Regio- and Stereoselective Synthesis of Vinylallenes by 1,5-(S_N2'')-Substitution of Enyne Acetates and Oxiranes with Organocuprates

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Dedicated to Prof. Dr. Reinhard W. Hoffmann on the occasion of his 65th birthday

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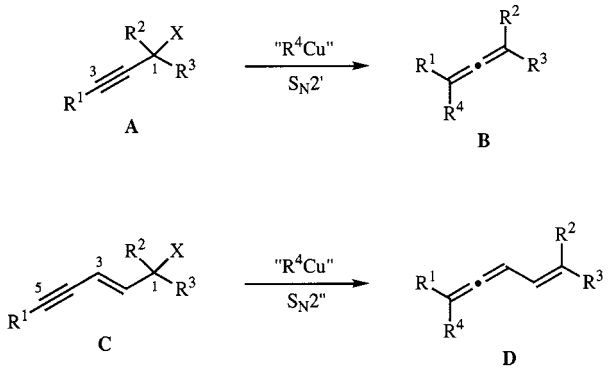
Enyne acetates **2**, **4**, **6**, and **8**, as well as enyne oxiranes **10**, with different substitution patterns react with organocuprates regioselectively under 1,5-(S_N2'')-substitution to provide vinylallenes **11** and **12**. With lithium dimethylcuprate, reduced vinylallenes originating from a (formal) transfer of a hydride ion to the substrate are formed in some cases. The products are usually obtained as mixtures of (*E*/*Z*)-isomers; however, pure (*E*)-vinylallenes are formed occasionally. The 1,5-substitutions can also be carried out with catalytic amounts of copper reagents. The reaction of chiral enyne acetate (*S*)-**2a** with *t*Bu_2CuLi · LiCN proceeds enantioselectively, so that this transformation constitutes a new case of remote stereocontrol.

Introduction

Allenes are fascinating and useful molecules for several reasons: the allenic moiety is found in many natural products, it can be utilized for the assembly of complex target molecules of biological and/or pharmacological relevance, and it constitutes an axis of chirality if substituted suitably.[1] Among several known methods for the synthesis of allenes,[1,2] the reaction of propargylic electrophiles **A** with organocopper reagents is of particular importance because it usually leads to the desired products **B** with high regio- and stereoselectivity (i.e. as *anti*-S_N2' substitution with propargylic rearrangement).[1,3] This opens a reliable stereoselective route to chiral allenes since the starting materials are easily accessible in enantiomerically and/or diastereomerically pure form.[4] Additional virtues of the method are its applicability to substrates with many different leaving groups X (among others, propargylic acetates, mesylates, halides and epoxides have been converted into allenes successfully) and the possibility to perform it catalytically, i.e. with Grignard reagents and catalytic amounts of copper salts.[1,3]

In contrast to this well-established transformation, there is almost no precedent for the corresponding reactions of enynoic electrophiles **C**.[5,6] Of course, the introduction of an additional double bond into the substrate causes an increase of the number of possible regioisomeric products: the nucleophile may attack at C-1, C-3, or C-5. The latter case, i.e. a S_N2'' or 1,5-substitution, would be the most interesting, as this would lead directly to vinylallenes **D** which, inter alia, are valuable dienes in regio- and stereoselective Diels−Alder reactions.[7] Additionally, it would be interesting to study the stereochemical course of such transformations, i.e. the possibility to control the configuration of the olefinic double bond of the vinylallene, and to perform the reactions enantio- or diastereoselectively (this would constitute one of the few cases of remote stereocontrol in organocopper chemistry[6,8]). We therefore examined the reactions of enyne electrophiles with organocopper reagents in greater detail; our first results concerning the scope of 1,5-substitutions of enyne acetates and oxiranes are presented here.



Scheme 1

Results and Discussion

After preliminary studies had shown that the acetate group is a suitable leaving group for 1,5-substitutions of primary, secondary, and tertiary enyne electrophiles,[2b] we synthesized several enyne acetates with different steric and electronic properties. Thus, the secondary acetates **2a**−**c** bearing different substituents at the triple bond were ob-

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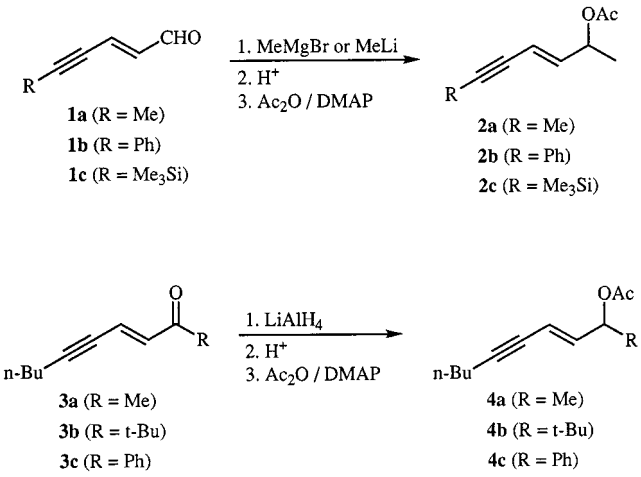
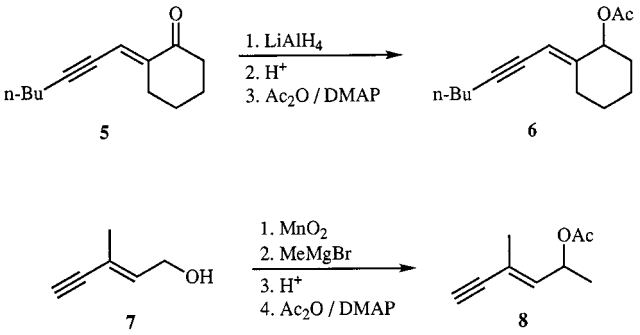
tained from the aldehydes **1** by addition of MeLi or MeMgBr and esterification of the crude alcohols (for details see Experimental Section). Similarly, reduction of the ketones **3** followed by acylation gave acetates **4a**−**c**.



