Preparation of Propargylic Carbenoids and Reactions with Carbonyl Compounds − A Stereoselective Synthesis of Propargylic Halohydrins and Oxiranes[‡]

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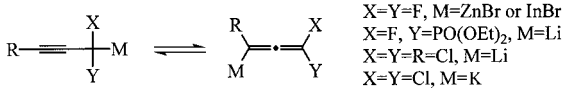
The preparation and the reactivity of the zincioallene **3** is described. This organometallic compound reacts with aldehydes to yield propargylic halohydrins with good diastereoselectivities. These halohydrins can easily be converted into propargylic oxiranes.

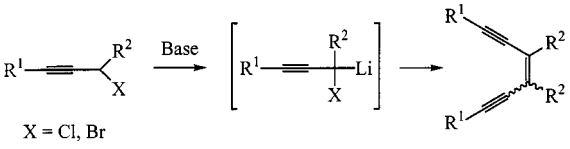
Introduction

Whereas much work concerning allenyl- and propargylmetal compounds has been done,[1,2] little is known concerning propargylic carbenoids. α,α-Difluoropropargylzinc[3,4] (Scheme 1, X = Y = F, M = ZnBr) and propargylindium[5,6] (Scheme 1, X = Y = F, M = InBr) carbenoids have been described, as have α,α-dichloropropargyllithium[7] (Scheme 1, X = Y = R = Cl, M = Li), α,α-dichloropropargylpotassium[8] (Scheme 1, X = Y = Cl, M = K), and lithiated α-fluoropropargylphosphonate[9] [Scheme 1, X = F, Y = $PO(OEt)_2$, M = Li].



Scheme 1

On the other hand, it has been shown that the simplest propargylic lithiocarbenoids[10−14] (Scheme 1, X = H or alkyl, Y = Cl or Br, M = Li), prepared by deprotonation of propargyl halides, display low thermal stabilities and undergo coupling to form enediynes (Scheme 2). This methodology has been applied in the synthesis of enediyne crown ethers.[15]



Scheme 2

[‡] Propargylic Carbenoids, 1

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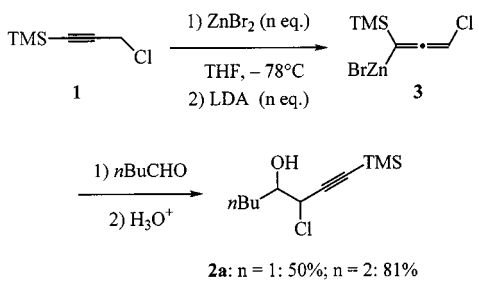
Results and Discussion

Preparation of Propargylic Chlorohydrins

We have recently shown that propargylic oxiranes are ideal substrates from which to prepare *syn*- or *anti*-1,2-disubstituted homopropargylic alcohols in stereospecific manner.[16] One possible preparation of these propargylic oxiranes might be by treatment of a propargylic carbenoid with an aldehyde, followed by ring closure, as has already been described in a similar approach involving propargylic ylides.[17−20] To circumvent the tendency of these carbenoids to undergo self-coupling, two possibilities can be envisaged. Deprotonation of propargyl halides in the presence of the electrophile (Barbier conditions) might be usable, but this method suffers from severe limitations in the choice of electrophile. On the other hand, it should be possible to trap the lithiocarbenoid in situ with a metal salt, to produce a new carbenoid with better thermal stability and lower reactivity. We chose zinc salts, because propargylic and allenic zinc compounds have afforded very good regioselectivities in their additions to aldehydes.[21,22]

Dropwise addition of LDA to an equimolar mixture of 3-chloro-1-trimethylsilylpropyne (**1**)[23,24] and zinc bromide in THF at −78 °C, followed by treatment with *n*-butanal, gave the corresponding desired halohydrin **2a** in 50% yield. To our pleasure, the use of 2 equiv. of both LDA and zinc bromide improved this yield to 81%[25] (Scheme 3).

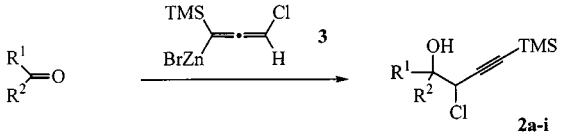


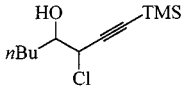
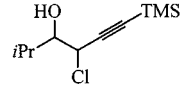
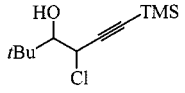
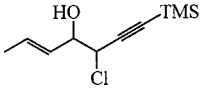
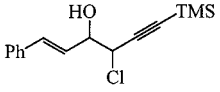
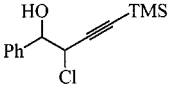
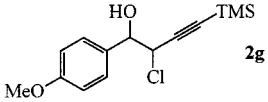
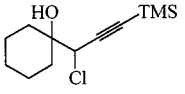
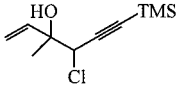
Scheme 3

  1434−193X/01/0917−3295 $ 17.50+.50/0

We tested the reactivity of this new carbenoid (which can best be represented as an allenic carbenoid **3**[26]). This zinc carbenoid displays good thermal stability; decomposition occurs only at or above −10 °C, giving a complex mixture of unidentified products. The reaction with aldehydes or ketones is very general, giving good yields of propargylic halohydrins, with no trace (by ^{1}H NMR) of the allenic regioisomer. Our results are summarized in Table 1.

