JOC The Journal of Organic Chemistry

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Three-Carbon Homologation of Diorganozincs with Lithiated Acetylenic Epoxides

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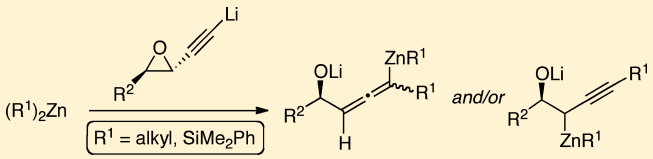
Supporting Information

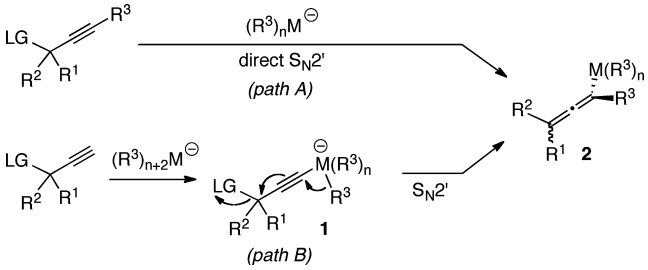
ABSTRACT: Reaction of dialkylzincs with lithiated acetylenic epoxides is described to give zincates that undergo a 1,2-metallate rearrangement by an *anti*-S_N2' pathway. This rearrangement occurs with the transfer of an alkyl or a silyl group affording allenylzinc intermediates. Allenic and/or homopropargylic alcohols are obtained upon hydrolysis. Quenching the reaction mixture with aldehydes or ketones is shown to give access to 2-alkynyl-1,3-diols in a stereoselective manner.



INTRODUCTION

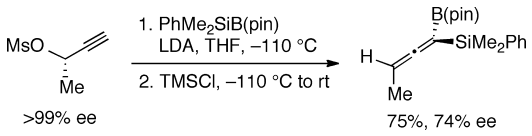
Allenylmetals are versatile reagents intensively used in organic synthesis.[1] The preparation of allenylmetals (with boron, copper, tin, indium, or zinc as the metal) through the direct S_N2' substitution reaction of metallic reagents to propargylic substrates bearing a leaving group at the propargylic position is well-documented (Scheme 1, path A).[2] Conversely, little is known on the alternate preparation of allenylmetals by the 1,2-metallate rearrangement of alkynylogous carbenoids of type **1**.[3] The overall process leading to allenylmetals **2** involves the initial formation of **1** through metalation at the acetylenic terminus and the subsequent 1,2-migration of the R^3 substituent with displacement of the leaving group through an S_N2' pathway (Scheme 1, path B).

Scheme 1. Three-Carbon Homologation with Propargylic Substrates



In seminal works, this approach was successfully applied to the preparation of allenylborons from propargylic chlorides,[4] acetates,[4d,5] acetals,[6] or mesylates.[4d] An enantioenriched allenylboron could be obtained with a good level of selectivity from an enantiopure chiral propargylic mesylate as the result of the stereoselective transfer of a dimethylphenylsilyl group through an *anti*-S_N2' mechanism (Scheme 2).[4d]

Scheme 2. Preparation of an Enantioeneriched Allenylboron



Allenyl aluminums[4c] and zirconiums[7] have been analogously obtained from propargylic chlorides, mesylates, or tosylates. Moreover, allenylzincs **3** have been generated by the three-carbon homologation of lithium triorganozincates, a process that involves the intermediate formation of alkynylogous zinco-carbenoids undergoing a 1,2-migration (Scheme 3).[8]

Allenylzincs **3** are particularly interesting and have been reacted with several electrophiles to provide allenes **4** (via an S_E2 pathway)[7a] or homopropargylic **5**[7b] as well as propargylic alcohols **6**[7c] (via an S_E2' pathway).

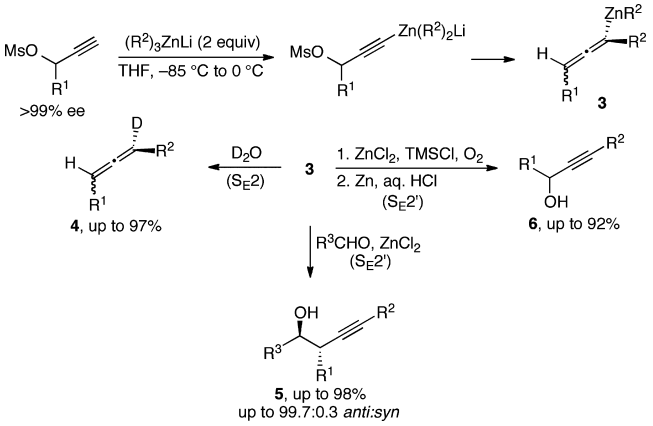
A related reaction involving an acetylenic epoxide and lithium tributylzincate was described by Marshall in 1994 (Scheme 4).[9,10] However, unlike propargylic mesylates, in this case, the reaction was evidenced to proceed to some extent (ca. 25%) by direct S_N2' displacement, thus without intermediate formation of an alkynylogous zinco-carbenoid. Deuterated allenic alcohol **8** was indeed obtained (through an S_E2 process) upon quenching of the allenylzinc intermediate **7** with D_2O with only ca. 75% D-incorporation.

Despite this promising preliminary result, no other example of the use of acetylenic epoxides for three-carbon homologation of organozinc reagents has been reported to date. We thus

Special Issue: Robert Ireland Memorial Issue

Received: September 28, 2012
Published: December 4, 2012

Scheme 3. Preparation and Use of Allenylzincs by Three-Carbon Homologation of Lithium Triorganozincates with Propargylic Mesylates



envisioned reinvestigating this reaction, and we report herein our recent results in this field (Scheme 5).

RESULTS AND DISCUSSION

Preliminary Study. In order to circumvent the competitive direct S_N2' mechanism observed by Marshall, we envisioned generating the alkynylogous zinco-carbenoid by deprotonation of the epoxide at the acetylenic terminus followed by transmetalation with a diorganozinc. Our study was initially conducted with acetylenic epoxide **9a** prepared from cyclohexanecarboxaldehyde using a known methodology (Scheme 6).[11]

When using a slight excess of *n*BuLi, the deprotonation was complete within 10 min at −80 °C in THF. Deuterated epoxide D-**9a** with >95% D-content was indeed quantitatively formed upon addition of D_2O. Note that the control of the amount of *n*BuLi used is crucial to avoid α-deprotronation of the epoxide, followed by 1,2-H shift rearrangement and the formation of the corresponding allenic ketone.[12]

The anticipated formation of allenic alcohol **10a** from lithium dibutylzincate Zn-**9a** by reacting Li-**9a** with various zinc species and then carrying out an acidic hydrolysis was examined (Scheme 6). Unexpectedly, when a commercially available salt-free solution of dibutylzinc was used, no reaction was observed at all within 1 h at 20 °C, and epoxide **9a** was quantitatively recovered upon hydrolysis (Table 1, entry 1).

In contrast, the successive addition of 1 equiv of $ZnBr_2$ and 2 equiv of *n*BuLi led, within 0.5 h at 20 °C, to a mixture of inseparable allenic and homopropargylic alcohols, **10a** and **10a′**, respectively, upon hydrolysis, albeit in a modest 39% combined yield and with no regioselectivity (Table 1, entry 2). The regioselectivity observed here contrasts with the study of Marshall in which only the allenic alcohol was obtained (Scheme 4).[9] This difference could be attributed to the metallotropic equilibrium totally shifted toward allenylzinc **7** in Marshall's case due to the disfavored isomerization of **7** into α,α,α-trisubstituted propargylzinc **7′**. Conversely, in our case, isomerization of allenylzinc **11** into α,α-disubstituted propargylzinc **11′** should be more favorable, leading to a mixture of alcohols **10a** and **10a′** upon hydrolysis, through an S_E2' process (Scheme 7).[13]

Although the diastereomeric ratio of allenic isomer **10a** could not be determined, two diastereomers could be observed by ^{13}C NMR.

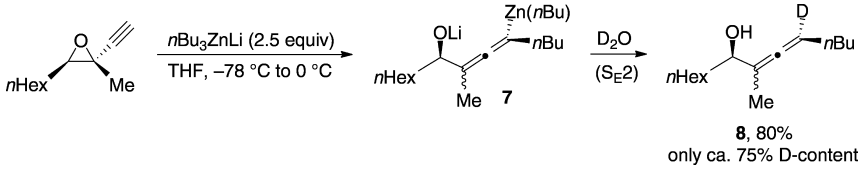
Analogous results were obtained with a similar procedure at −20 °C (Table 1, entry 3). Interestingly, when dibutylzinc (*n*Bu_2Zn) was preformed prior to the addition to Li-**9a**, by mixing 1 equiv of $ZnBr_2$ and 2 equiv of *n*BuLi (giving *n*Bu_2Zn·2LiBr), upon hydrolysis a significantly higher 74% yield in **10a** and **10a′** was obtained, yet with poor 48:52 regioselectivity (Table 1, entry 4). Note that in all cases similar results were obtained upon quenching with aqueous HCl or MeOH.

The positive results observed with Zn-**9a** generated from Li-**9a** by the addition of 1 equiv of $ZnBr_2$ followed by 2 equiv of *n*BuLi or by the addition of preformed dibutylzinc were attributed to the presence of 2 equiv of Lewis acidic LiBr that could facilitate the epoxide ring opening. Consistent with this hypothesis, the addition of HMPA (hexamethylphosphoric triamide), known to be able to coordinate lithium cations,[14] prevented the reaction with preformed *n*Bu_2Zn·2LiBr even at 20 °C (Table 1, entries 5−7). In contrast, when the reaction was run with a salt-free commercial dibutylzinc solution and adding 2 equiv of LiBr, no reaction was observed at −20 °C (Table 1, entry 8). We attributed this failure to the low solubility of this salt in the reaction medium as a turbid mixture was obtained. Strikingly, when using $MgBr_2$, assumed to be a stronger Lewis acid than LiBr, the reaction did not occur below 0 °C, and only degradation of the substrate was noted at 20 °C (Table 1, entries 9−11). Similarly, in the presence of only 1 equiv of LiBr, no reaction occurred at −20 °C, and decomposition was observed above 0 °C (Table 1, entry 12).

All of these results indicated that the formation of allenylzincs from acetylenic epoxides by three-carbon homologation of diorganozincs was possible, provided it was conducted in the presence of 2 equiv of LiBr, even though the exact role of this salt was not clear.