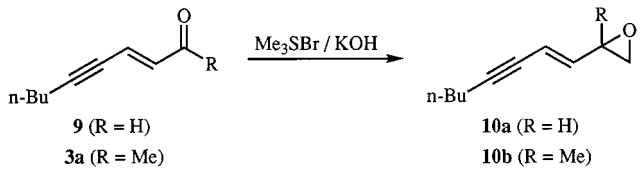
Scheme 2

Different substitution patterns were elaborated from ketone **5** and the commercially available alcohol **7**. Thus, reduction and esterification of **5** provided the cyclic acetate **6**, and oxidation of **7** to the aldehyde with activated manganese dioxide, followed by addition of MeMgBr and acylation gave substrate **8**.



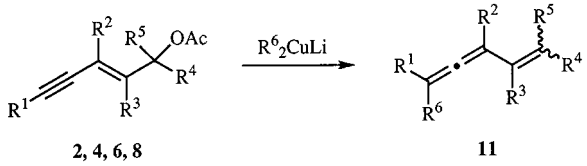
Scheme 3

Another leaving group which has been used frequently in S_N2' substitutions is the oxirane moiety; in contrast to simpler substrates which furnish unfunctionalized hydrocarbons, oxiranes give substitution products with an additional alcohol function which can be elaborated further.[3] In order to examine substrates of this type also here, we synthesized the enyne oxiranes **10a/b** by treatment of the corresponding carbonyl compounds **3a** and **9** with the sulfur ylide formed from trimethylsulfonium bromide and base.[9]



Scheme 4

With this set of different enyne electrophiles at hand, we examined their behavior in substitution reactions in greater detail. The results of the reaction of the enyne acetates **2**, **4**, **6** and **8** with organocuprates are summarized in Table 1.



Scheme 6

Treatment of enyne acetate **2a** with 2.0 equiv. of lithium di-*n*-butylcuprate (nBu$_2$CuLi · LiI) in diethyl ether at −80°C resulted in complete consumption of the starting material within 1 h. After aqueous workup and purification of the crude product by column chromatography, the desired 1,5-substitution product, vinylallene **11a**, was isolated with 90% yield as a 2:1 mixture of (*E*/*Z*) isomers (Table 1, entry 1). The structural assignment of this hydrocarbon bases on the typical allenic resonances in the ^{13}C-NMR spectrum at δ = 203.5 (C-5), 100.6/100.5 (C-6), and 93.2/88.6 (C-4), as well as on the appearance of the characteristic peak at $\tilde{\nu}$ = 1948 cm^{-1} in the IR spectrum. Very similar values were found for all other substitution products obtained in this work. In this case, as in all other cases examined here, the isomers could not be separated by column chromatography. Unfortunately, the resonances for the olefinic and allenic protons in the ^{1}H-NMR spectrum could not be resolved; consequently an assignment of the configuration of the olefinic double bond of **11a** with the vicinal coupling constant $^3J_{2,3}$ (or with NOE experiments) was not possible. However, the ^{13}C-NMR resonances observed of C-4 for (*E*)-**11a** (δ = 93.2) and (*Z*)-**11a** (δ = 88.6) are characteristic for the geometrical isomers (see below) and were used for the assignment in this case.

When THF was employed instead of diethyl ether as solvent, the reaction of **2a** and n-Bu$_2$CuLi · LiI proceeded only sluggishly even at elevated temperatures. Therefore, diethyl ether was used as solvent for 1,5-substitutions throughout this work, and the analogouos reaction of **2a** with the cyano-Gilman reagent tBu$_2$CuLi · LiCN[10] under these conditions furnished vinylallene **11b** with 93% yield as a 1:3 mixture of (*E*/*Z*)-isomers (entry 2). Thus, the steric demand of the cuprate affects the (*E*/*Z*)-selectivity, but not the regioselectivity of the substitution. Again, the isomers could not be separated chromatographically; nevertheless, all ^{1}H- and ^{13}C-NMR resonances could be assigned, allowing an unambigous distinction of the isomers. Particularly indicative are the coupling constants $^3J_{2,3}$ = 15.5 Hz for (*E*)-**11b** and $^3J_{2,3}$ = 10.6 Hz for (*Z*)-**11b**. Also the differences of chemical shifts of the (*E*)- and (*Z*)-isomer observed for 2-H (δ = 5.58 vs. 5.38), 4-H (δ = 5.70 vs. 5.99), and C-4 (δ = 93.6 vs. 89.1) are very useful for the assignment of the configuration of the olefinic double bond since similar patterns were found for many more vinylallenes prepared in this work.