Table 1. Preparation of propargylic chlorohydrins **2**



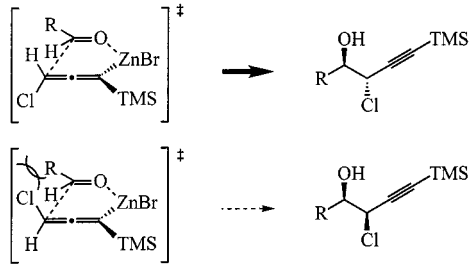
Entry	Chlorohydrin		Yield (%)	*anti* / *syn* ratio
1		**2a**	81	85 / 15
2		**2b**	75	95 / 5
3		**2c**	82	>98 / 2
4		**2d**	82	84 / 16
5		**2e**	75	80 / 20
6		**2f**	85	64 / 36
7		**2g**	85	63 / 37
8		**2h**	70	
9		**2i**	91	50 / 50

In the case of aliphatic aldehydes, the diastereoselectivity of the reaction shows a high tendency towards formation of *anti* isomers (Table 1, Entries 1−5). Less selectivity is observed with aromatic aldehydes (Table 1, Entries 6 and 7), as has also been observed for other allenic organometallic compounds.[1,2] Identification of the diastereomers was achieved by transformation of the chlorohydrins **2** (see below) into propargylic oxiranes **6** or **7** and comparison of the coupling constants of the two oxiranyl protons. However, it should be noted that the *dr* can be determined directly from the coupling constant between the propargylic proton and the one in α-position to the alcohol group, this constant being greater for the *syn* isomer than for the *anti* one (this also holds for the corresponding oxiranes) in all cases we examined. The values of these coupling constants are listed in Table 2.

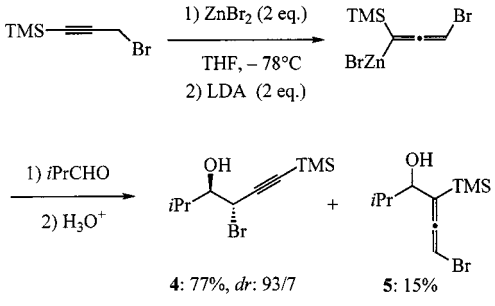
Table 2. Coupling constants $J(H_a\text{-}H_b)$ for *anti*- and *syn*-chlorohydrins **2a−g**

Entry	Halohydrin	*anti* / *syn* ratio	J_{anti} (Hz)	J_{syn} (Hz)
1	**2a**	85 / 15	4.1	6.5
2	**2b**	95 / 5	4.7	6.8
3	**2c**	>98/ 2	1.8	
4	**2d**	84 / 16	4.6	6.6
5	**2e**	80 / 20	4.2	6.5
6	**2f**	64 / 36	4.6	7.6
7	**2g**	63 / 37	4.9	7.4

The excellent diastereoselectivity of this reaction with aliphatic aldehydes[21,22] can be explained by a chelate-type transition state in which the allenyl moiety and the C=O bond are eclipsed (Scheme 4). In this transition state, the R group of the aldehyde and the chlorine atom adopt an *anti*-position, to minimize steric interactions. The stereoselectivity with aromatic aldehydes cannot be explained by this transition state. We are currently investigating this abnormal behavior.



Scheme 4

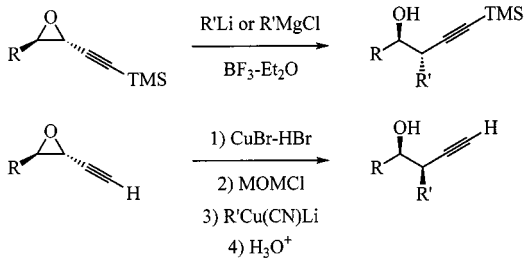


Scheme 5

Replacement of the chlorine atom in the allenyl moiety by a bromine atom was attempted, starting from 3-bromo-1-trimethylsilylpropyne.[23,24] Metalation of this reagent under the same conditions gave, after treatment with *i*PrCHO, the corresponding bromohydrin **4** in a similar yield (77%) and also with similar diastereoselectivity (*anti*/*syn* = 93:7). However, this product was accompanied by a small amount of a single diastereomer of the bromoallenyl regioisomer **5**, the relative configuration of which was not ascertained (Scheme 5). Owing to this lower regioselectivity, this approach was not subjected to further investigation.

Ring-Closure into Propargylic Oxiranes

Having in hand a good and stereoselective method for the preparation of propargylic chlorohydrins **2**, we then turned to their transformation into propargylic oxiranes. We have already described a diastereodivergent synthesis of homopropargylic alcohols,[16] and so we needed propargylic oxiranes *both protected and not protected* by TMS moieties on the acetylenic terminus (Scheme 6). Our goal, then, was to prepare both from chlorohydrins **2**.

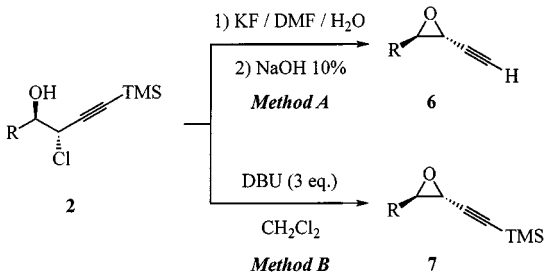


Scheme 6

The preparation of unprotected propargylic oxiranes **6** was achieved by protodesilylation (KF/DMF/H_2O), followed by a simple wash with aqueous NaOH (Table 3). It should be noted that, after the first step, a small amount (10−20%) of the propargylic oxirane is already present in the reaction mixture. Some oxiranes (those derived from chlorohydrins **2a**−**d** and **2i**) could not be obtained by this method, because of their low boiling points. This two-step protodesilylation/ring-closure process was completely stereospecific, the *anti*/*syn* ratio of the propargylic oxiranes **6** reflecting the *anti*/*syn* ratio of the starting chlorohydrins **2**.