Scope of the Three-Carbon Homologation. The scope of the three-carbon homologation was next investigated under the optimized conditions. To this end, various acetylenic epoxides **9** were subjected to the reaction with preformed dibutylzinc (*n*Bu_2Zn·2LiBr) at −20 °C for 1.5 h prior to hydrolysis with aqueous HCl (Scheme 8). In all cases, mixtures of the allenic and homopropargylic alcohols **10** and **10′**, respectively, were obtained. Although the combined isolated yield was always good, the nature of the starting acetylenic epoxide **9** highly impacted both the sense and the level of the regioselectivity (Table 2). Moreover, in all cases, the

Scheme 4. Formation of an Allenylzinc from an Acetylenic Epoxide



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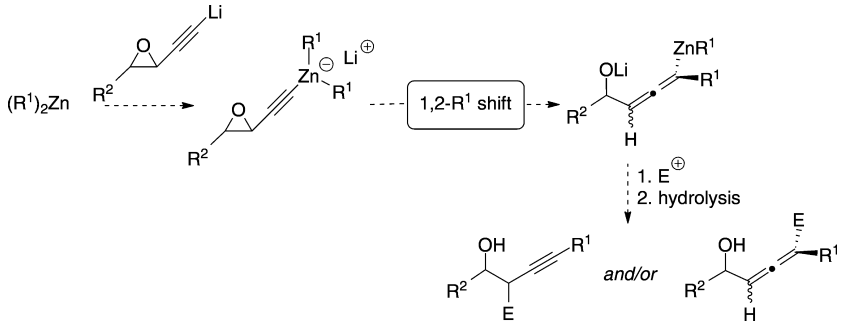
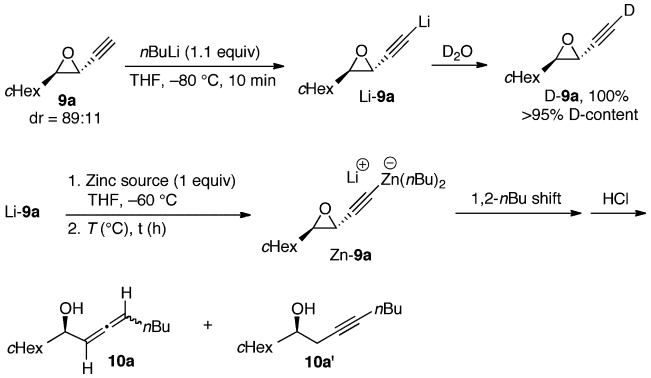
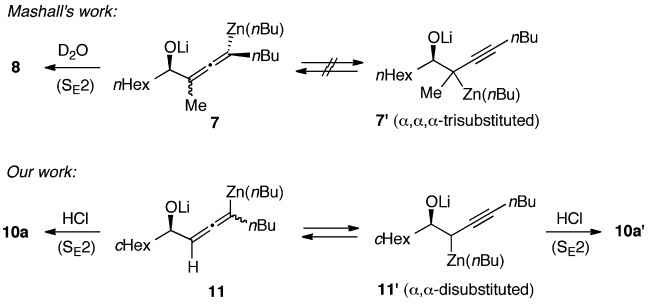
Scheme 5. Our Work



Scheme 6. Optimization of the Three-Carbon Homologation



Scheme 7. Origin of the Regioselectivity



diastereomeric ratio of allenic alcohols **10** could not be determined.

The three-carbon homologation of various dialkylzincs was next examined through their reaction with acetylenic epoxide **9a** (Scheme 9). These dialkylzincs were preformed as before by the reaction of 1 equiv of $ZnBr_2$ with 2 equiv of of the corresponding alkyllithiums (see the Experimental Section for details).

Except in the case of lithium dimethyzincate (Table 3, entry 1), high combined yields of allenic alcohols **12a**−**14a** and homopropargylic alcohols **12a**′−**14a**′ were attained, albeit with moderate selectivities (Table 3, entries 2 and 3). As before, the diastereomeric ratio of allenic alcohols **12a**−**14a** could not be determined.

Interestingly, the dimethylphenylsilyl group could also be transferred efficiently using bis(dimethylphenylsilyl)zinc (Scheme 10), preformed from the parent silyllithium species[15] (see the Experimental Section for details).

The best yields were obtained when the rearrangement was carried out for 2 h at −20 °C followed by an additional stirring of 45 min at 0 °C prior to quenching with MeOH. To our delight, the transfer of the silyl group occurred with high regioselectivity, leading to 4-silylated homopropargylic alcohols **15**′ as unique or major regioisomers (Table 4).

The corresponding allenic alcohols **15** could only be detected as minor isomers with acetylenic epoxides **9b** and **9i**

Table 1. Optimization of the Three-Carbon Homologation (Scheme 6)

entry	zinc source[a]	T (°C)	t (h)	**10a**:**10a**′ ratio[b]	yield (%)[c]
1	salt-free nBu_2Zn[d]	20	1		0[e]
2	$ZnBr_2$ then 2 equiv of nBuLi	20	0.5	50:50	39
3	$ZnBr_2$ then 2 equiv of nBuLi	−20	1.5	50:50	40
4	$nBu_2Zn{\cdot}2LiBr$[f]	−20	1.5	48:52	74
5	$nBu_2Zn{\cdot}2LiBr$[f] + HMPA	−20	1.5		(0)
6	$nBu_2Zn{\cdot}2LiBr$[f] + HMPA	0	1		(0)
7	$nBu_2Zn{\cdot}2LiBr$[f] + HMPA	20	8		0[e]
8	salt-free nBu_2Zn[d] + 2 equiv of LiBr	−20	1		0[e]
9	$nBu_2Zn{\cdot}2MgBr_2$[g]	−20	2		0[e]
10	$nBu_2Zn{\cdot}2MgBr_2$[g]	0	2		0[e]
11	$nBu_2Zn{\cdot}2MgBr_2$[g]	20	2		decomposition
12	$nBu_2Zn{\cdot}LiBr{\cdot}MgBr_2$[h]	−20	1		(0)

[a]See the Experimental Section for the preparation of the zinc species. [b]Regioselectivity determined by ^{1}H NMR analysis at 400 MHz of the crude reaction mixture. [c]Combined isolated yield in **10a** and **10a**′. In parentheses is the conversion rate as measured by ^{1}H NMR at 400 MHz. [d]Commercial 1 M solution in heptane. [e]Epoxide **9a** was quantitatively recovered. [f]Preformed dibutylzinc: freshly prepared by the reaction of nBuLi (2 equiv) with $ZnBr_2$ (1 equiv) in THF from −80 to 0 °C. [g]Preformed dibutylzinc: freshly prepared by the reaction of nBuMgBr (2 equiv) with $ZnBr_2$ (1 equiv) in THF from −80 to 0 °C. [h]Preformed dibutylzinc: freshly prepared by the reaction of nBuMgBr (1 equiv) and nBuLi (1 equiv) with $ZnBr_2$ (1 equiv) in THF from −80 to 0 °C.

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Scheme 8. Three-Carbon Homologation of nBu$_2$Zn·2LiBr with Epoxides 9

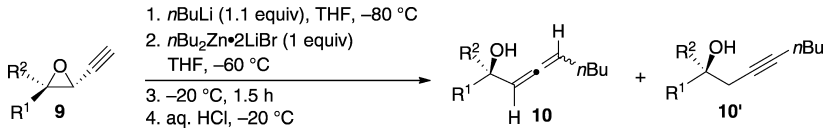

Table 2. Three-Carbon Homologation of nBu$_2$Zn·2LiBr with Epoxides 9 (Scheme 8)

entry	R^1	R^2	epoxide	**10**:**10′** ratio[a]	yield (%)[b]
1	$Ph(CH_2)_2$	H	**9b** (dr = 81:19)	**10b**:**10b′** = 58:42	70
2	Et_2CH	H	**9c** (dr = 94:06)	**10c**:**10c′** = 69:31	68
3	*t*Bu	H	**9d** (dr > 98:02)	**10d**:**10d′** = 83:17	72
4	Ph	H	**9e** (dr = 62:38)	**10e**:**10e′** = 58:42	57[c]
5	Ph	Ph	**9f**	**10f**:**10f′** = 13:87	62[d]

[a]Regioselectivity determined by ^{1}H NMR analysis at 400 MHz of the crude reaction mixture. [b]Combined isolated yield in **10** and **10′**. The same regioselectivity as in the crude material was observed. [c]Conversion rate of 94%. [d]Conversion rate of 89%. The reaction was carried out for 4 h at 0 °C then 1.5 h at 20 °C.

Scheme 9. Three-Carbon Homologation of R$_2$Zn·2LiBr

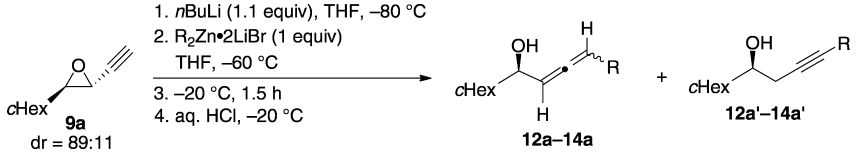

Table 3. Three-Carbon Homologation of R$_2$Zn·2LiBr (Scheme 9)

entry	R	regioselectivity[a]	yield (%)[b]
1	Me	**12a**:**12a′** = 76:24	28
2	Et	**13a**:**13a′** = 68:32	75
3	*t*Bu	**14a**:**14a′** = 65:35	85
4	Ph		decomposition

[a]Regioselectivity determined by ^{1}H NMR analysis at 400 MHz of the crude reaction mixture. [b]Combined isolated yield in **12a**–**14a** and **12a′**–**14a′**. The same regioselectivity as in the crude material was observed.

bearing a primary alkyl substituent (Table 4, entries 2 and 3) and with aromatic epoxide **9e** (Table 4, entry 6). Their configuration could not be determined. Intriguingly, only decomposition was observed in the case of alkenyl epoxide **9h** under the same conditions (Table 4, entry 9). The reason why **9h** behaves differently from the others remains unexplained even though the vinylogous nature of the epoxide, prone to substitution giving multiple of products, could be invoked. Interestingly, trisubstituted epoxides **9f** and **9g** led to the corresponding quaternary homopropargylic alcohols in good yields as unique regioisomers (Table 4, entries 7 and 8).

Diverse alkyl groups as well as the dimethylphenylsilyl group could thus be transferred affording the corresponding allenic and/or homopropargylic alcohols through ring opening of the epoxide following an S_N2' process. In most cases, yields are good while the regioselectivity highly depends on the nature of the epoxide and/or of the group transferred. The exact reason why the regioselectivity varies in such a way is unknown, even through it is undoubtedly related to the metallotropic allenylzinc/propargylzinc equilibrium.