Table 1: Reaction of enyne acetates **2**, **4**, **6**, and **8** with organocuprates

Entry	Substrate	Cuprate	Product	R^1	R^2	R^3	R^4	R^5	R^6	Yield [%]	(*E*)/(*Z*)
1	**2a**	nBu$_2$CuLi · LiI	**11a**	Me	H	H	Me	H	nBu	90	67:33
2	**2a**	tBu$_2$CuLi · LiCN	**11b**	Me	H	H	Me	H	tBu	93	25:75
3	**2b**	tBu$_2$CuLi · LiCN	**11c**	Ph	H	H	Me	H	tBu	80	50:50
4	**2c**	nBu$_2$CuLi · LiCN	**11d**	Me$_3$Si	H	H	Me	H	nBu	80	60:40
5	**2c**	tBu$_2$CuLi · LiCN	**11e**	Me$_3$Si	H	H	Me	H	tBu	96	40:60
6	**4a**	Me$_2$CuLi · LiI	**11a**	nBu	H	H	Me	H	Me	[a]	[a]
7	**4a**	tBu$_2$CuLi · LiCN	**11f**	nBu	H	H	Me	H	tBu	78	33:67
8	**4b**	Me$_2$CuLi · LiI	**11g**	nBu	H	H	tBu	H	Me	92	>99:<1
9	**4b**	tBu$_2$CuLi · LiCN	**11h**	nBu	H	H	tBu	H	tBu	95	60:40
10	**4c**	Me$_2$CuLi · LiI	**11i**	nBu	H	H	Ph	H	Me	66	>99:<1
11	**4c**	tBu$_2$CuLi · LiCN	**11j**	nBu	H	H	Ph	H	tBu	94	40:60
12	**6**	Me$_2$CuLi · LiI	**11k**	nBu	H	(CH$_2$)$_4$		H	Me	83	–
13	**6**	tBu$_2$CuLi · LiCN	**11l**	nBu	H	(CH$_2$)$_4$		H	tBu	85	–
14	**8**	tBu$_2$CuLi · LiCN	**11m**	H	Me	H	Me	H	tBu	83	>99:<1

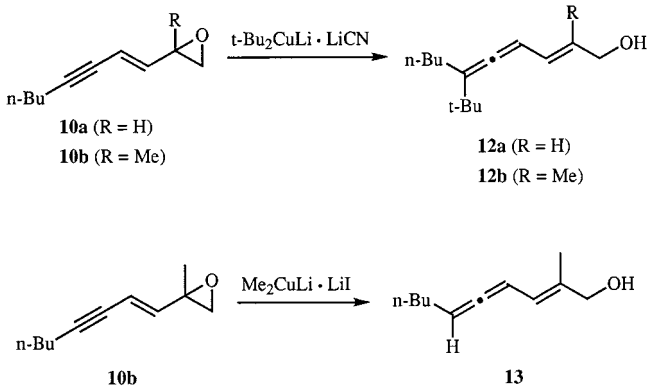
[a] Formation of a 1:1-mixture of **11a** and the corresponding "reduced" vinylallene with R^6 = H (see text).

Next, we examined the possible influence of the substituent at the triple bond of the enyne acetate on the course of the substitution. The reaction of the phenyl-substituted acetate **2b** with tBu$_2$CuLi · LiCN, as well as the reactions of the silylated substrate **2c** with both the *n*-butyl and *tert*-butyl cuprate, proceeded without difficulty to give the 1,5-substitution products **11c**–**e** with high chemical yields and (*E*)/(*Z*) ratios around 1:1 (Table 1, entries 3–5). Thus, the introduction of bulky or electron-releasing groups at this position does not alter the course of the reaction with organocuprates. The structural assignment was again made as outlined above with the typical coupling constants and chemical shifts (see Experimental Section). A surprising observation was then made when we tried to prepare the vinylallene **11a** by addition of lithium dimethylcuprate (Me$_2$CuLi · LiI) to the *n*-butyl-substituted acetate **4a** (entry 6): the desired product was formed, but only as a 1:1-mixture with the corresponding "reduced" vinylallene bearing a hydrogen atom instead of a methyl group at C-6 (i.e. R^6 = H). Both products were obtained as 2:1 mixtures of (*E*/*Z*)-isomers with a combined yield of 80%. A similar product mixture was isolated when the cyano-Gilman reagent Me$_2$-CuLi · LiCN was used. There is some precedent for the formation of (formal) reduction products in organocopper chemistry[8b,11] (also in substitution reactions of propargylic electrophiles[11c,11f]), and this has been attributed to electron transfer processes, reactions of copper hydride species or protonation of organometallic intermediates. Interestingly, with enyne acetates as substrates reduction only occurred when methyl cuprates were employed as reagents. Thus, the reaction of **4a** with the *tert*-butyl cuprate tBu$_2$-CuLi · LiCN under the usual conditions (diethyl ether, −80°C) proceeded cleanly to give the vinylallene **11f** as a 1:2-mixture of (*E*/*Z*)-isomers with 78% yield (Table 1, entry 7). Again, the characteristic ^{13}C-NMR resonances of C-4 at δ = 96.3 and 91.7 served for the assignment of the geometrical isomers.