In contrast, simple ring closure of the chlorohydrins **2** surprisingly proved very difficult to achieve. No reaction was observed on treatment variously with aqueous NaOH, K_2CO_3 in refluxing THF,[27] or NaH in THF. Treatment with LDA or *n*BuLi gave only mixtures of unidentified products. Finally, we found that on treatment with DBU (3 equiv.) in CH_2Cl_2, the desired ring closure to propargylic oxiranes **7** protected at the acetylenic position occurs smoothly, in excellent yields (Table 3). Again, this ring-closure reaction was totally stereospecific. The yield for the oxirane derived from chlorohydrin **2b** (Table 3, Entry 1) is underestimated, again because of its low boiling point.

Table 3. Conversion of chlorohydrins **2** into oxiranes **6** and **7**



Entry	Chlorohydrin	Method	Oxirane	Yield (%)
1	**2b**	A	**6b**	35
2	**2c**	B	**7c**	97
3	**2d**	B	**7d**	93
4	**2e**	A	**6e**	90
5		B	**7e**	98
6	**2f**	A	**6f**	95
7		B	**7f**	99
8	**2g**	A	**6g**	97
9		B	**7g**	94
10	**2h**	A	**6h**	74
11		B	**7h**	96
12	**2i**	B	**7i**	98

Conclusion

We report a stereoselective synthesis of propargylic chlorohydrins by preparation of a new allenylzinc carbenoid and its condensation with aldehydes or ketones. This methodology permits the formation of propargylic oxiranes in two high-yielding steps after ring closure. We are currently working on some other applications of this promising new carbenoid.

Experimental Section

General Remarks: Experiments involving organometallic compounds were carried out in dried glassware under a positive pressure of dry N_2. Liquid nitrogen was used as a cryoscopic fluid. A four-necked, round-bottomed flask equipped with an internal thermometer, a septum cap, a nitrogen inlet, and a mechanical stirrer was used. − THF was freshly distilled from sodium benzophenone ketyl prior to use. − Zinc bromide (98%) was purchased from Aldrich. It was melted under dry N_2 and, immediately after cooling to room temperature, was dissolved in anhydrous THF. − All other reagents and solvents were of commercial quality and were used without purification. − Flash column chromatographic separations were carried out on Merck silica gel 60 (0.015−0.040 mm). − ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker ARX 400 or AC 200 spectrometers. Chemical shifts are reported in δ relative to an internal standard of residual chloroform (δ = 7.27 for ^{1}H NMR and δ = 77.1 for ^{13}C NMR). − IR spectra were recorded with a Perkin−Elmer 1420 spectropho-

tometer. − Elemental analyses were performed by the Service de Microanalyses de l'Université Pierre et Marie Curie.

General Procedure 1. − Preparation of Chlorohydrins 2: 3-Chloro-1-trimethylsilyl-1-propyne (1 equiv.) was added at −20 °C to a 1 M solution of $ZnBr_2$ (2 equiv.) in THF. The resulting mixture was cooled to −80 °C, and a freshly prepared 1 M solution of lithium diisopropylamide (2 equiv.) in anhydrous THF was slowly added dropwise. The yellow mixture was stirred at −80 °C for 1 h, and the aldehyde (1 equiv.) was added in one portion. After further stirring for 1 h at −80 °C, the solution was allowed to warm to −20 °C, stirred for 45 min at this temperature, and then quenched with a 2:1 mixture of a saturated aqueous NH_4Cl solution and NH_3. After warming up to room temperature, the aqueous layer was extracted with Et_2O (three times). The combined organic layers were washed with water (twice) and brine, dried with anhydrous $MgSO_4$, and then concentrated to dryness in vacuo. The crude, oily product was purified by flash chromatography eluting with 10% ethyl acetate/cyclohexane to give chlorohydrins **2**.

(3*S,4*R**)-3-Chloro-1-(trimethylsilyl)oct-1-yn-4-ol (2a):** Prepared by general procedure 1, from butyraldehyde (0.145 mL, 2.00 mmol) in 81% yield (377 mg, 1.62 mmol); *anti*/*syn* = 85:15. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3450, 2950, 2890, 2170, 1250, 840 cm^{-1}. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.19 (s, 9 H), 0.92 (t, ^3J = 6.5 Hz, 3 H), 1.25−1.80 (m, 6 H), 2.43 (d, ^3J = 5.6 Hz, 1 H), 3.75 (m, 1 H), 4.45 (d, ^3J = 6.4 Hz, 1 H *syn*), 4.57 (d, ^3J = 4.1 Hz, 1 H *anti*). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.1, 14.0, 22.5, 27.8, 32.6, 54.4, 74.3, 93.6, 99.9.