Stereoselective Access to 2-Alkynyl-1,3-diols. The mixture of allenylzinc **11** and propargylzinc **11′**, obtained from acetylenic epoxide **9a** (see Scheme 7), was first reacted with cyclohexanecarboxaldehyde. Within 1 h at −20 °C, upon hydrolysis, inseparable diastereomeric 2-alkynyl-1,3-diols[16,17] **16** and **17** were isolated in good yield with a complete control of the regioselectivity (the corresponding allenic isomers not being observed) and with a ratio of 85:15 in favor of **16** (Scheme 11). The exclusive formation of homopropargylic diols was rationalized by the reactivity of **11** being greater with carbonyl derivatives than that of **11′** through an S_E2' process. Everything thus happened as if **11** were the only existing metallotropic form in the medium.[18]

Stereochemical assignment was achieved by NMR studies. The major diastereomer **16** was first shown to be a symmetrical 1,3-diol by ^{1}H NMR analysis, showing that hydrogens H^1 and H^3 are identical and appear as a unique doublet of doublet at 3.37 ppm (Scheme 11). Similarly, the minor diastereomer **17** could be determined to be unsymmetrical by its ^{1}H NMR analysis, showing that H^1 and H^3 are different.

The relative configuration of **16** was next deduced from its quantitative transformation into dioxolane **18** in which coupling constants of 2.2 Hz were measured between H^2 and H^1 as well as H^3 (Scheme 12). These are typical of equatorial−equatorial and/or axial−equatorial interactions meaning that the

Scheme 10. Three-Carbon Homologation of (PhMe$_2$Si)$_2$Zn·2LiBr

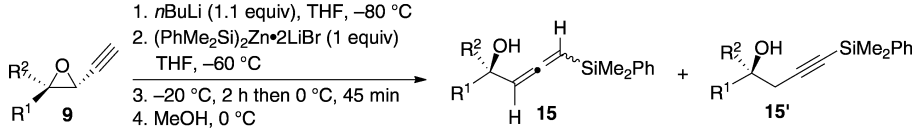

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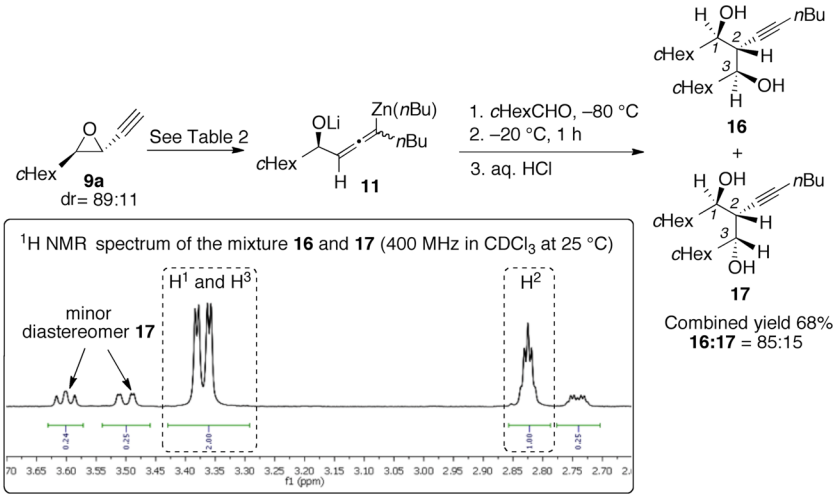
Table 4. Three-Carbon Homologation of $(PhMe_2Si)_2Zn{\cdot}2LiBr$ (Scheme 10)

entry	R^1	R^2	epoxide **9**	**15**:**15′** ratio[a]	yield (%)[b]
1	*c*Hex	H	**9a** (dr = 89:11)	<02:98	72
2	*n*Bu	H	**9i** (dr = 80:20)	17:83	64
3	$Ph(CH_2)_2$	H	**9b** (dr = 81:19)	07:93	65
4	Et_2CH	H	**9c** (dr = 94:06)	<02:98	72
5	*t*Bu	H	**9d** (dr > 98:02)	<02:98	79
6	Ph	H	**9e** (dr = 62:38)	16:84	86
7	Ph	Ph	**9f**	<02:98	72
8	*n*Pent	*n*Pent	**9g**	<02:98	76
9	(*E*)-PhCH=CH_2	H	**9h** (dr > 98:02)		decomposition

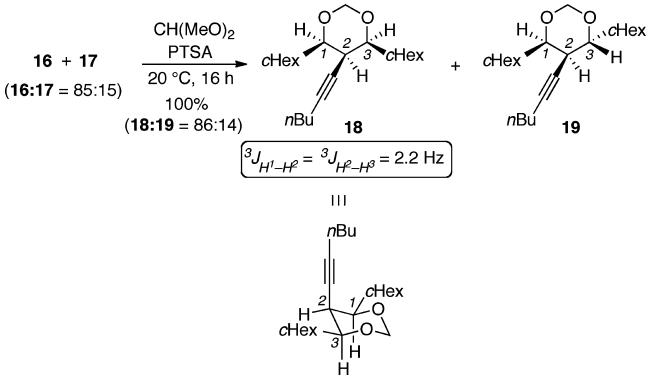
[a]Regioselectivity determined by ^{1}H NMR analysis at 400 MHz of the crude reaction mixture. [b]Combined isolated yield in **15** and **15′**. The same regioselectivity as in the crude material was observed.

Scheme 11. Access to 2-Alkynyl-1,3-diols



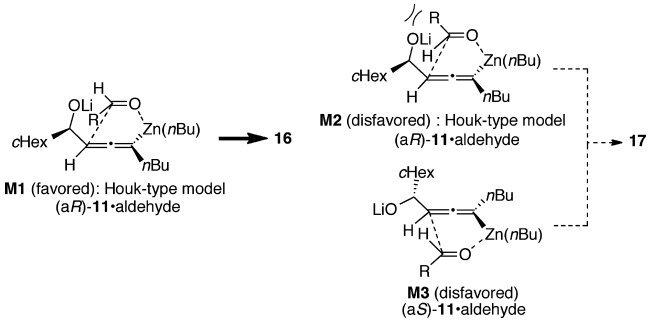
(1*R**,2*r**,3*S**) stereochemistry could be unambiguously attributed to **16**.

Scheme 12. Determination of the Configuration of 16



The preferred formation of diastereomer **16** could be rationalized by the favored Chodkiewicz–Yamamoto-type[19] transition state model **M1** in which allenylzinc (a*R*)-**11** reacts with the aldehyde (Scheme 13). Analogously, **17** could be arise from the disfavored competitive more energetic chelate models **M2** or **M3**. Transition state model **M1** is favored relative to **M2** due to less steric interactions between the allenylzinc and the aldehyde. The preference for **M1** versus **M3** was explained by the "inside alkoxy effect" that enhances the nucleophilicity of the allenylzinc (Houk-type model).[20,21]

Scheme 13. Possible Transition State Models



These results suggest that **16** arises only from allenylzinc (a*R*)-**11** while the formation of **17** can be formed either from (a*R*)-**11** or (a*S*)-**11** (Scheme 13). In order to gain insight into the stereoselectivity of the formation of **11** and its subsequent reaction with aldehydes, we carried out a series of reactions with epoxide **9a** and varying the trapping conditions (Scheme 14).

Interestingly, when cyclohexanecarboxaldehyde was rapidly added dropwise at −20 °C only 5 min following the addition of dibutylzinc to Li-**9a**, adducts **16** and **17** were obtained in low 35% yield and with a **16**:**17** ratio of 57:43. The diastereoselectivity was considerably lower than that observed when adding the aldehyde 90 min after dibutylzinc (Table 5, entry 1 vs 2). Moreover, the sense of the diastereoselectivity could be reversed when the aldehyde was rapidly and

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Scheme 14. Study of the Configurational Stability of 11

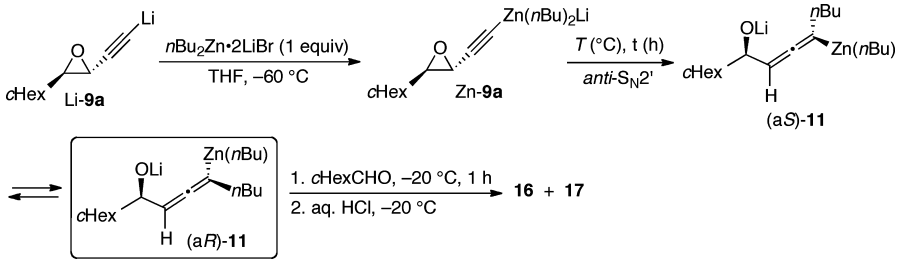


Table 5. Study of the Configurational Stability of 11 (Scheme 14)

entry	T (°C)	t (min)[a]	addition rate (min)[b]	16:17[c]	yield (%)[d]
1	−20	90	0.33	85:15	66
2	−20	5	0.33	57:43	35
3	−60	0[e]	0.33	27:73	7[f]
4	−20	90	210	84:16	79

[a]Time of stirring at the appropriate temperature after completion of the addition of dibutylzinc to Li-**9a** and before the addition of cyclohexanecarboxaldehyde. [b]Addition rate of cyclohexanecarboxaldehyde to the reaction mixture. [c]Ratio determined by ^{1}H NMR analysis at 400 MHz of the crude reaction mixture. [d]Isolated combined yield in **16** and **17**. [e]Cyclohexanecarboxaldehyde was added immediately after preformed dibutylzinc. [f]The major product resulted from the addition of cyclohexanecarboxaldehyde at the acetylenic terminus of **9a**.

immediately added after dibutylzinc at −60 °C. In this case, the expected **16** and **17** adducts were obtained with a **16**:**17** ratio of 27:73 in very poor 7% yield, the main product resulting from the direct nucleophilic attack of the zincate to the aldehyde (Table 5, entry 3).