Until now, only enyne acetates with R^4 = Me had been used as substrates for 1,5-substitutions; we next extended our study to the acetates **4b**/**c** with *tert*-butyl and phenyl groups, respectively, at this position (entries 8–11). Also in these cases, the reactions with the methyl and *tert*-butyl cuprates proceeded with the desired regioselectivity to give the vinylallenes with good (**11i**) to excellent yields (**11g**, **h**, **j**), and the substitution products formed from tBu$_2$CuLi · LiCN were isolated with (*E*)/(*Z*) ratios of about 1:1. However, distinct differences from the previous results were observed in the reactions of **4b**/**c** with lithium dimethylcuprate (Me$_2$CuLi · LiI): no reduction products with R^6 = H were formed, and the vinylallenes **11g**/**i** were isolated as (*E*)-isomers exclusively. The configuration of the olefinic double bond was assigned with the vicinal coupling constant $^3J_{H,H}$ (15.0/15.8 Hz), and also the characteristic chemical shifts in the ^{1}H- and ^{13}C-NMR spectra (see above) were observed as expected. The reactions of the remaining enyne acetates **6** and **8** with the cuprates Me$_2$CuLi · LiI or tBu$_2$CuLi · LiCN (Table 1, entries 12–14) confirm the observations made with the previous substrates: the regioselectivity does not depend on the structure of the reactants, and in all cases 1,5-substitution takes place exclusively to give the vinylallenes **11k**–**m** with good yields (83–85%). In the case of the acyclic vinylallene **11m**, only one isomer was formed which, according to the vicinal coupling constant $^3J_{2,3}$ = 15.5 Hz, has the (*E*)-configuration.

So far, our study has shown that the 1,5-substitution of enynoic acetates is a general method for the generation of vinylallenes with different substitution patterns. Although these products were often formed as mixtures of (*E*/*Z*)-isomers, pure (*E*)-vinylallenes could be obtained in some cases. We then extended our studies to the enyne oxiranes **10a**/**b** which were treated with lithium dimethylcuprate (Me$_2$CuLi · LiI) or tBu$_2$CuLi · LiCN under the usual conditions. It turned out that both substrates react cleanly with the *tert*-butyl cuprate to give the vinylallenes **12** with good yields (61–72%); whereas **12a** was obtained as (*E*)-isomer only, an (*E*)/(*Z*) ratio of 80:20 was determined for **12b**. In the latter case, the (*E*)-configuration of the major isomer was assigned with NOE experiments which confirmed the proximity of 1-H and 3-H, as well as of the methyl group at C-2 and 4-H (see Experimental Section). The unpredictable behavior of lithium dimethylcuprate in these transformations was again unraveled when oxirane **10b** was treated

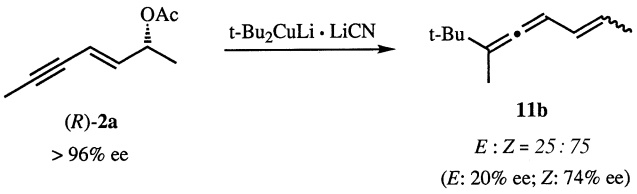
with this reagent: exclusive reduction to the vinylallene **13** took place, which was isolated with 54% yield as single isomer. The similarity of the NMR data with those of (*E*)-**12b** let us assume that this also possesses the (*E*)-configuration.



Scheme 6

Finally, we wanted to establish whether the 1,5-substitutions of enyne electrophiles can also be carried out with catalytic amounts of copper salts, and whether they take place enantioselectively with chirality transfer from the substrate to the vinylallene. Complex product mixtures were obtained when enyne acetate **2a** was treated with *n*BuMgCl or *t*BuMgCl in the presence of catalytic amounts of CuCl according to procedures for S_N2'-substitutions of propargylic acetates[3], and the use of stoichiometric amounts of magnesium cuprates $R_2CuMgCl$ (prepared from 2 equiv. of Grignard reagents and 1 equiv. of copper salts) gave rise to the formation of the S_N2'-(1,3)-substitution product. These findings clearly indicate that the presence of *lithium* cuprates is essential for the desired 1,5-substitutions. Accordingly, we tested a different procedure which has been used successfully in catalytic 1,6-addition reactions to acceptor-substituted enynes,[2b] i.e. the simultaneous addition of substrate and organolithium reagent to catalytic amounts of the cuprate. Indeed, the reaction of **2a** with 1 equiv. of *t*BuLi and 10 mol% of $t\text{Bu}_2\text{CuLi} \cdot \text{LiI}$ in diethyl ether at −50°C under these conditions proceeded cleanly to give vinylallene **11b** with 90% yield as 1:2 mixture of (*E*/*Z*) isomers. Thus, the 1,5-substitutions can also be performed efficiently with reduced amounts of organolithium and copper reagents; it is reasonable to assume that the cuprate R_2CuLi is also responsible for the product formation in the catalytic procedure, and it is regenerated continuously by reaction of the organocopper reagent RCu produced in the 1,5-substitution with the added RLi.

In order to explore whether the 1,5-substitution of chiral enyne acetates takes place enantioselectively with efficient chirality transfer from the center of chirality of the substrate to the stereogenic axis of the vinylallene, the enantiomerically pure enyne acetate (*R*)-**2a** (> 96% ee by GC analysis) was generated by kinetic deracemization of the racemic acetate in the presence of the lipase from *Pseudomonas fluorescens*. In a preliminary experiment, this was treated with the cyano-Gilman reagent $t\text{Bu}_2\text{CuLi} \cdot \text{LiCN}$; as in the corresponding reaction of racemic **2a** (Table 1, entry 2), vinylallene **11b** was formed as a 1:3 mixture of (*E*/*Z*)-isomers, and the GC analysis with octakis(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin as chiral stationary phase revealed enantiomeric excesses of 20% ee for (*E*)-**11b** and 74% ee for (*Z*)-**11b**. Thus, the 1,5-substitution of chiral enyne acetates does indeed take place enantioselectively with remote stereocontrol.