(3*S,4*R**)-3-Chloro-5-methyl-1-(trimethylsilyl)hex-1-yn-4-ol (2b):** Prepared by general procedure 1, from isobutyraldehyde (0.180 mL, 2.00 mmol) in 75% yield (328 mg, 1.50 mmol); *anti*/*syn* = 95:5. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3460, 2950, 2920, 2875, 2170, 1245, 840 cm^{-1}. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.20 (s, 9 H), 0.98 (d, ^3J = 6.8 Hz, 3 H), 1.01 (d, ^3J = 6.8 Hz, 3 H), 1.99 (m, 1 H), 2.31 (d, ^3J = 5.0 Hz, 1 H, *syn*), 2.41 (d, ^3J = 5.2 Hz, 1 H, *anti*), 3.45 (m, 1 H), 4.60 (d, ^3J = 6.8 Hz, 1 H, *syn*), 4.63 (d, ^3J = 4.7 Hz, 1 H, *anti*). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.1, 16.2 (*syn*), 17.6 (*anti*), 19.3 (*anti*), 19.8 (*syn*), 30.5 (*syn*), 30.9 (*anti*), 52.2 (*anti*), 54.1 (*syn*), 79.3, 93.8, 99.8. − $C_{10}H_{19}ClOSi$ (218.80): calcd. C 54.89, H 8.75; found C 54.90, H 8.77.

(3*S,4*R**)-3-Chloro-5,5-dimethyl-1-(trimethylsilyl)hex-1-yn-4-ol (2c):** Prepared by general procedure 1, from pivaldehyde (173 mg, 2.00 mmol) in 82% yield (381 mg, 1.50 mmol); *anti*/*syn* > 98:2. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3550, 2950, 2895, 2170, 1475, 1250, 840 cm^{-1}. − ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.10 (s, 9 H), 0.94 (s, 9 H), 2.32 (s, 1 H), 3.44 (d, ^3J = 1.8 Hz, 1 H), 4.73 (d, ^3J = 1.8 Hz, 1 H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.1, 26.8, 36.1, 52.0, 82.9, 96.3, 100.3. − $C_{11}H_{21}ClOSi$ (232.82): calcd. C 56.75, H 9.09; found C 56.88, H 9.16.

(3*S,4*R**)-3-Chloro-1-(trimethylsilyl)hept-5-en-1-yn-4-ol (2d):** Prepared by general procedure 1, from crotonaldehyde (0.235 mL, 2.85 mmol) in 82% yield (506 mg, 2.34 mmol); *anti*/*syn* = 84:16. Pale yellow oil. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.20 (s, 9 H, *syn*), 0.21 (s, 9 H *anti*), 1.78 (d, ^3J = 6.6 Hz, 3 H), 2.30 (d, ^3J = 7.6 Hz, 1 H, *anti*), 2.43 (d, ^3J = 4.6 Hz, 1 H, *syn*), 4.24−4.32 (m, 1 H), 4.45 (d, ^3J = 6.6 Hz, 1 H, *syn*), 4.58 (d, ^3J = 4.6 Hz, 1 H, *anti*), 5.55−5.69 (m, 1 H), 5.84−5.87 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 18.2, 54.2 (*syn*), 54.3 (*anti*), 75.4 (*anti*), 75.9 (*syn*), 94.1 (*syn*), 94.4 (*anti*), 99.3 (*anti*), 100.4 (*syn*), 128.0 (*syn*), 128.2 (*anti*), 131.1 (*anti*), 131.3 (*syn*). − $C_{10}H_{17}ClOSi$ (216.78): calcd. C 55.41, H 7.90; found C 55.52, H 8.07.

(3*R,4*S**)-4-Chloro-1-phenyl-6-(trimethylsilyl)hex-1-en-5-yn-3-ol (2e):** Prepared by general procedure 1, from (*E*)-cinnamaldehyde (0.250 mL, 2.00 mmol) in 75% yield (418 mg, 1.50 mmol); *anti*/*syn* = 80:20. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3400, 3070, 3050, 3020, 2950, 2890, 2170, 1660, 1490, 1250, 840 cm^{-1}. − ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.14 (s, 9 H, *syn*), 0.16 (s, 9 H, *anti*), 2.65 (s, 1 H, *anti*), 2.80 (s, 1 H, *syn*), 4.40−4.50 (m, 1 H), 4.51 (d, ^3J = 6.5 Hz, 1 H, *anti*), 4.64 (d, ^3J = 4.2 Hz, 1 H, *syn*), 6.29 (dd, ^3J = 6.0 and 15.9 Hz, 1 H, *syn*), 6.30 (dd, ^3J = 6.0 and 15.9 Hz, 1 H, *anti*), 6.70 (dd, ^3J = 1.0 and 16.0 Hz, 1 H, *anti*), 6.75 (dd, ^3J = 1.0 and 16.0 Hz, 1 H, *syn*), 7.28−7.40 (m, 5 H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.2, 54.0 (*anti*), 54.1 (*syn*), 75.1 (*anti*), 75.6 (*syn*), 94.2 (*syn*), 94.6 (*anti*), 99.6 (*anti*), 100.0 (*syn*), 125.9 (*anti*), 126.1 (*syn*), 126.8, 128.2, 128.7, 133.8 (*syn*), 136.3 (*anti*). − $C_{15}H_{19}ClOSi$ (252.81): calcd. C 64.61, H 6.87; found C 64.61, H 6.79.

(3*S,4*R**)-3-Chloro-4-phenyl-1-(trimethylsilyl)but-1-yn-4-ol (2f):** Prepared by general procedure 1, from benzaldehyde (0.290 mL, 2.85 mmol) in 85% yield (608 mg, 2.41 mmol); *anti*/*syn* = 64:36. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3420, 3080, 3060, 3020, 2960, 2890, 2180, 1450, 1250 cm^{-1}. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.13 (s, 9 H, *syn*), 0.20 (s, 9 H, *anti*), 2.85 (d, ^3J = 4.6 Hz, 1 H, *anti*), 2.93 (d, ^3J = 3.0 Hz, 1 H, *syn*), 4.63 (d, ^3J = 7.6 Hz, 1 H, *syn*), 4.72 (d, ^3J = 4.6 Hz, 1 H, *anti*), 4.86 (dd, ^3J = 3.0 and 7.6 Hz, 1 H, *syn*), 4.93 (t, ^3J = 4.6 Hz, 1 H, *anti*), 7.37−7.50 (m, 5 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.2, 54.2 (*anti*), 55.6 (*syn*), 76.7, 94.5 (*syn*), 94.8 (*anti*), 99.4 (*anti*), 100.0 (*syn*), 127.1 (*syn*), 127.4 (*anti*), 128.3, 128.7, 138.4 (*syn*), 138.5 (*anti*). − $C_{13}H_{17}ClOSi$ (252.81): calcd. C 61.76, H 6.78; found C 62.20, H 7.00.