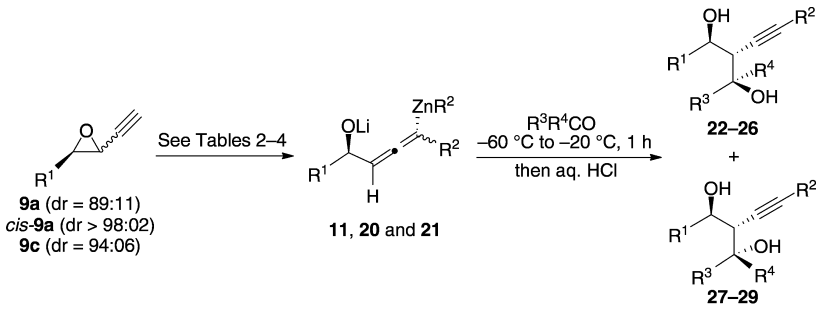
These results were in accord with a mechanistic picture involving the initial formation of (a*S*)-**11**, via the classical *anti*-S_N2' migration of a butyl substituent from zincate Zn-**9a**, and isomerization to give (a*R*)-**11**. In this context, a last experiment was carried out by slowly adding the aldehyde at −20 °C 90 min after dibutylzinc. In this case, both the yield and the diastereoselectivity were close to those obtained when the aldehyde was rapidly added under the same conditions (Table 5, entry 1 vs 4). This last experiment suggested that the Curtin−Hammet principle applies at −20 °C and thereby means that the equilibration of (a*S*)-**11** is faster than its reaction with the aldehyde at this temperature. Indeed, in the case of a slow equilibration, an increased diastereoselectivity would have been observed by giving more time to (a*S*)-**11** to isomerize into (a*R*)-**11**. On the other hand, the result obtained at −60 °C could be interpreted by a slow isomerization of (a*S*)-**11** relative to the rate of its reaction with the aldehyde. However, we cannot currently provide an explanation why (a*S*)-**11** rapidly epimerizes into (a*R*)-**11**, and to why the equilibrium is shifted toward (a*R*)-**11**.[18,22] Nevertheless, a greater reactivity of (a*R*)-**11** (through **M1**) than that of (a*S*)-**11** (through **M3**) might be invoked (see Scheme 13).

We next studied the scope of this new diastereoselective access to 2-alkynyl-1,3-diols by trapping allenylzincs (a*R*)-**11**, **20**, and **21**, generated from the appropriate acetylenic epoxides **9** and dialkylzincs R_2Zn·2LiBr, with carbonyl derivatives (Scheme 15).

When allenylzinc **11** was trapped with propanal and pivaldehyde, the corresponding 2-alkynyl-1,3-diols were obtained with a complete regioselectivity in good yields and diastereoselectivities ≥85:15 (Table 6, entries 1 and 2). The relative configuration of major diastereomers **22** and **23** was inferred by analogy with that of **16** and can be explained on the basis of the favored transition state model **M1** (Scheme 13). The stereochemistry of minor isomers **27** and **28** could not be assigned. It is, however, worth noting that the bulkiness of the R substituent of the aldehyde has no influence on the diastereoselectivity, thereby suggesting that these adducts are obtained *via* model **M3** rather than **M2** (Scheme 13). Hence, their relative configuration could be assigned.

When the 1,3-diol preparation was carried out with tBu$_2$Zn·2LiCl and **9a**, a reversal of the diastereoselectivity was observed, the generated allenylzinc **20** leading to major isomer

Scheme 15. Diastereoselective Preparation of 2-Alkynyl-1,3-diols



11: R^1 = *c*Hex, R^2 = *n*Bu
20: R^1 = *c*Hex, R^2 = *t*Bu
21: R^1 = Et_2CH, R^2 = $SiMe_2Ph$

22 and **27:** R^1 = *c*Hex, R^2 = *n*Bu, R^3 = Et, R^4 = H
23 and **28:** R^1 = *c*Hex, R^2 = *n*Bu, R^3 = *t*Bu, R^4 = H
24 and **29:** R^1 = *c*Hex, R^2 = *t*Bu, R^3 = *c*Hex, R^4 = H
25: R^1 = *c*Hex, R^2 = *n*Bu, R^3 = Me, R^4 = Me
26: R^1 = Et_2CH, R^2 = $SiMe_2Ph$, R^3 = Me, R^4 = Me

dx.doi.org/10.1021/jo302128n | *J. Org. Chem.* 2013, 78, 134−145

Table 6. Diastereoselective Preparation of 2-Alkynyl-1,3-diols (Scheme 15)

entry	R^1 (epoxide)	allenylzinc	R^2	R^3	R^4	stereoselectivity[a]	yield (%)
1	*c*Hex (**9a**)	**11**	*n*Bu	Et	H	**22:27** = 87:13	78[b]
2	*c*Hex (**9a**)	**11**	*n*Bu	*t*Bu	H	**23:28** = 85:15	59[b]
3	*c*Hex (**9a**)	**20**	*t*Bu	*c*Hex	H	**24:29** = 36:64	88[b]
4	*c*Hex (**9a**)	**11**	*n*Bu	Me	Me	*c*	77[d]
5	*c*Hex (*cis*-**9a**)	**11**	*n*Bu	Me	Me	*e*	59[d]
6	Et_2CH (**9c**)	**21**	$SiMe_2Ph$	Me	Me	*f*	42[d,g]

[a]Stereoselectivity determined by ^1H NMR analysis at 400 MHz of the crude reaction mixture. [b]Combined isolated yield. The same regioselectivity as in the crude material was observed. [c]Only compound **25** was obtained with 94:06 regioselectivity. [d]Yield in purified major products. [e]Only compound **25** was obtained with 93:07 regioselectivity. [f]Only compound **26** was obtained with 88:12 regioselectivity. [g]Reaction carried out for 2.5 h at −40 °C.

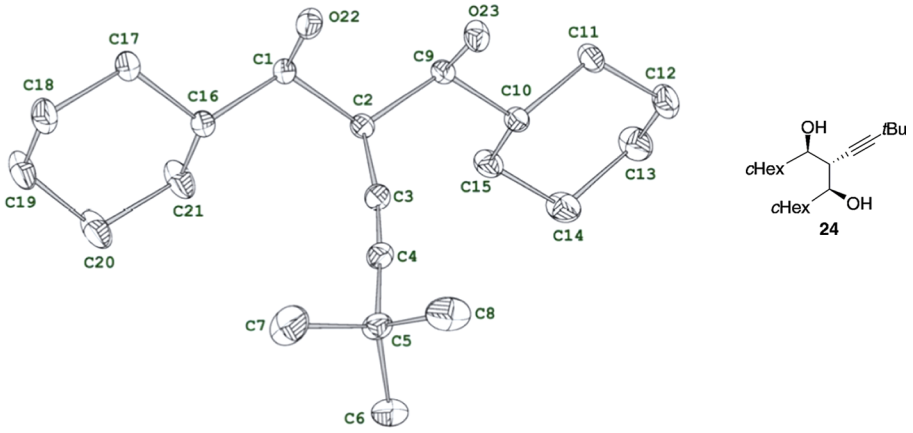
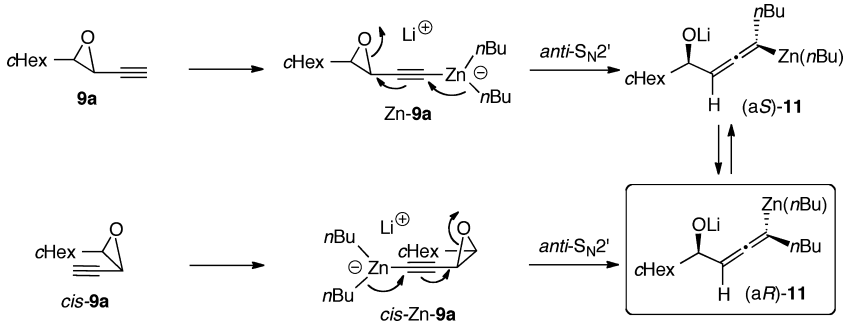


Figure 1. ORTEP drawing of **24** (hydrogens have been omitted for clarity).

Scheme 16. Diastereoconvergent Generation of Allenylzinc (a*R*)-11



29, albeit with a modest selectivity of 64:36 (Table 6, entry 3). The stereochemistry of the minor isomer **24** could be unambiguously assigned from crystal X-ray analysis (Figure 1).[23] This reversal of the stereoselectivity remains puzzling.

In addition to aldehydes, trapping of allenylzincs **11** and **21** could be efficiently performed with acetone, thus leading to the corresponding 2-alkynyl-1,3-diols in good yields with good regio- and stereoselectivities (Table 6, entries 4–6). Interestingly, diastereoconvergent results were obtained from isomeric acetylenic epoxides **9a** and *cis*-**9a** that gave exclusively the same adduct **25** (Table 6, entries 4 and 5). Most likely, *cis*-Zn-**9a** undergoes an *anti*-S_N2' migration of the butyl group, leading directly to allenylzinc intermediate (a*R*)-**11** (Scheme 16).

CONCLUSION

Allenylzinc formation from acetylenic epoxides has been developed through deprotonation at the acetylenic position and subsequent transmetalation with diorganozincs, leading to zincates that undergo migration of an alkyl or silyl group. In the case of (2*R*,3*R*)-2-alkyl-3-ethynyl epoxides, the migration occurs by an *anti*-S_N2' pathway, leading to (a*S*) allenylzinc intermediates. The latter rapidly epimerize and afford the corresponding (a*R*) allenylzincs, which are the reactive species. In the case of the (2*R*,3*S*) diastereomeric epoxides, the same (a*R*) allenylzincs are directly formed following the same *anti*-S_N2' pathway. When dialkylzincs are used in the transmetalation step, mixtures of homopropargylic and allenic alcohols are obtained with modest regioselectivites upon hydrolysis. Conversely, the reactions involving bis(dimethylphenylsilyl)zinc lead to the corresponding homopropargylic alcohols in high yields and excellent regioselectivity. Trapping of allenylzinc intermediates with carbonyl derivatives has been shown to give stereoselectively 2-alkynyl-1,3-diols. The extension of this methodology to acetylenic aziridines is under investigation in our group and will be reported in due course.

dx.doi.org/10.1021/jo302128n | *J. Org. Chem.* 2013, 78, 134–145

EXPERIMENTAL SECTION

General Methods. Experiments involving organometallics were carried out in dried glassware under a positive pressure of dry nitrogen. Liquid nitrogen was used as a cryoscopic fluid. A three-necked, round-bottomed flask equipped with an internal thermometer, a septum cap, and a nitrogen inlet was used. Anhydrous THF and Et_2O were obtained by distillation over sodium benzophenone ketyl. Zinc bromide was purchased from Aldrich, melted under argon, and, immediately after cooling to room temperature, dissolved in anhydrous THF or Et_2O. Commercial solutions of *n*BuLi and *t*BuLi were titrated with *s*BuOH (1 M solution in toluene) in the presence of 2,2′-dichinolyl or with Suffert's reagent.[24] All other reagents and solvents were of commercial quality and were used without further purification. Flash chromatographies were carried out over silica gel 60 (230−400 mesh). IR spectra were recorded with an ATR diamant spectrophotometer. Chemical shifts are reported in δ units relative to an internal standard of residual chloroform (δ = 7.27 ppm for ^{1}H NMR and δ = 77.1 ppm for ^{13}C NMR). HRMS were obtained using a Q-TOF instrument equipped with ESI source.