Scheme 7

Conclusion

In this work we have shown that 1,5-(S_N2'')-substitutions of enyne acetates and oxiranes with organocuprates take place with complete regiocontrol to provide vinylallenes, regardless of the steric and electronic properties of the reactants. With lithium dimethylcuprate, however, reduced vinylallenes originating from a (formal) transfer of a hydride ion to the substrate are formed in some cases. The products are usually obtained as mixtures of (*E*/*Z*)-isomers; however, pure (*E*)-vinylallenes are formed occasionally. We were also able to show that the 1,5-substitution of chiral enyne acetates proceeds enantioselectively, so that this reaction constitutes a new type of remote stereocontrol. Further work will be devoted to the optimization of a catalytic version of these transformations, as well as to the investigation of the chirality transfer and the determination of the absolute configuration of the products.

Experimental Section

General Information: NMR spectra were recorded with a Bruker WM 400 spectrometer at 400 MHz (^{1}H) and 100.6 MHz (^{13}C) in $CDCl_3$ as solvent and internal standard (δ = 7.27 for ^{1}H, δ = 77.05 for ^{13}C). The signals of a major component of a product mixture are marked with an asterisk (*). − IR spectra were obtained with a Perkin-Elmer 1600 FT-IR spectrometer, mass spectra with A.E.I. MS-30 and MS-50 spectrometers (EI, 70 eV). GC-MS spectra were recorded with a Hewlett Packard HP 5850 Series II spectrometer. − GC analyses were carried out with a Dani 86.10 or a Carlo Erba GC 8000 gaschromatograph with hydrogen as carrier gas and OV-1701 or octakis(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin capillary colums. − Elemental analyses were obtained with Perkin-Elmer CHN 240 A and B analyzers. Due to their tendency to polymerization and oxidation, correct elemental analyses of the vinylallenes prepared in this work could not be obtained; instead, they were characterized by high-resolution mass spectra (HRMS), and GC analysis showed them to be at least 90% pure. − The reactions were carried out in thoroughly dried glassware under argon. Diethyl ether was distilled from $LiAlH_4$ prior to use. MeLi, *n*BuLi, and *t*BuLi were titrated with diphenylacetic acid according to the procedure of Kofron and Baclawski.[12]

2-Acetoxy-3-hepten-5-yne (2a): The crude aldehyde **1a** prepared from 6.91 g (50.0 mmol) of ethyl 2-hexen-4-ynoate according to ref.[7] was dissolved in 100 mL of diethyl ether and treated at −80°C with 17 mL (51.0 mmol) of MeMgBr (3.0 M in diethyl ether). Within 2 h the mixture was warmed with stirring to −40°C and then hydrolyzed by addition of 30 mL of a saturated NH_4Cl solution. After extraction with diethyl ether, the combined organic layers were washed with water and dried with $MgSO_4$. The solvent was removed in vacuo, and the crude alcohol thus obtained was dissolved in 150 mL of diethyl ether and treated with 10.2 g (0.10 mol) of acetic anhydride and a small amount of 4-(dimethylamino)-pyridine (DMAP). After stirring for 2 h at room temperature, 10 mL of methanol was added, and the mixture was stirred for another 15 min before neutralization with a saturated $NaHCO_3$ solution. Separation of the layers was followed by washing of the aqueous phase with diethyl ether. The combined organic layers were dried with K_2CO_3; the crude product obtained removal of the solvent in vacuo was purified by column chromatography (SiO_2, cyclohexane/diethyl ether, 10:1) to give 5.60 g (74%) of **2a** as colorless oil. − ^{1}H NMR: δ = 5.96 (dd, *J* = 15.9/6.5 Hz, 1 H, 3-H), 5.67 (dq, *J* = 15.9/2.2 Hz, 1 H, 4-H), 5.33 (qi, *J* = 6.5 Hz, 1 H, 2-H), 2.02 (s, 3 H, $OCOCH_3$), 1.92 (d, *J* = 2.2 Hz, 3 H, 7-H), 1.28 (d, *J* = 6.5 Hz, 1 H, 1-H). − ^{13}C NMR: δ = 170.1 (x, C=O), 140.4 (+, C-3), 112.0 (+, C-4), 96.1 (x, C-6), 77.2 (x, C-5), 70.2 (+, C-2), 21.3 (+,C-1), 20.0 (+,$OCOCH_3$), 4.3 (+, C-7). − IR: $\tilde{\nu}$ = 2921 cm^{-1} (s, C−H), 2222 (m, C≡C), 1743 (s, C=O), 1237 (s, C−O−C). − MS: *m/z* (%) = 152 (13) [M^+], 137 (25) [M − CH_3], 109 (73) [M − $COCH_3$], 91 (100). − $C_9H_{12}O_2$ (152.19): calcd. C 71.03, H 7.95; found C 70.66, H 8.02.