(3*S,4*R**)-3-Chloro-4-(4-methoxyphenyl)-1-(trimethylsilyl)but-1-yn-4-ol (2g):** Prepared by general procedure 1, from *p*-methoxybenzaldehyde (272 mg, 2.00 mmol) in 85% yield (458 mg, 1.70 mmol); *anti*/*syn* = 63:37. Viscous yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3440, 2990, 2980, 2950, 2170, 1610, 1510, 1245 cm^{-1}. − ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.10 (s, 9 H, *syn*), 0.17 (s, 9 H, *anti*), 2.79 (d, ^3J = 4.0 Hz, 1 H, *anti*), 2.90 (d, ^3J = 3.0 Hz, 1 H, *syn*), 3.80 (s, 3 H), 4.55 (d, ^3J = 7.4 Hz, 1 H, *syn*), 4.63 (d, ^3J = 4.9 Hz, 1 H, *anti*), 4.76 (dd, ^3J = 2.5 and 7.4 Hz, 1 H, *syn*), 4.84 (t, ^3J = 4.4 Hz, 1 H, *anti*), 6.87 (dd, ^3J = 8.4, ^{5}J = 1.5 Hz, 2 H), 7.37 (dd, ^3J = 8.4, ^5J = 1.5 Hz, 2 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.2, 54.3 (*anti*), 55.4, 55.5 (*syn*), 76.3 (*anti*), 77.1 (*syn*), 94.2 (*syn*), 94.4 (*anti*), 99.7 (*anti*), 100.2 (*syn*), 113.6, 128.4 (*anti*), 128.6 (*syn*), 130.7, 130.8, 159.8, 159.9 − $C_{14}H_{19}ClO_2Si$ (282.84): calcd. C 59.45, H 6.77; found C 59.50, H 6.86.

1-[1-Chloro-3-(trimethylsilyl)prop-2-ynyl]cyclohexanol (2h): Prepared by general procedure 1, from cyclohexanone (196 mg, 2.00 mmol) in 70% yield (342 mg, 1.40 mmol). Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3440, 2930, 2850, 2170, 1445, 1245 cm^{-1}. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.21 (s, 9 H), 1.55−1.85 (m, 10 H), 1.90 (s, 1 H), 4.48 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.0, 21.8, 22.0, 25.9, 32.9, 34.0, 60.1, 73.8, 93.9, 100.8. − $C_{12}H_{21}ClOSi$ (244.83): calcd. C 58.87, H 8.65; found C 58.84, H 8.70.

4-Chloro-3-methyl-6-(trimethylsilyl)hex-1-en-5-yn-3-ol (2i): Prepared by general procedure 1, from methyl vinyl ketone (210 mg, 3.00 mmol) in 91% yield (591 mg, 2.73 mmol); *dr*: 50:50. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3450, 3180, 2950, 2890, 2170, 1250, 840 cm^{-1}. − ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.19 (s, 9 H), 1.47 (s, 9 H), 2.40 and 2.44 (2 × s, 1 H), 4.47 and 4.51 (2 × s, 1 H), 5.27 (t, ^3J = 10.9 Hz, 1 H, for one diastereomer), 5.45 (dd, ^3J =

9.2 and 17.2 Hz, for one diastereomer), 6.04 and 6.17 (2 × dd, ^3J = 10.8 and 17.2 Hz, 1 H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.0, 23.9, 25.1, 58.5, 58.9, 75.4, 75.7, 94.1, 94.3, 100.5, 115.8, 139.8, 140.1.

(3*S,4*R**)-3-Bromo-5-methyl-1-(trimethylsilyl)hex-1-yn-4-ol (4):** 3-Bromo-1-trimethylsilyl-1-propyne (380 mg, 2 mmol) was added at −20 °C to a suspension of $ZnBr_2$ (1 M in THF, 2 mL, 2 mmol). The mixture was cooled to −80 °C and a freshly prepared solution of lithium diisopropylamide (1 M in THF, 2 mL, 2 mmol) was slowly added dropwise. The yellow solution was stirred at −80 °C for 1 h and isobutyraldehyde (0.090 mL, 1.00 mmol) was added in one portion. After further stirring for 1 h at −80 °C, the solution was allowed to warm to −20 °C, stirred for 1 h at this temperature, and then quenched with a 2:1 mixture of a saturated aqueous NH_4Cl solution and NH_3 (20 mL). After warming up to room temperature, the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with water and brine, and dried with anhydrous $MgSO_4$. Concentration to dryness in vacuo afforded a mixture of bromohydrin **4** and allenyl bromide **5** as a pale yellow oil.