Standard Procedure for the Three-Carbon Homologation of Dialkylzincs (SP1). Under a nitrogen atmosphere, to $ZnBr_2$ (1.00 M solution in THF, 0.55 mL, 0.55 mmol) in THF (0.5 mL) was added RLi (1.1 mmol) at −80 °C. After 5 min of stirring at −80 °C, the mixture was allowed to warm to 0 °C. The resulting solution of dialkylzinc (R_2Zn·2LiBr) was immediately used in the reaction with lithiated epoxides.

Under a nitrogen atmosphere, at −80 °C to a solution of epoxide (0.50 mmol) in THF (4 mL) was added dropwise *n*BuLi (2.20 M in hexanes, 0.25 mL, 0.55 mmol). After 10 min of stirring at −80 °C, the mixture was allowed to warm to −60 °C and the above prepared dialkylzinc was added. The resulting mixture was warmed to −20 °C then stirred for 1.5 h at this temperature. The reaction was quenched with a 0.5 M aqueous HCl solution (10 mL), and Et_2O (10 mL) was added. The layers were separated, and the aqueous one was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with water (15 mL) and brine (15 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuum and purification by flash chromatography (10% Et_2O/pentane) afforded mixtures of alcohols **10**, **12**−**14** and **10**′, **12**′−**14**′ (Tables 2 and 3).

Mixture of (±)-1-Cyclohexylocta-2,3-dien-1-ol (10a) and (±)-1-Cyclohexyloct-3-yn-1-ol and (10a′): Colorless yellow oil (78 mg, 74%, **10a**:**10a**′ = 48:52, indeterminable dr for **10a**) obtained according to **SP1** from epoxide **9a** (76 mg, 0.50 mmol) and nBu_2Zn·2LiBr; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.33−5.27 (m, 1 H **10a**), 5.27−5.14 (m, 1 H **10a**), 3.89−3.85 (m, 1 H **10a**), 3.41−3.38 (m, 1 H **10a**′), 2.41 (ABX system, *J* = 16.5, 4.4, 2.4 Hz, 1 H **10a**′), 2.29 (ABX system, *J* = 16.5, 7.6, 2.4 Hz, 1 H **10a**′), 2.18−2.14 (m, 1 H), 2.0−1.93 (m, 1 H), 1.92−1.73 (m, 1 H), 1.72−1.57 (m, 5 H), 1.50−1.39 (m, 5 H), 1.38−0.94 (m, 5 H), 0.93−0.87 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.7 and 202.3 (two isomers of **10a**), 94.4 and 94.3 (two isomers of **10a**), 83.3 (**10a**′), 76.5, 74.4, 74.1, 44.2, 44.1, 42.76, 31.4, 31.2, 29.1, 28.9, 28.62, 28.60, 28.5, 28.4, 28.3, 26.3, 26.25, 26.23, 26.17, 26.15, 25.1, 22.3, 22.2, 22.1, 18.6, 14.0, 13.7; IR (neat) ν 3349, 2922, 2852, 1962 cm^{-1}; HMRS (ESI) *m*/*z* calcd for $C_{14}H_{25}O^+$ 209.1900 [*M* + H$^+$], found 209.1896.

Mixture of (±)-1-Phenyldeca-4,5-dien-3-ol (10b) and (±)-1-Phenyldec-3-yn-1-ol (10b′): Colorless oil (81 mg, 70%, **10b**:**10b**′ = 58:42, indeterminable dr for **10b**) obtained according to **SP1** from epoxide **9b** (87 mg, 0.51 mmol) and nBu_2Zn·2LiBr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.26 (m, 2 H), 7.23−7.17 (m, 3 H), 5.36−5.29 (m, 1 H **10b**), 5.29−5.23 (m, 1 H **10b**), 4.19−4.13 (m, 1 H **10b**), 3.75−3.68 (m, 1 H **10b**′), 2.84−2.65 (m, 2 H), 2.42 (ABX system, *J* = 16.5, 4.6, 2.3 Hz, 1 H **10b**′), 2.31 (ABX system, *J* = 16.5, 6.7, 2.3 Hz, 1 H **10b**′), 2.19−2.16 (m, 1 H), 2.07−1.92 (m, 1 H), 1.91−1.63 (m, 3 H), 1.51−1.21 (m, 4 H), 0.93−0.89 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3 and 202.2 (two isomers of **10b**) 142.11, 142.07, 142.0, 128.59, 128.57, 128.5, 126.0, 125.9, 95.7, and 95.6 (two isomers of **10b**), 94.8 and 94.6 (two isomers of **10b**), 83.6 (**10b**′), 75.9, 69.54, 69.51, 69.2, 39.23, 39.21, 38.0, 32.1, 31.9, 31.8, 31.38, 31.36, 31.2, 28.60, 28.58, 28.0, 22.3, 22.1, 18.5, 14.0, 13.7; IR (neat) ν 3340, 2925, 1972 cm^{-1}; HMRS (ESI) *m*/*z* calcd for $C_{16}H_{23}O^+$ 231.1743 [*M* + H$^+$], found 231.1750.

Mixture of (±)-3-Ethylundeca-5,6-dien-4-ol (10c) and (±)-3-Ethylundec-6-yn-4-ol (10c′): Colorless oil (66 mg, 68%, **10c**:**10c**′ = 69:31, indeterminable dr for **10c**) obtained according to **SP1** from epoxide **9c** (68 mg, 0.50 mmol) and nBu_2Zn·2LiBr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34−5.26 (m, 1 H **10c**), 5.26−5.15 (m, 1 H **10c**), 4.21−4.09 (m, 1 H **10c**), 3.67 (m, 1 H **10c**′), 2.38 (ABX system, *J* = 16.5, 4.6, 2.4 Hz, 1 H **10c**′), 2.31 (ABX system, *J* = 16.5, 7.9, 2.4 Hz, 1 H **10c**′), 2.20−2.12 (m, 1 H **10c**), 2.08−1.97 (m, 1 H), 1.92−1.88 (m, 1 H **10c**′), 1.62−1.52 (m, 1 H), 1.52−1.18 (m, 9 H), 0.96−0.77 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7 (**10c**), 94.7 and 94.5 (two isomers of **10c**), 94.24 and 94.17 (two isomers of **10c**), 83.3 (**10c**′), 76.7, 71.8, 71.6, 71.2, 47.3, 45.5, 31.5, 31.2, 28.7, 25.2, 22.3, 22.1, 22.0, 21.8, 21.6, 21.1, 18.6, 14.0, 13.7, 11.9, 11.8, 11.7, 11.5; IR (neat) ν 3328, 2924, 2172 (**10c**′), 1961 (**10c**) cm^{-1}; HMRS (ESI) *m*/*z* calcd for $C_{13}H_{25}O^+$ 197.1900 [*M* + H$^+$], found 197.1896.

Mixture of (±)-2,2-Dimethyldeca-4,5-dien-3-ol (10d) and (±)-2,2-Dimethyldec-5-yn-3-ol (10d′): Colorless yellow oil (70 mg, 72%, **10d**:**10d**′ = 83:17, indeterminable dr for **10d**) obtained according to **SP1** from epoxide **9d** (65 mg, 0.53 mmol) and nBu_2Zn·2LiBr. Further purification by flash chromatography afforded analytically pure products. *Data for* ***10d***: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36−5.30 (m, 1 H), 5.29−5.25 (m, 1 H), 3.76 (dd, *J* = 5.7, 2.8 Hz, 1H), 2.06−2.00 (m, 2 H), 1.67 (br s, 1 H), 1.43−1.28 (m, 4 H), 0.90 (s, 9 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7 and 202.3 (two isomers), 94.8 and 94.1 (two isomers), 92.9 and 92.6 (two isomers), 77.8, 35.5, and 35.4 (two isomers), 28.54 and 28.46 (two isomers), 25.47 and 25.45 (two isomers), 21.5, 13.9. *Data for* ***10d***′: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (dd, *J* = 10.0, 2.8 Hz, 1 H), 2.42−2.35 (m, 1 H), 2.26−2.10 (m, 3 H), 2.06−1.79 (m, 1 H), 1.52−1.11 (m, 4 H), 0.97−0.80 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.3, 77.7, 77.4, 34.5, 31.2, 25.8, 23.0, 18.6, 13.7; IR (neat) ν 3419, 2955, 2930, 2870, 1962 cm^{-1}; HMRS (ESI) *m*/*z* calcd for $C_{12}H_{23}O^+$ 183.1743 [*M* + H$^+$], found 183.1746.

Mixture of (±)-1-Phenylocta-2,3-dien-1-ol (10e) and (±)-1-Phenyloct-3-yn-1-ol (10e′): Pale yellow oil (58 mg, 57%, **10e**:**10e**′ = 58:42) obtained according to **SP1** from epoxide **9e** (72 mg, 0.50 mmol) and nBu_2Zn·2LiBr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.29 (m, 5 H), 5.45−5.35 (m, 2 H **10e**), 5.26−5.22 (m, 1 H **10e**), 4.82 (dd, *J* = 7.5, 5.2 Hz, 1 H **10e**′), 2.62−2.47 (m, 3 H **10e**′), 2.28−2.17 (m, 2 H **10e** and 1 H **10e**′), 2.17−2.00 (m, 1 H), 1.51−1.29 (m, 4 H), 0.90 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3 and 202.0 (two isomers of **10e**), 143.2, 143.1, 142.8, 128.5, 128.4, 127.8, 127.72, 127.67, 126.2, 126.1, 125.8, 96.2 and 96.1 (two isomers of **10e**), 95.4, and 95.1 (two isomers of **10e**), 83.6 (**10e**′), 77.3, 76.0, 72.7, 72.4, 72.2, 31.3, 31.2, 31.0, 30.1, 28.5, 22.2, 22.0, 18.5, 14.0, 13.7; IR (neat) ν 3419, 2955, 2930, 2870, 1962 cm^{-1}; HMRS (ESI) *m*/*z* calcd for $C_{14}H_{19}O^+$ 203.1430 [*M* + H$^+$], found 203.1434.

