John Wiley&Sons: New York, **1984**, 272−280.
[48] G. Linstrumelle, D. Michelot, *J. Chem. Soc., Chem. Commun.* **1975**, 561.
[49] D. K. Black, S. R. Landor, *J. Chem. Soc (C)* **1968**, 283; S. R. Landor, P. D. Landor, P. F. Whiter, *J. Chem. Soc., Perkin Trans. 1* **1977**, 1710.
[50] G. Linstrumelle, T. Jeffery-Luong, *Tetrahdron Lett.* **1980**, *21*, 5019.

[51] K. Ruitenberg, H. Kleijn, H. Westmijze, J. Meijer, P. Vermeer, *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 405.
[52] A. M. Caporusso, L. Lardicci, F. De Settimo, *Tetrahedron Lett.* **1986**, *27*, 1067.
[53] A. M. Caporusso, F. De Settimo, L. Lardicci, *Tetrahedron Lett.* **1985**, *26*, 5101.
[54] E. J. Corey, N. W. Boaz, *Tetrahedron Lett.* **1984**, *25*, 3059.
[55] A. M. Caporusso, C. Polizzi, L. Lardicci, *Tetrahedron Lett.* **1987**, *28*, 6073; C. Polizzi, C. Consoloni, L. Lardicci, A. M. Caporusso, *J. Organomet. Chem.* **1991**, *417*, 289.
[56] E. J. Corey, J. Kang, *J. Am. Chem. Soc.* **1981**, *103*, 4619; E. J. Corey, S. G. Pyne, A. I. Schafer, *Tetrahedron Lett.* **1983**, *24*, 3291; E. J. Corey, B. De, *J. Am. Chem. Soc.* **1984**, *106*, 2735; P. A. Bartlett, P. C. Ting, *J. Org. Chem.* **1986**, *51*, 2230.
[57] H. Westmijze, P. Vermeer, *Synthesis* **1979**, 390.
[58] J. M. Oostveen, H. Westmijze, P. Vermeer, *J. Org. Chem.* **1980**, *45*, 1158.
[59] M. Kalli, P. D. Landor, S. R. Landor, *J. Chem. Soc., Perkin Trans. 1* **1973**, 1347.
[60] F. D′Aniello, A. Mann, A. Schoenfeldre, M. Taddei, *J. Org. Chem.* **1996**, *61*, 9631.
[61] N. Bernard, F. Chemla, J. Normant, *Tetrahedron Lett.* **1999**, *40*, 1649.
[62] T. M. Bargar, R. M. Lett, P. L. Johnson, J. E. Hunter, C. P. Chang, D. J. Pernich, M. R. Sabol, M. R. Dick, *J. Agric. Food. Chem.* **1995**, *43*, 1044.
[63] Very recently, an enantioselective synthesis of propargylic oxiranes by oxidation of enynes was reported: G. Cao, Z. Wang, Y. Tu, Y. Shi, *Tetrahedron Lett.* **1998**, *39*, 4425.

Received February 25, 1999
[O99118]