2-Acetoxy-6-phenyl-3-hexen-5-yne (2b): Crude phenylpropynal was prepared from 6.13 g (60.0 mmol) of phenylacetylene according to ref.[13] and dissolved in 50 mL of THF. After addition of 1.36 g (6.0 mmol) of anhydrous $ZnBr_2$, a solution of 14.6 g (60.0 mmol) of α,α-bis(trimethylsilyl)-*tert*-butylacetaldimine[14] in 25 mL of THF was added dropwise with stirring. The mixture was stirred for 1 h at room temperature and then treated with 120 mL of diethyl ether and a solution of 10.0 g (74.0 mmol) of $ZnCl_2$ in 100 mL of water. After stirring for another hour at room temperature, the mixture was filtered through Celite, and the layers were separated. The aqueous layer was washed with diethyl ether, and the combined organic layers were washed with water and dried with $MgSO_4$. Removal of the solvent in vacuo gave crude aldehyde **1b** which was converted into acetate **2b** according to the procedure given for **2a** by treatment with 38 mL (61 mmol) of MeLi (1.6 M solution in diethyl ether) and 12.2 g (0.12 mol) of acetic anhydride. Yield: 6.70 g (52%) of **2b** as colorless oil after purification by column chromatography (SiO_2, cyclohexane/diethyl ether, 10:1). − ^{1}H NMR: δ = 7.42−7.30 (m, 5 H, Phenyl-H), 6.17 (dd, *J* = 16.0/6.4 Hz, 1 H, 3-H), 5.92 (dd, *J* = 16.0/1.2 Hz, 1 H, 4-H), 5.43 (qid, *J* = 6.4/1.2 Hz, 1 H, 2-H), 2.07 (s, 3 H, $OCOCH_3$), 1.36 (d, *J* = 6.4 Hz, 1 H, 1-H). − ^{13}C NMR: δ = 170.2 (x, C=O), 141.8 (+, C-3), 131.6 (+, C-2′), 128.5/128.4 (+, C-3′/4′), 123.1 (x, C-1′), 111.4 (+, C-4), 90.8 (x, C-6), 86.9 (x, C-5), 70.1 (+, C-2), 21.3 (+,C-1), 20.0 (+,$OCOCH_3$). − IR: $\tilde{\nu}$ = 2958 cm^{-1} (s, C−H), 2144 (m, C≡C), 1742 (s, C=O), 1251 (s, C−O−C). − MS: *m/z* (%) = 214 (24) [M^+], 199 (18) [M − CH_3], 171 (100), 153 (50). − $C_{14}H_{14}O_2$ (214.26): calcd. C 78.48, H 6.59; found C 78.46 H 6.70.

2-Acetoxy-6-trimethylsilyl-3-hexen-5-yne (2c): According to the procedure given for **2b**, crude 3-trimethylsilylpropynal prepared from 5.89 g (60.0 mmol) of trimethylsilylacetylene was converted into enyne acetate **2c** by treatment with 1.36 g (6.0 mmol) of anhydrous $ZnBr_2$, 14.6 g (60.0 mmol) of α,α-bis(trimethylsilyl)-*tert*-butylacetaldimine, 38 mL (61 mmol) of MeLi (1.6 M solution in diethyl ether) and 12.2 g (0.12 mol) of acetic anhydride. Yield: 6.30 g (50%) of **2c** as colorless oil after purification by column chromatography (SiO_2, cyclohexane/diethyl ether, 10:1). − ^{1}H NMR: δ = 6.10 (dd, *J* = 16.0/6.4 Hz, 1 H, 3-H), 5.69 (dd, *J* = 16.0/1.2 Hz, 1 H, 4-H), 5.33 (qid, *J* = 6.4/1.2 Hz, 1 H, 2-H), 2.02 (s, 3 H, $OCOCH_3$), 1.28 (d, *J* = 6.4 Hz, 1 H, 1-H), 0.15 [s, 9 H, $Si(CH_3)_3$]. − ^{13}C NMR: δ = 170.4 (x, C=O), 143.4 (+, C-3), 111.4 (+, C-4), 101.8 (x, C-6), 96.2 (x, C-5), 70.1 (+, C-2), 21.4 (+, C-1), 20.3 (+,$OCOCH_3$), 0.1 [+, $Si(CH_3)_3$]. − IR: $\tilde{\nu}$ = 2978 cm^{-1} (s, C−H), 2252 (m, C≡C), 1735 (s, C=O), 1240 (s, C−O−C). − MS: *m/z* (%) = 210 (21) [M^+], 195 (16) [M − CH_3], 167 (59), 73 (100). − $C_{11}H_{18}O_2Si$ (210.34): calcd. C 62.81, H 8.63; found C 62.95, H 9.34.

2-Acetoxy-3-decen-5-yne (4a): 7.50 g (50.0 mmol) of ketone **3a** (prepared with 96% yield by olefination of 2-heptynal[13] with (diethoxyphosphoryl)acetone[15] in the presence of K_2CO_3/H_2O[16]) in 50 mL of diethyl ether was added dropwise at −60°C to a stirred suspension of 1.90 g (50.0 mmol) of $LiAlH_4$ in 100 mL of diethyl ether. After stirring for 1 h at −60°C, 20 mL of a saturated NH_4Cl solution was added dropwise with vigorous stirring and the mixture was filtered through Celite. The crude alcohol obtained after removal of the solvent in vacuo was esterified according to the procedure given for **2a** by treatment with 10.2 g (0.10 mol) of acetic anhydride. Chromatographic purification (SiO_2, cyclohexane/diethyl ether, 10:1) gave 9.00 g (93%) of **4a** as yellow oil. − ^{1}H NMR: δ = 5.95 (dd, *J* = 15.9/6.5 Hz, 1 H, 3-H), 5.65 (d, *J* = 15.9 Hz, 1 H, 4-H), 5.32 (qi, *J* = 6.5 Hz, 1 H, 2-H), 2.27 (t, *J* = 5.1 Hz, 2 H, 7-H), 2.01 (s, 3 H, $OCOCH_3$), 1.98−1.32 (m, 4 H, 8/9-H), 1.27 (d, *J* = 6.4 Hz, 1 H, 1-H), 0.89 (t, *J* = 6.9 Hz, 3 H, 10-H). − ^{13}C NMR: δ = 170.1 (x, C=O), 140.2 (+, C-3), 112.1 (+, C-4), 92.1 (x, C-6), 77.9 (x, C-5), 70.2 (+, C-2), 30.7 (−, C-8), 21.9 (−, C-7), 21.2 (+, C-1), 19.9 (+, $OCOCH_3$), 19.0 (−, C-9), 13.6 (+, C-10). − IR: $\tilde{\nu}$ = 2932 cm^{-1} (s, C−H), 2216 (m, C≡C), 1742 (s, C=O), 1237 (s, C−O−C). − MS: *m/z* (%) = 194 (20) [M^+], 179 (9) [M − CH_3], 151 (71) [M − $COCH_3$], 95 (100). − $C_9H_{12}O_2$ (194.27): calcd. C 74.19, H 9.34; found C 74.15, H 9.61.