Mixture of (±)-1,1-Diphenylocta-2,3-dien-1-ol (10f) and (±)-1,1-Diphenyloct-3-yn-1-ol (10f′): Pale yellow oil (81 mg, 62%, **10f**:**10f**′ = 13:87) obtained according to **SP1** from epoxide **9f** (65 mg, 0.53 mmol) and nBu_2Zn·2LiBr. Further purification by flash chromatography afforded analytically pure products. *Data for* ***10f***: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.44 (m, 4 H), 7.34−7.30 (m, 4 H), 7.27−7.23 (m, 2 H), 5.90 (dt, *J* = 6.2, 3.0 Hz, 1 H), 5.41 (q, *J* = 6.2 Hz, 1 H), 2.67 (s, 1 H), 2.05−1.98 (m, 2 H), 1.27−1.21 (m, 2 H), 0.86 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 146.5, 128.1, 127.3, 126.9, 126.8, 101.0, 97.5, 77.3, 31.3, 28.6, 22.3, 14.0. *Data for* ***10f***′: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.42 (m, 4 H), 7.34−7.30 (m, 4 H), 7.26−7.20 (m, 2 H), 3.12 (t, *J* = 2.3 Hz, 2 H), 3.08 (br s, 1 H), 2.09 (tt, *J* = 7.0, 2.3 Hz, 2 H), 1.39−1.32 (m, 2 H), 1.28−1.19 (m, 2 H), 0.82 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 128.2, 127.2, 126.3, 85.2, 77.2, 75.8, 33.9, 30.9, 21.8, 18.5, 13.7; HMRS (ESI) *m*/*z* calcd for $C_{20}H_{23}O^+$ 279.1743 [*M* + H$^+$], found 279.1747.

Mixture of (±)-1-Cyclohexylpenta-2,3-dien-1-ol (12a) and (±)-1-Cyclohexylpent-3-yn-1-ol (12a′): Colorless oil (23 mg, 28%, **12a**:**12a**′ = 76:24, indetermibable dr for **12a**) obtained according **SP1** from epoxide **9a** (75 mg, 0.50 mmol) and Me_2Zn·2LiBr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32−5.22 (m, 1 H **12a**), 5.22−5.16 (m, 1 H

dx.doi.org/10.1021/jo302128n | J. Org. Chem. 2013, 78, 134−145

12a), 3.92−3.85 (m, 1 H **12a**) 3.47−3.39 (m, 1 H **12a**), 2.45−2.38 (m, 1 H, **12a**), 2.33−2.25 (m, 1 H **12a**), 2.00−1.57 (m, 8 H), 1.51−1.37 (m, 1 H), 1.37−0.92 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5 and 203.2 (two isomers of **12a**), 93.7 and 93.6 (two isomers of **12a**), 88.8 and 88.4 (two isomers of **12a**), 78.4 (**12a′**), 75.7, 75.6, 74.3, 74.1, 44.2, 44.1, 42.6, 29.1, 28.8, 28.4, 28.3, 26.6, 26.5, 26.2, 25.0, 14.52, 14.46, 3.7; IR (neat) ν 3395, 2962, 1961 cm^{-1}; HMRS (ESI) m/z calcd for $C_{11}H_{19}O^+$ 167.1430 [M + H$^+$], found 167.1427.

Mixture of (±)-1-Cyclohexylhex-2,3-dien-1-ol (13a) and (±)-1-Cyclohexylhex-3-yn-1-ol (13a′): Colorless oil (60 mg, 75%, **13a**:**13a′** = 68:32, indeterminable dr for **13a**) obtained according **SP1** from epoxide **9a** (75 mg, 0.50 mmol) and Et_2Zn·2LiBr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42−5.33 (m, 1 H **13a**), 5.28−5.19 (m, 1 H **13a**), 3.88−3.79 (m, 1 H **13a**), 3.47−3.38 (m, 1 H **13a′**), 2.45−2.37 (m, 1 H **13a′**), 2.28 (ddt, J = 16.5, 7.8, 2.3 Hz, 1 H **13a′**), 2.20−2.17 (m 2 H **13a′**), 2.07−1.99 (m, 1 H **13a** and 2 H **13a**), 1.99−1.78 (m, 1 H), 1.78−1.64 (m, 5 H), 1.46−1.37 (m, 1 H), 1.29−0.95 (m, 4 H), 1.15−0.98 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3 and 201.8 (two isomers of **13a**), 96.3 and 95.6 (two isomers of **13a**), 95.1 and 94.8 (two isomers of **13a**), 84.6 (**13a′**), 77.3, 75.9, 74.7, 74.3, 74.0, 44.3, 44.2, 44.1, 42.6, 28.8, 28.2, 26.6, 26.5, 26.24, 26.19, 26.1, 22.0, 14.3, 13.5, 12.5; IR (neat) ν 3346, 2922, 1960 cm^{-1}; HMRS (ESI) m/z calcd for $C_{12}H_{21}O^+$ 188.1587 [M + H$^+$], found 188.1584.

Mixture of (±)-1-Cyclohexyl-5,5-dimethylhex-2,3-dien-1-ol (14a) and (±)-1-Cyclohexyl-5,5-dimethylhex-3-yn-1-ol (14a′): Colorless oil (41 mg, 85%, **14a**:**14a′** = 65:35 indeterminable dr for **14a**) obtained according to **SP1** from epoxide **9a** (75 mg, 0.50 mmol) and tBu$_2$Zn·2LiBr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36−5.24 (m, 2 H **14a**), 3.91−3.87 (m, 1 H **14a**), 3.45−3.37 (m, 1 H **14a′**), 2.40 (ABX system, J = 16.4, 4.0 Hz, 1 H **14a′**), 2.27 (ABX system, J = 16.4, 8.0 Hz, 1 H **14a′**), 2.02 (br s, 1 H **14a′**), 1.92−1.77 (m, 2 H **14a** and 1 H **14a′**), 1.77−1.65 (m, 5 H), 1.50−1.37 (m, 1 H), 1.37−1.09 (m, 6 H), 1.09−0.98 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1 and 199.1 (two isomers of **14a**), 106.9 and 105.8 (two isomers of **14a**), 96.3 and 96.0 (two isomers of **14a**), 92.1 (**14a′**), 77.3, 74.9, 74.8, 74.1, 73.9, 73.9, 44.3, 44.1, 42.7, 32.0,1, 31.97, 31.3, 30.3, 29.0, 28.94, 28.87, 28.6, 38.5, 28.4, 28.3, 27.5, 26.6, 26.3, 26.2, 26.12, 26.10, 25.0; IR (neat) ν 3395, 2960, 2925, 2853, 1961 cm^{-1}; HMRS (ESI) m/z calcd for $C_{14}H_{25}O^+$ 209.1900 [M + H$^+$], found 209.1903.

Standard Procedure for the Three-Carbon Homologation of Bis(dimethylphenylsilyl)zinc (SP2). Li (50 mg, 7.23 mmol) was cut into pieces and placed in a round-bottomed flask under an argon atmosphere. Li was washed with pentane (2 × 3 mL), followed by THF (2 × 3 mL), and then suspended into THF (3 mL). Chlorotrimethylsilane (0.50 mL, 3.97 mmol) was added, and the suspension was sonicated for 15 min. The solution was removed, and activated Li was washed with THF (2 × 6 mL) and finally suspended into THF (3 mL). The mixture was degassed at the sonicator for 3 min and then cooled to 0 °C. Dimethylphenyl chlorosilane (0.31 mL, 1.87 mmol) was added, and the mixture was sonicated for 2 h at 0 °C. The deep red solution obtained was cooled to −60 °C, and $ZnBr_2$ (1.00 M solution in THF, 0.75 mL, 0.75 mmol) was added. The solution was stirred for 10 min at −20 °C to give a dark orange solution of bis(dimethylphenylsilyl)zinc [$(PhMe_2Si)_2$Zn·2LiBr] ready for use.

Under a nitrogen atmosphere, at −80 °C to a solution of epoxide (0.50 mmol) in THF (4 mL) was added dropwise nBuLi (2.20 M in hexanes, 0.25 mL, 0.55 mmol). After 10 min of stirring at −80 °C, the mixture was allowed to warm to −60 °C, stirred 20 min at this temperature, and then canulated to the above prepared solution of bis(dimethylphenylsilyl)zinc (0.75 mmol). The resulting mixture was warmed to −20 °C and then stirred for 2 h at this temperature followed by an additional stirring of 45 min at 0 °C. The reaction was quenched with MeOH (10 mL), and Et_2O (10 mL) was added. The layers were separated, and the aqueous one was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with water (15 mL) and brine (15 mL) and then dried over anhydrous $MgSO_4$. Removal of the solvent in vacuum and purification by flash chromatography (40% CH_2Cl_2/cyclohexane) afforded homopropargylic alcohols **15′** (Table 4).

(±)-1-Cyclohexyl-4-[(dimethyl)phenylsilyl]but-3-yn-1-ol (15a′): Colorless oil (103 mg, 72%) obtained according to **SP2** from epoxide **9a** (75 mg, 0.50 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.60 (m, 2 H), 7.45−7.35 (m, 3 H), 3.53 (m, 1H), 2.56 (ABX system, J = 16.9, 4.5 Hz, 1 H), 2.43 (ABX system, J = 16.9, 7.6 Hz, 1 H), 2.05−1.60 (m, 6 H), 1.57−1.40 (m, 1 H), 1.38−0.9 (m, 4 H), 0.42 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 133.7, 129.5, 128.0, 105.9, 85.6, 74.0, 42.8, 29.1, 28.2, 26.5, 26.4, 26.3, 26.1, −0.6; IR (neat) ν 3424, 3069, 2925, 2853, 2175 cm^{-1}; HMRS (ESI) m/z calcd for $C_{18}H_{26}OSiNa^+$ 309.1645 [M + Na$^+$], found 309.1649.

(±)-6-(Dimethyl)phenylsilyl-1-phenylhex-5-yn-3-ol (15b′): Colorless oil (100 mg, 65%, **15b**:**15b′** = 07:93, indeterminable dr for **15b**) obtained according to **SP2** from epoxide **9b** (88 mg, 0.50 mmol). For the mixture of **15b** and **15b′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.61 (m, 2 H), 7.47−7.35 (m, 4 H), 7.35−7.26 (m, 4 H), 7.26−7.18 (m, 2 H), 5.32 (dd, J = 6.7, 2.3 Hz, 1 H **15b**), 5.00 (app t, J = 8.7, 1 H **15b**), 4.25−4.15 (br s, 1 H **15b**), 3.78 (app quint, J = 6.4 Hz, 1 H), 2.83−2.71 (m, 1 H, m), 2.69−2.64 (m, 1 H), 2.56 (ABX system, J = 16.8, 5.2 Hz, 1 H), 2.49 (ABX system, J = 16.8, 6.6 Hz, 1 H), 2.10 (br s, 1 H), 1.95−1.86 (m, 2 H), 0.46 (s, 6 H), 0.45 (s, 6 H **15b**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (**15b**), 137.3 (**15b**), 133.7, 133.2 (**15b**), 129.7 (**15b′**), 129.5, 128.5, 128.0, 126.0, 105.0, 85.9, 69.3, 37.9, 31.9, 29.2, 0.1, −0.6; IR (neat) ν 3337, 3025, 2955, 2174 (**15b′**), 1938 (**15b**) cm^{-1}; HMRS (ESI) m/z calcd for $C_{20}H_{24}OSiNa^+$ 331.1489 [M + Na$^+$], found 331.1494.