Compound 4: (394 mg, 0.77 mmol), 77% yield; *anti*/*syn* = 93:7. − IR (NaCl film): $\tilde{\nu}$ = 3450, 2950, 2890, 2860, 2170, 1465 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.20 (s, 9 H), 1.00 (d, ^3J = 6.7 Hz, 3 H), 1.04 (d, ^3J = 6.7 Hz, 3 H), 2.00 (m, 1 H), 2.30 (d, ^3J = 5.2 Hz, 1 H), 3.50 (m, 1 H), 4.60 (d, ^3J = 6.2 Hz, 1 H, *syn*), 4.70 (d, ^3J = 4.4 Hz, 1 H, *anti*). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.1, 18.1, 19.7, 31.8, 42.0, 79.7, 95.1, 100.4.

Compound 5: (75 mg, 0.15 mmol), 15% yield. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.00 (s, 9 H), 0.95 (d, ^3J = 6.8 Hz, 3 H), 1.01 (d, ^3J = 6.8 Hz, 3 H), 1.83 (m, 1 H), 4.05 (m, 1 H), 5.94 (d, ^3J = 1.6 Hz, 1 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.7, 16.4, 20.4, 34.0, 42.0, 72.2, 75.6, 113.4, 201.6.

General Procedure 2. − Preparation of Desilylated Oxiranes 6: KF (1.2 equiv.) and 4 drops of water were added successively at room temperature to a 0.3 M solution of chlorohydrins **2** in DMF. The mixture was stirred for 1 h at this temperature until completion of the reaction, and was then quenched with a saturated aqueous NH_4Cl solution. The aqueous phase was extracted with Et_2O (three times) and the combined organic layers were stirred for 1 h with a 10% aqueous NaOH solution (20 mL). The layers were separated and the ethereal layer was washed with brine, dried with anhydrous $MgSO_4$, and then concentrated in vacuo to afford desilylated oxiranes **6**.

(2*R,3*R**)-2-Ethynyl-3-isopropyloxirane (6b):** Prepared by general procedure 2, from chlorohydrin **2b** (6.57 g, 25 mmol) in 35% yield (1.67 g, 8.75 mmol) after distillation of the crude product; *trans*/*cis* > 98:2. Colorless oil. − IR (NaCl film): $\tilde{\nu}$ = 3290, 2960, 2920, 2860, 2120, 1465, 1380, 1360, 1280, 1230 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.00 (d, ^3J = 6.7 Hz, 3 H), 1.04 (d, ^3J = 6.7 Hz, 3 H), 1.55 (m, 1 H), 2.32 (d, ^3J = 1.7 Hz, 1 H), 2.93 (dd, ^3J = 2.3 and 6.8 Hz, 1 H), 3.15 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 18.4, 19.0, 30.7, 44.3, 65.8, 50.9, 72.0, 81.1

(2*R,3*R**)-2-Ethynyl-3-(2-styryl)oxirane (6e):** Prepared by general procedure 2, from chlorohydrin **2e** (278 mg, 1.00 mmol) in 90% yield (153 mg, 0.90 mmol); *trans*/*cis* = 80:20. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3290, 3090, 3050, 3020, 2920, 2840, 2115, 1445 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.44 (d, ^3J = 1.7 Hz, 1 H, *trans*), 2.48 (d, ^3J = 1.6 Hz, 1 H, *cis*), 3.38 (t, ^3J = 1.8 Hz, 1 H), 3.70 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1 H), 5.85 (dd, ^3J = 7.7 and 13.1 Hz, 1 H, *trans*), 6.20 (dd, ^3J = 8.1 and 16.0 Hz, 1 H, *cis*), 6.80 (d, ^3J = 16.0 Hz, 1 H), 7.25−7.52 (m, 5 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 46.8 (*cis*), 47.4 (*trans*), 58.4 (*cis*), 60.4 (*trans*), 73.0 (*trans*), 74.7 (*cis*), 78.9 (*cis*), 80.1 (*trans*), 123.5 (*cis*), 124.6 (*trans*), 126.7, 128.7, 129.0 (*cis*), 135.9, 136.1 (*trans*), 137.7 (*cis*).

(2*R,3*R**)-3-Ethynyl-2-phenyloxirane (6f):** Prepared by general procedure 2, from chlorohydrin **2f** (253 mg, 1.00 mmol) in 95% yield (137 mg, 0.95 mmol); *trans*/*cis* = 62:38. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3290, 2960, 2920, 2860, 2120, 1110 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.25 (d, ^3J = 1.7 Hz, 1 H, *cis*), 2.42 (d, ^3J = 1.8 Hz, 1 H, *trans*), 3.36 (t, ^3J = 1.8 Hz, 1 H, *trans*), 3.76 (dd, ^3J = 4.0, ^4J = 1.6 Hz, 1 H, *cis*), 4.06 (d, ^3J = 1.8 Hz, 1 H, *trans*), 4.12 (d, ^3J = 4.0 Hz, 1 H, *cis*), 7.30−7.50 (m, 5 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 48.3 (*cis*), 49.3 (*trans*), 59.0 (*cis*), 60.2 (*trans*), 72.7 (*trans*), 75.1 (*cis*), 78.0 (*cis*), 80.3 (*trans*), 126.0 (*cis*), 127.3 (*trans*), 128.3, 129.0 (*cis*), 129.2 (*trans*), 134.9 (*cis*), 135.8 (C *trans*).