3-Acetoxy-2,2-dimethyl-4-undecen-6-yne (4b): The reduction of 6.92 g (36.0 mmol) of ketone **3b** (obtained with 87% yield from 2-heptynal[13] and 1-(diethoxyphosphoryl)-3,3-dimethyl-2-butanone[15] according to ref.[16]) with 1.37 g (36.0 mmol) of $LiAlH_4$ and the subsequent esterification with 7.40 g (72.0 mmol) of acetic anhydride was carried out as described for **4a** and provided 8.00 g (94%) of **4b** as yellow oil after chromatographic purification of the crude product (SiO_2, cyclohexane/diethyl ether, 10:1). − ^{1}H NMR: δ = 5.93 (dd, *J* = 16.0/7.6 Hz, 1 H, 4-H), 5.63 (dm, *J* = 16.0 Hz, 1 H, 5-H), 4.96 (dd, *J* = 7.6/1.0 Hz, 1 H, 3-H), 2.27 (td, *J* = 6.6/2.0 Hz, 2 H, 8-H), 2.03 (s, 3 H, $OCOCH_3$), 1.52−1.33 (m, 4 H, 9/10-H), 0.88 [s, 9 H, $C(CH_3)_3$], 0.84 (t, *J* = 7.3 Hz, 3 H, 11-H). − ^{13}C NMR: δ = 170.2 (x, C=O), 136.6 (+, C-4), 114.1 (+, C-5), 91.7 (x, C-7), 80.9 (+, C-3), 78.2 (x, C-6), 34.5 (x, C-2), 30.7 (−, C-8), 25.7 [+, $C(CH_3)_3$], 22.0 (+, $OCOCH_3$), 21.1 (−, C-9), 19.1 (−, C-10), 13.6 (+, C-11). − IR: $\tilde{\nu}$ = 2958 cm^{-1} (s, C−H), 2144 (m, C≡C), 1742 (s, C=O), 1251 (s, C−O−C). − MS: *m/z* (%) = 236 (8) [M^+], 179 (10), 152 (11), 137 (100). − $C_{15}H_{24}O_2$ (236.35): calcd. C 76.23, H 10.23; found C 76.10, H 10.37.

1-Acetoxy-1-phenyl-2-nonen-4-yne (4c): The reduction of 7.00 g (33.0 mmol) of ketone **3c** (obtained with 79% yield from 2-heptynal[13] and 2-(diethoxyphosphoryl)-1-phenylethanone[15] according to ref.[16]) with 1.30 g (33.0 mmol) of $LiAlH_4$ and the subsequent esterification with 6.70 g (66.0 mmol) of acetic anhydride was carried out as described for **4a** and provided 8.20 g (97%) of **4c** as orange oil after chromatographic purification of the crude

product (SiO_2, cyclohexane/diethyl ether, 10:1). − ^{1}H NMR: δ = 7.24−7.17 (m, 5-H, Phenyl-H), 6.19 (dd, *J* = 6.4/1.0 Hz, 1 H, 1-H), 6.06 (dd, *J* = 15.8/6.4 Hz, 1 H, 2-H), 5.63 (dm, *J* = 15.8 Hz, 1 H, 3-H), 2.20 (td, *J* = 6.9/2.2 Hz, 2 H, 6-H), 2.01 (s, 3 H, OCOCH$_3$), 1.45−1.25 (m, 4 H, 7/8-H), 0.82 (t, *J* = 7.2 Hz, 3 H, 9-H). − ^{13}C NMR: δ = 170.0 (x, C=O), 138.8 (+, C-2), 138.4 (x, Phenyl), 128.6, 128.3, 127.2 (3+, Phenyl), 113.2 (+, C-3), 92.8 (x, C-5), 80.0 (x, C-4), 75.4 (+, C-1), 30.7 (−, C-6), 21.9 (−, C-7), 21.2 (+, OCO*C*H$_3$), 19.1 (−, C-8), 13.6 (+, C-9). − IR: $\tilde{\nu}$ = 2957 cm^{-1} (s, C−H), 2217 (m, C≡C), 1740 (s, C=O), 1229 (s, C−O−C). − MS: *m/z* (%) = 256 (19) [M$^+$], 241 (5) [M − CH$_3$], 214 (54), 105 (100). − $C_{17}H_{20}O_2$ (256.34): calcd. C 79.65, H 7.86; found C 79.27, H 8.24.