(±)-6-(Dimethyl)phenylsilyl-1-phenylhex-5-yn-3-ol (15c′): Colorless oil (99 mg, 72%) obtained according to **SP2** from epoxide **9c** (69 mg, 0.50 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.62 (m, 2 H), 7.41−7.39 (m, 3 H), 3.80 (br s, 1 H), 2.54 (ABX system, J = 16.8, 4.7 Hz, 1 H), 2.48 (ABX system, J = 16.8, 7.5 Hz, 1 H), 1.51−1.23 (m, 5 H), 0.93−0.89 (m, 6 H), 0.43 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 133.7, 129.5, 129.4, 128.0, 106.0, 85.6, 83.5, 71.4, 47.5, 26.5, 21.9, 21.1, 11.6, −0.6; IR (neat) ν 3390, 3069, 2960, 2875, 2174 cm^{-1}; HMRS (ESI) m/z calcd for $C_{17}H_{26}OSiNa^+$ 297.1645 [M + Na$^+$], found 297.1650.

(±)-2,2-Dimethyl-6-[(dimethyl)phenylsilyl]hex-5-yn-3-ol (15d′): Colorless oil (102 mg, 79%) obtained according to **SP2** from epoxide **9d** (62 mg, 0.50 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.62 (m 2 H), 7.44−7.35 (m, 3 H), 3.49 (dd, J = 9.9, 3.0 Hz, 1 H), 2.56 (ABX system, J = 16.8, 3.0 Hz, 1 H), 2.38 (ABX system, J = 16.8, 9.9 Hz, 1 H), 2.08 (br s, 1 H), 0.95 (s, 9 H), 0.44 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 133.7, 129.5, 128.0, 106.7, 85.6, 77.4, 34.7, 25.8, 24.4, −0.6; IR (neat) ν 3579, 3069, 2957, 2870, 2174 cm^{-1}; HMRS (ESI) m/z calcd for $C_{16}H_{24}OSiNa^+$ 283.1489 [M + Na$^+$], found 283.1496.

(±)-4-(Dimethyl)phenylsilyl-1-phenylhex-5-yn-3-ol (15e′): Colorless oil (121 mg, 86%, **15e**:**15e′** = 16:84, indeterminable dr for **15e**) obtained according to **SP2** from epoxide **9e** (72 mg, 0.50 mmol). For the mixture of **15e** and **15e′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.57 (m, 4 H), 7.44−7.30 (m, 6 H), 5.33−5.28 (m, 1 H **15e**), 5.26−5.17 (m, 1 H **15e**), 4.90 (t, J = 6.2 Hz, 1 H), 2.74 (d, J = 6.2 Hz, 2 H), 2.43 (br s, 1 H), 0.41 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.2, 133.8, 133.2, 129.8, 129.5, 128.6, 128.0, 125.9, 104.9, 86.1, 72.5, 31.3, 0.1 (**15e**), −0.7; IR (neat) ν 3320, 3068, 2958, 2176 cm^{-1}; HMRS (ESI) m/z calcd for $C_{18}H_{20}OSiNa^+$ 303.1176 [M + Na$^+$], found 303.1180.

(±)-6-(Dimethyl)phenylsilyl-1,1-diphenylhex-5-yn-3-ol (15f′): Pale yellow oil (129 mg, 72%) obtained according to **SP2** from epoxide **9f** (110 mg, 0.50 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.48 (m, 4 H, m), 7.40−7.26 (m, 11 H), 3.25 (s, 2 H), 2.98 (s, 1 H), 0.31 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 137.1, 133.7, 129.4, 128.3, 128.0, 127.4, 126.4, 104.8, 87.7, 35.3, −0.8; IR (neat) ν 3555, 3064, 2957, 2174 cm^{-1}; HMRS (ESI) m/z calcd for $C_{24}H_{24}OSiNa^+$ 379.1489 [M + Na$^+$], found 379.1495.

(±)-6-(Dimethyl)phenylsilyl-1,1-dipentylhex-5-yn-3-ol (15g′): Pale yellow oil (131 mg, 76%) obtained according to **SP2** from epoxide **9g** (104 mg, 0.50 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.61 (m, 2 H′), 738−7.33 (m, 3 H), 2.44 (s, 2 H), 1,68 (br s, 1 H), 1.61−1.52 (m, 4 H), 1.26−1.40 (m, 12 H), 0.90 (t, J = 7.0 Hz, 6 H), 0.40 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 133.7, 129.4,

dx.doi.org/10.1021/jo302128n | J. Org. Chem. 2013, 78, 134−145

128.0, 105.6, 85.9, 73.7, 39.4, 39.1, 32.6, 32.4, 31.9, 23.3, 22.8, 14.2, −0.6; IR (neat) ν 3400, 3050, 2931, 2860, 2139 cm^{-1}; HMRS (ESI) m/z calcd for $C_{22}H_{36}OSiNa^+$ 367.2428 [M + Na^+], found 367.2433.

(±)-6-[(Dimethyl)phenylsilyl]oct-1-yn-4-ol (15i′): Colorless oil (87 mg, 64%, **15i**:**15i′** = 17:83, indeterminable dr for **15i**) obtained according to **SP2** from epoxide **9i** (69 mg, 0.50 mmol). For the mixture of **15i** and **15i′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.60 (m, 2 H), 7.59−7.53 (m, 2 H **15i**), 7.49−7.28 (m, 3 H), 5.28 (dd, J = 6.9, 2.2 Hz, 1 H), 4.99 (t, J = 6.9 Hz, 1 H **15i**), 4.14 (app qd, J = 6.9 Hz, 1 H **15i**), 3.80 (app quint, J = 6.7 Hz, 1 H), 2.52 (ABX system, J = 16.8, 4.8 Hz, 1 H), 2.42 (ABX system, J = 16.8, 6.8 Hz, 1 H), 1.63−1.55 (m, 2 H), 1.50−1.28 (m, 4 H), 0.95 (t, J = 6.9 Hz, 3 H), 0.42 (s, 6 H), 0.40 (s, 6 H **15i**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5 (**15i**), 138.1, 137.3, 133.8 (**15i**), 133.7, 133.1 (**15i**), 129.5, 128.0, 105.4, 88.9 (**15i**), 85.6, 83.6 (**15i**), 70.5 (**15i**), 70.0, 37.5 (**15i**), 39.1, 36.0, 29.1, 27.8, 22.7, 14.1, 0.1 (**15i**), −0.6; IR (neat) ν 3361, 3069, 2958, 2932, 2175 (**15i′**), 1939 (**15i**) cm^{-1}; HMRS (ESI) m/z calcd for $C_{16}H_{25}OSi^+$ 260.1596 [M + H^+], found 260.1604.

(±)-(1*R,2*r**,3*S**)-1,3-Dicyclohexyl-2-(hex-1-ynyl)propane-1,3-diol (16):** Under a nitrogen atmosphere, cyclohexanecarboxaldehyde (0.09 mL, 0.73 mmol) was added at −80 °C to allenylzinc **11**, freshly prepared from epoxide **9a** (99 mg, 0.56 mmol) and nBu$_2$Zn·2LiBr according to **SP1**. The mixture was warmed to −20 °C and stirred at this temperature for 1 h. The reaction was quenched with aqueous 1 M HCl solution (10 mL). Et_2O (10 mL) was added, the layers were separated, and the aqueous one was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with water (15 mL) and brine (15 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the crude reaction was purified by flash chromatography (20% Et_2O/pentane) to afford a mixture of **16** and **17** (144 mg, 68%, **16**:**17** = 85:15) as a white crystalline solid. For the mixture of **16** and **17**: mp 113−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (dd, J = 6.8, 5.4 Hz, 1 H **17**), 3.50 (dd, J = 9.0, 1.9 Hz, 1 H **17**), 3.36 (dd, J = 8.1, 2.3 Hz, 2 H), 2.83−2.82 (m, 1 H), 2.73−2.72 (m, 1 H **17**), 2.26−2.19 (m, 2 H), 2.12−2.09 (m, 1 H **17**), 2.05−2.02 (m, 2 H), 1.79−0.81 (m, 26 H), 0.92 (t, J = 7.2 Hz, 3 H) 0.90−0.87 (m, 1 H **17**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.5, 85.5 (**17**), 79.2, 76.74 (**17**), 76.68 (**17**), 79.2, 74.5, 74.2 (**17**), 42.6 (**17**), 42.3, 40.6 (**17**), 38.4 (**17**), 38.1, 31.2, 30.2 (**17**), 29.7, 29.4, 29.1, 28.9, 27.1 (**17**), 26.6, 26.5, 26.2, 26.0, 22.0, 18.7, 18.6 (**17**), 13.8; IR (neat) ν 3313, 2910, 2848, 2238 cm^{-1}; HMRS (ESI) m/z calcd for $C_{21}H_{37}O_2^+$ 321.2788 [M + H^+], found 321.2794.

(±)-(1*S*,*,5*r,6*R**)-4,6-Dicyclohexyl-5-(hex-1-ynyl)-1,3-dioxane (18):** At 20 °C, to **16** (17 mg, 0.05 mmol, **16**:**17** = 85:15) in dimethoxymethane (2 mL) was added PTSA (a spatula tip). After 16 h of stirring, the reaction was quenched with a mixture of a saturated aqueous NH_4Cl solution (10 mL) and Et_2O (10 mL) was added. The layers were separated, and the aqueous one was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with water (10 mL) then brine (10 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent afforded a mixture of **18** and **19** (17 mg, 100%, **18**:**19** = 86:14) as a white crystalline solid. For the mixture of **18** and **19**: mp 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (d, J = 6.2 Hz, 1 H), 4.89 (d, J = 6.0 Hz, 1 H **19**), 4.83 (d, J = 6.0 Hz, 1 H **19**), 4.61 (d, J = 6.2 Hz, 1 H), 3.60 (dd, J = 9.9, 1.5 Hz, 1 H **19**), 3.27 (dd, J = 9.4, 2.5 Hz, 1 H **19**), 3.04 (dd, J = 9.6, 2.2 Hz, 2 H), 2.64−2.62 (m, 1 H **19**), 2.52 (br s, 1 H), 2.22 (dt, J = 6.7, 2.2 Hz, 2 H), 2.11−2.08 (m, 2 H), 1.94−1.90 (m, 2 H **19**), 1.83−1.64 (m, 10 H), 1.53−1.39 (m, 4 H), 1.32−1.10 (m, 6 H), 0.93 (t, J = 7.2 Hz, 3 H), 1.00−0.74 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 94.3, 86.6 (**19**), 83.9, 83.7, 82.2 (**19**), 81.8 (**19**), 79.0 (**19**), 77.7 (**19**), 75.0, 39.9 (**19**), 39.8, 35.8 (**19**), 33.1, 31.3, 31.2 (**19**), 31.0 (**19**), 29.8 (**19**), 29.7, 29.6 (**19**), 29.1, 27.6 (**19**), 27.5, 26.7, 26.4, 26.1, 26.0, 25.9 (**19**), 25.8, 25.7, 22.04 (**19**), 21.98, 18.7, 13.8; HMRS (ESI) m/z calcd for $C_{22}H_{37}O_2^+$ 333.2788 [M + H^+], found 333.2790.