(2*R,3*R**)-3-Ethynyl-2-(4-methoxyphenyl)oxirane (6g):** Prepared by general procedure 2, from chlorohydrin **2g** (175 mg, 0.62 mmol) in 97% yield (111 mg, 0.60 mmol); *trans*/*cis* = 60:40. Pale yellow oil. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.28 (d, ^3J = 1.8 Hz, 1 H, *cis*), 2.42 (d, ^3J = 1.6 Hz, 1 H, *trans*), 3.36 (t, ^3J = 1.6 Hz, 1 H, *trans*), 3.75 (dd, ^3J = 3.8, ^4J = 1.6 Hz, 1 H, *cis*), 3.82 (s, 3 H, *trans*), 3.83 (s, 3 H, *cis*), 4.02 (d, ^3J = 2.0 Hz, 1 H, *trans*), 4.08 (d, ^3J = 3.8 Hz, 1 H, *cis*), 6.91 (m, 2 H), 7.20 (dd, ^3J = 6.6, ^5J = 2.0 Hz, 2 H, *trans*), 7.36 (d, ^3J = 8.7 Hz, 2 H, *cis*). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 48.3 (*cis*), 49.1 (*trans*), 55.5 (*cis*), 55.6 (*trans*), 58.8 (*cis*), 60.0 (*trans*), 49.3 (*trans*), 59.0 (*cis*), 60.2 (*trans*), 72.6 (*trans*), 75.1 (*cis*), 78.6 (*cis*), 80.4 (*trans*), 113.8 (*cis*), 114.4 (*trans*), 126.1 (*cis*), 127.3 (C *trans*), 127.6 (*trans*), 128.5 (*cis*), 160.2 (*cis*), 160.4 (*trans*).

(1*R,2*R**)-2-Ethynyl-1-oxaspiro[2.5]octane (6h):** Prepared by general procedure 2, from chlorohydrin **2h** (245 mg, 1.00 mmol) in 74% yield (101 mg, 0.74 mmol). Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3300, 2940, 2910, 2815, 2110, 1445 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.80−1.30 (m, 10 H), 2.30 (d, ^3J = 1.7 Hz, 1 H), 3.11 (d, ^3J = 1.7 Hz, 1 H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 24.5, 24.8, 25.1, 30.6, 33.9, 50.9, 64.6, 73.3, 79.3.

General Procedure 3. − Preparation of Silylated Oxiranes 7: DBU (3 equiv.) was added at room temperature to a 0.2 M solution of chlorohydrins **2** in dry CH_2Cl_2. After the reaction mixture had been stirred at this temperature for 1 h, CH_2Cl_2 was added and the mixture was quenched with aqueous 1 M HCl. The aqueous layer was extracted with CH_2Cl_2 (twice) and the combined organic layers were washed with brine and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo. The residue was then purified by flash chromatography, eluting with 5% ethyl acetate/cyclohexane, to afford silylated oxiranes **7**.

(2*R,3*R**)-2-*tert*-Butyl-3-(trimethylsilylethynyl)oxirane (7c):** Prepared by general procedure 3, from chlorohydrin **2c** (232 mg, 1.00 mmol) in 97% yield (190 mg, 0.97 mmol); *trans*/*cis* > 98:2. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 2950, 2900, 2860, 2170, 1475, 1460, 1420, 1385, 1360, 1320, 1245, 1050, 825 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.18 (s, 9 H), 0.93 (s, 9 H), 2.92 (d, ^3J = 2.3 Hz, 1 H), 3.20 (d, ^3J = 2.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.0, 25.8, 31.2, 43.0, 68.5, 89.1, 92.8, 102.7.

(2*S,3*R**)-2-(Prop-1-enyl)-3-(trimethylsilylethynyl)oxirane (7d):** Prepared by general procedure 3, from chlorohydrin **2d** (112 mg, 0.52 mmol) in 93% yield (86 mg, 0.48 mmol); *trans*/*cis* = 83:17. Yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3080, 3050, 3020, 2950, 2920, 2840, 2170, 1445, 1245, 1035, 840 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 200 MHz):

δ = 0.17 (s, 9 H, *trans*), 0.19 (s, 9 H, *cis*), 1.75 (dd, ^3J = 1.9 and 5.0 Hz, 3 H, *trans*), 1.82 (dd, ^3J = 1.9 and 4.9 Hz, 3 H, *cis*), 3.23 (d, ^3J = 2.0 Hz, 1 H, *trans*), 3.46 (dd, ^3J = 3.9 and 8.3 Hz, 1 H, *cis*), 3.48 (dd, ^3J = 2.0 and 5.9 Hz, 1 H, *trans*), 3.56 (d, ^3J = 3.9 Hz, 1 H, *cis*), 5.10 (m, 1 H, *trans*), 5.42 (m, 1 H, *cis*), 6.00 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.3, 17.9 (*trans*), 18.2 (*cis*), 46.6 (*cis*), 47.2 (*trans*), 58.2 (*cis*), 60.4 (*trans*), 89.7, 101.4, 101.2 (*trans*), 125.4 (*cis*), 126.8 (*trans*), 133.4 (*trans*), 134.7 (*cis*).

(2*R,3*R**)-2-(2-Styryl)-3-(trimethylsilylethynyl)oxirane (7e):** Prepared by general procedure 3, from chlorohydrin **2e** (140 mg, 0.50 mmol) in 98% yield (118 mg, 0.49 mmol); *trans*/*cis*: 80:20. Yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3080, 3050, 3020, 2950, 2920, 2840, 2170, 1445, 1245, 1035, 840 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.17 (s, 9 H), 3.32 (d, ^3J = 2.0 Hz, 1 H, *trans*), 3.58 (d, ^3J = 4.0 Hz, 1 H, *cis*), 3.65 (dd, ^3J = 2.0 and 7.7 Hz, 1 H, *trans*), 5.79 (dd, ^3J = 7.7 and 16.0 Hz, 1 H, *trans*), 6.14 (dd, ^3J = 7.8 and 16.0 Hz, 1 H, *cis*), 6.78 (d, ^3J = 16.0 Hz, 1 H, *trans*), 6.83 (d, ^3J = 16.0 Hz, 1 H, *cis*), 7.15−7.40 (m, 5 H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 0.3, 47.1 (*cis*), 47.7 (*trans*), 58.3 (*cis*), 60.6 (*trans*), 90.1 (*trans*), 92.8 (*cis*), 100.0 (*cis*), 101.2 (*trans*), 124.7, 128.4, 128.7, 128.0 (*trans*), 135.6 (*trans*), 135.8 (*cis*).