(±)-(1*R,2*R**,3*S**)-1-Cyclohexyl-2-(hex-1-ynyl)pentane-1,3-diol (22):** Under a nitrogen atmosphere, propanal (0.07 mL, 1.00 mmol) was added at −80 °C to allenylzinc **11**, freshly prepared from epoxide **9a** (75 mg 0.50 mmol) and nBu$_2$Zn·2LiBr according to **SP1**. The same workup as for **16** was followed to afford a mixture of **22** and **27** (104 mg, 78%, **22**:**27** = 87:13). Further purification by flash chromatography afforded analytically pure **22** as a white crystalline solid: mp 49−51 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65−3.59 (m, 1 H), 3.39−3.34 (m, 1 H), 2.94 (m, 1 H), 2.76 (m, 1 H), 2.64 (m, 1 H), 2.21 (dt, J = 6.9, 2.3 Hz, 2 H), 2.06−2.02 (m, 1 H), 1.88−0.88 (m, 22 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.6, 79.1, 76.1, 74.3, 42.3, 40.6, 31.2, 29.2, 29.1, 28.9, 26.5, 26.2, 25.9, 22.0, 18.6, 13.7, 10.2; HMRS (ESI) m/z calcd for $C_{17}H_{31}O_2^+$ 267.2319 [M + H^+], found 267.2322.

(±)-(1*R,2*S**,3*R**)-1-Cyclohexyl-4,4-dimethyl-2-(hex-1-ynyl)-pentane-1,3-diol (23):** Under a nitrogen atmosphere, pivalaldehyde (0.11 mL, 1.00 mmol) was added at −80 °C to allenylzinc **11**, freshly prepared from epoxide **9a** (71 mg 0.47 mmol) and nBu$_2$Zn·2LiBr according to **SP1**. The same workup as for **16** was followed to afford a mixture of **23** and **28** (82 mg, 59%, **23**:**28** = 85:15) as a white crystalline solid. For the mixture of **23** and **28**: mp 64−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.21−3.47 (m, 2 H **28**), 3.31−3.28 (m, 2 H), 2.89−2.87 (m, 1 H), 2.79−2.71 (m, 3 H), 2.33 (d, J = 9.6 Hz, 1 H **28**), 2.21 (dt, J = 7.0, 2.3 Hz, 2 H), 2.19 (dt, J = 7.0, 2.2 Hz, 2 H **28**), 2.09 (d, J = 5.8 Hz, 1 H **28**), 2.06−2.01 (m, 1 H), 1.87−1.83 (m, 1 H **28**), 1.78−1.64 (m, 4 H), 1.60−1.36 (m, 5 H), 1.31−1.11 (m, 3 H), 1.04−0.88 (m, 2 H), 0.98 (s, 9 H **28**), 0.96 (s, 9 H), 0.90 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.0, 87.3 (**28**), 81.3, 80.7, 77.3 (**28**), 75.8, 75.0, 41.7, 40.4, 37.5 (**28**), 36.7, 36.1, 35.8 (**28**), 31.04, 30.98 (**28**), 30.4 (**28**), 29.3, 28.9, 26.63 (**28**), 26.61 (**28**), 26.54, 26.5, 26.47, 26.3 (**28**), 26.25, 26.22, 26.0, 22.1, 18.7, 18.6 (**28**), 13.7; IR (neat) ν 3278, 2954, 2944, 2233 cm^{-1}; HMRS (ESI) m/z calcd for $C_{19}H_{34}O_2^+$ 295.2632 [M + H^+], found 295.2637.

Mixture of (±)-(1*R,2*r**,3*S**)-1,3-Dicyclohexyl-2-(3,3-dimethylbut-1-ynyl)propane-1,3-diol (24) and (±)-(1*R**,3*R**)-1,3-Dicyclohexyl-2-(3,3-dimethylbut-1-ynyl)propane-1,3-diol (29):** Under a nitrogen atmosphere, cyclohexanecarboxaldehyde (0.07 mL, 0.60 mmol) was added at −80 °C to allenylzinc **20**, freshly prepared from epoxide **9a** (69 mg 0.46 mmol) and tBu$_2$Zn·2LiBr according to **SP1**. The same workup as for **16** was followed to afford a mixture of **24** and **29** (129 mg, 88%, **24**:**29** = 36:64) as a white crystalline solid. For the mixture of **24** and **29**: mp 156−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (dd, J = 6.4, 5.7 Hz, 1 H), 3.49 (dd, J = 8.6, 1.7 Hz, 1 H), 3.36 (dd, J = 7.6, 2.8 Hz, 2 H **24**), 2.79 (t, J = 2.8 Hz, 1 H), 2.70 (dd, J = 6.4, 1.7 Hz, 1 H), 2.11−2.08 (m, 2 H **24**), 2.01−1.86 (m, 2 H), 1.23 (s, 9 H **24**), 1.22 (s, 9 H), 1.75−0.85 (m, 22 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 95.4 (**24**), 94.5, 78.5, 75.9, 74.9, 74.0, 72.9 (**24**), 42.9, 42.4, 40.8, 38.7, 38.1 (**24**), 31.4 (**24**), 31.3 (**24**), 30.3, 29.8, 29.3, 29.1, 28.9, 28.8, 27.7 (**24**), 27.6, 26.6, 26.53, 26.50. 26.4, 26.31, 26.26, 26.1, 26.0, 25.5; HMRS (ESI) m/z calcd for $C_{21}H_{37}O_2^+$ 321.2788 [M + H^+], found 321.2794.

(±)-(1*R,2*S**)-1-Cyclohexyl-2-(hex-1-ynyl)-3-methylbutane-1,3-diol (25):** Under a nitrogen atmosphere, acetone (0.12 mL, 1.60 mmol) was added at −80 °C to allenylzinc **11**, freshly prepared from epoxide **9a** (77 mg 0.51 mmol) and nBu$_2$Zn·LiBr according to **SP1**. The same workup as for **16** was followed to afford **25** (98 mg, 77%) as a white crystalline solid. Also prepared in 59% yield from epoxide *cis*-**9a** following the same procedure: mp 56−58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56−3.53 (m, 1 H), 2.89 (d, J = 5.6, 1 H), 2.69 (s, 1 H), 2.50−2.49 (m, 1 H), 2.24 (dt, J = 7.0, 2.3 Hz, 2 H), 2.14−2.08 (m, 1 H), 1.84−1.65 (m, 4 H), 1.65−1.38 (m, 5 H), 1.35 (s, 3 H), 1.31 (s, 3 H), 1.29−1.10 (m, 3 H), 1.00−0.80 (m, 2 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.8, 75.8, 74.9, 73.0, 45.8, 42.8, 31.2, 29.7, 29.4, 29.0, 27.1, 26.5, 26.1, 26.0, 22.1, 18.6, 13.7; IR (neat) ν 3354, 2922, 2852, 2232 cm^{-1}; HMRS (ESI) m/z calcd for $C_{17}H_{30}O_2^+$ 267.2319 [M + H^+], found 267.2324.

(±)-(3*S,4*R**)-3-[(Dimethyl)phenylsilyl]ethynyl-5-ethyl-2-methylheptane-2,4-diol (26):** Under a nitrogen atmosphere, acetone (0.19 mL, 2.50 mmol) was added at −80 °C to allenylzinc **21**, freshly prepared from epoxide **9c** (69 mg 0.50 mmol) and $(PhMe_2Si)_2$Zn·2LiBr according to **SP2**. The mixture was warmed to −40 °C over a period of 10 min and stirred at this temperature for 2.5 h. The same procedure workup as for **16** was followed, and the crude material was purified by flash chromatography (40% CH_2Cl_2/cyclohexane) to afford **26** (70 mg, 42%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.64 (m, 2 H), 7.42−7.36 (m, 3 H), 4.11

dx.doi.org/10.1021/jo302128n | J. Org. Chem. 2013, 78, 134−145

(dd, J = 8.6, 1.7 Hz, 1 H), 2.77 (d, J = 1.7 Hz, 1 H), 1.72−1.65 (m, 1 H), 1.63−1.55 (m, 1 H), 1.55−1.40 (m, 1 H), 1.44 (s, 3 H), 1.39 (s, 3 H), 1.23−1.37 (m, 1 H), 0.91 (t, J = 7.4 Hz, 3 H), 0.88 (t, J = 7.5 Hz, 3 H), 0.45 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 133.8, 129.7, 128.1 105.4, 89.5, 73.0, 71.7, 47.7, 45.5, 29.6, 27.7, 21.2, 20.6, 10.8, 10.7, −0.4; IR (neat) ν 3355, 3069, 2961, 2169 cm^{-1}; HMRS (ESI) m/z calcd for $C_{20}H_{32}O_2SiNa^+$ 355.2064 [M + Na^+], found 355.2065.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures; ^{1}H and ^{13}C spectra of new compounds; crystallographic data for compound **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors wish to kindly thank the MESR for grants to A.D. and M.C., and Patrick Herson for the determination of the X-ray structure of compound **24**.

■ DEDICATION

Dedicated to the memory of Robert E. Ireland.

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(23) X-ray crystal data of compound **24**: $C_{26}H_{36}O_2$; M_w = 320.52; colorless; crystal size 0.08 × 0.12 × 0.19 mm; monoclinic; space group $P2_1/c$; Z = 4; a = 9.7491(15), b = 21.6842(77), c = 9.9916(14) Å, α = 90.000, β = 105.950(11), γ = 90.000(11)°; V = 2035.5(5) Å^3; ρ_{calcd} = 1.05 g cm^{-3}; λ = 0.710730 Å (Mo Kα); μ = 0.065 cm^{-1}; KAPPA type diffractometer; temperature 250 K; θ range 1−25°; min/max h = −13/13, min/max k = −30/23, min/max l = −10/14; 19 046 measured reflections, 5879 independent, 3159 used, 209 parameters; R = 0.051 ($R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$), Rw = 0.057 ($Rw = [\Sigma w(||F_0| - |F_c||)^2/\Sigma wF_0^2]^{1/2}$), goodness of fit = 1.013, max/min $\Delta\rho$ = −0.17/0.27 e Å^{-3}. CCDC903504 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

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