(2*R,3*R**)-2-Phenyl-3-(trimethylsilylethynyl)oxirane (7f):** Prepared by general procedure 3, from chlorohydrin **2f** (2.50 g, 10.00 mmol) in 99% yield (2.14 g, 9.91 mmol); *trans*/*cis* = 62:38. Colorless oil. − IR (NaCl film): $\tilde{\nu}$ = 2950, 2170, 1450, 1245 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.08 (s, 9 H, *cis*), 0.24 (s, 9 H, *trans*), 3.36 (d, ^3J = 2.0 Hz, 1 H, *trans*), 3.70 (d, ^3J = 4.0 Hz, 1 H, *cis*), 4.05 (d, ^3J = 2.0 Hz, 1 H, *trans*), 4.12 (d, ^3J = 4.0 Hz, 1 H, *cis*), 7.25−7.50 (m, 5 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.1, 48.7 (*cis*), 49.9 (*trans*), 59.4 (*cis*), 60.5 (*trans*), 90.1 (*trans*), 92.5 (*cis*), 99.9 (*cis*), 101.5 (*trans*), 125.9, 127.4 (*cis*), 128.0 (*trans*), 128.9 (*cis*), 129.0 (*trans*), 132.6 (*cis*), 135.9 (*trans*).

(2*R,3*R**)-2-(4-Methoxyphenyl)-3-(trimethylsilylethynyl)oxirane (7g):** Prepared by general procedure 3, from chlorohydrin **2g** (231 mg, 0.81 mmol) in 94% yield (188 mg, 0.76 mmol); *trans*/*cis* = 63:37. Colorless oil. − IR (NaCl film): $\tilde{\nu}$ = 3005, 2950, 2890, 2830, 2170, 1610, 1510, 1460, 1250 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.10 (s, 9 H, *cis*), 0.22 (s, 9 H, *trans*), 3.34 (d, ^3J = 2.0 Hz, 1 H, *trans*), 3.71 (d, ^3J = 4.0 Hz, 1 H, *cis*), 3.82 (s, 3 H, *trans*), 3.84 (s, 3 H, *cis*), 4.00 (d, ^3J = 2.0 Hz, 1 H, *trans*), 4.07 (d, ^3J = 4.0 Hz, 1 H, *cis*), 6.90 (d, ^3J = 8.7 Hz, 2 H, *trans*), 6.91 (d, ^3J = 8.7 Hz, 2 H, *cis*), 7.20 (d, ^3J = 8.7 Hz, 2 H, *trans*), 7.36 (d, ^3J = 8.7 Hz, 2 H, *cis*). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 48.9 (*cis*), 49.7 (*trans*), 55.6 (*trans*), 55.8 (*cis*), 59.5 (*cis*), 60.5 (*trans*), 90.0 (*trans*), 92.8 (*cis*), 100.4 (*cis*), 101.7 (*trans*), 113.7 (*cis*), 114.3 (*trans*), 126.5 (*cis*), 127.3 (*trans*), 129.0 (*cis*), 132.5 (*trans*), 160.3 (*cis*), 160.4 (*trans*).

2-(Trimethylsilylethynyl)-1-oxaspiro[2.5]octane (7h): Prepared by general procedure 3, from chlorohydrin **2h** (220 mg, 1.00 mmol) in 96% yield (200 mg, 0.96 mmol). Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 2930, 2850, 2170, 1445, 1295, 1045, 840 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.01 (s, 9 H), 1.31−1.60 (m, 10 H), 3.00 (d, ^3J = 4.4 Hz, 1 H), 3.20 (d, ^3J = 2.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 24.9, 25.2, 25.5, 31.0, 34.4, 51.9, 65.2, 90.9, 101.3.

2-Methyl-3-(trimethylsilylethynyl)-2-vinyloxirane (7i): Prepared by general procedure 3, from chlorohydrin **2i** (215 mg, 1.00 mmol) in 98% yield (176 mg, 0.98 mmol); *dr*: 55:45. Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 3080, 2950, 2920, 2890; 2850, 2170, 1440, 1410, 1375, 1245, 840 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.00 (s, 9 H), 1.29 (s, 3 H, *maj.*), 1.39 (s, 3 H, *min.*), 3.10 (s, 1 H, *min.*), 3.32 (s, 1 H, *maj.*), 5.07 (d, ^3J = 10.8 Hz, 1 H, *maj.*), 5.19−5.26 (m, 2 H, *min.* and 1 H, *maj.*), 5.43 (dd, ^3J = 10.8 and 17.6 Hz, 1 H, *min.*), 5.69 (dd, ^3J = 10.8 and 17.6 Hz, 1 H, *maj.*). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 0.0, 16.8 (*min.*), 19.5 (*maj.*), 53.3, 61.8, 92.0, 100.5, 117.9 (*min.*), 119.6 (*maj.*), 136.4 (*maj.*), 138.5 (*min.*).

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