1-Acetoxy-2-(2-heptynyliden)cyclohexene (6): The reduction of 7.40 g (39.0 mmol) of ketone **5**[17] with 1.50 g (39.0 mmol) of $LiAlH_4$ and the subsequent esterification with 8.00 g (78.0 mmol) of acetic anhydride was carried out as described for **4a** and provided 7.00 g (77%) of **6** as yellow oil after chromatographic purification of the crude product (SiO_2, cyclohexane/diethyl ether, 10:1). − ^{1}H NMR: δ = 5.36 (s, 1 H, 1′-H), 5.17 (m, 1 H, 1-H), 2.32−2.16 (m, 3 H, 4′-H), 2.01 (s, 3 H, OCOCH$_3$), 2.10−1.28 (m, 12 H, 3/4/5/6/5′/6′-H), 0.86 (t, *J* = 7.0 Hz, 3 H, 7′-H). − ^{13}C NMR: δ = 169.8 (x, C=O), 149.0 (x, C-2), 103.1 (+, C-1′), 94.4 (x, C-3′), 76.8 (x, C-2′), 74.0 (+, C-1), 33.2 (−, C-6), 30.8 (+, C-5′), 29.1 (−, C-3), 26.5 (−, C-4), 22.8 (−, C-5), 21.8 (−, C-6′), 21.0 (+,OCO*C*H$_3$), 19.1 (−, C-4′), 13.5 (+, C-7′). − IR: $\tilde{\nu}$ = 2933 cm^{-1} (s, C−H), 2212 (w, C≡C), 1740 (s, C=O), 1236 (s, C−O−C). − MS: *m/z* (%) = 234 (19) [M$^+$], 219 (4) [M − CH$_3$], 191 (36) [M − COCH$_3$], 91 (100). − $C_{15}H_{22}O_2$ (234.33): calcd. C 76.88, H 9.46; found C 76.44, H 9.68.

2-Acetoxy-4-methyl-3-hexen-5-yne (8): To a solution of 3.80 g (39.0 mmol) of **7** in 150 mL of diethyl ether was added 68.0 g (0.75 mol) of activated MnO_2 (Merck), and the mixture was stirred for 4 h at room temperature. After filtration through Celite, most of the solvent was removed by distillation. The conversion of the crude aldehyde thus obtained into acetate **8** was carried out according to the procedure given for **2a** by treatment with 13 mL (39 mmol) of MeMgBr (3.0 M solution in diethyl ether) and 8.00 g (78.0 mmol) of acetic anhydride. Yield: 3.80 g (64%) of **8** as yellow oil after purification by column chromatography (SiO_2, cyclohexane/diethyl ether, 10:1). − ^{1}H NMR: δ = 5.82 (dd, *J* = 8.9/1.2 Hz, 1 H, 3-H), 5.56 (dq, *J* = 8.9/6.5 Hz, 1 H, 2-H), 2.80 (s, 1 H, 6-H), 2.01 (s, 3 H, OCOCH$_3$), 1.87 (d, *J* = 1.2 Hz, 3 H, 4-CH$_3$), 1.27 (d, *J* = 6.5 Hz, 3 H, 1-H). − ^{13}C NMR: δ = 170.2 (x, C=O), 137.6 (+, C-3), 120.0 (x, C-4), 85.6 (+, C-6), 75.7 (x, C-5), 67.0 (+, C-2), 21.2 (+, C-1), 20.1 (+,OCO*C*H$_3$), 17.6 (+, 4-CH$_3$). − IR: $\tilde{\nu}$ = 3290 cm^{-1} (s, C≡C-H), 2097 (w, C≡C), 1730 (s, C=O), 1240 (s, C−O−C). − MS: *m/z* (%) = 152 (7) [M$^+$], 137 (27) [M − CH$_3$], 109 (86) [M − COCH$_3$], 91 (100). − $C_9H_{12}O_2$ (152.19): calcd. C 71.03, H 7.95; found C 70.90, H 8.21.

(1-Octen-3-yn-1-yl)oxirane (10a):[9,18] A mixture of 11.7 g (75.0 mmol) of trimethylsulfonium bromide, 19.7 g (0.30 mol) of K_2CO_3, and 0.23 g (12.0 mmol) of water in 70 mL of acetonitrile was stirred for 5 min at 60°C. With vigorous stirring, a solution of 6.70 g (49.0 mmol) of **9** (prepared from 2-heptynal[13] according to ref.[14]) in 25 mL of acetnitrile was added dropwise, and stirring was continued for further 2 h at 60°C. After cooling to room temp., the mixture was filtered, and 50 mL of diethyl ether was added to the filtrate which was filtered again. Washing of the filtrate with pentane, removal of the solvent in vacuo and purification of the crude product by column chromatography (SiO_2, cyclohexane/diethyl ether, 10:1) gave 5.90 g (80%) of **10a** as red oil. − ^{1}H NMR: δ = 5.85 (dt, *J* = 16.0/2.0 Hz, 1 H, 4-H), 5.64 (dd, *J* = 16.0/ 7.9 Hz, 1 H, 3-H), 3.29 (ddd, *J* = 7.9/4.2/2.7 Hz, 1 H, 2-H), 2.94 (dd, *J* = 5.4/4.2 Hz, 1 H, 1-H), 2.62 (dd, *J* = 5.4/2.7 Hz, 1 H, 1-H), 2.27 (td, *J* = 6.9/2.0 Hz, 2 H, 7-H), 1.54−1.29 (m, 4 H, 8/9-H), 0.88 (t, *J* = 7.2 Hz, 3 H, 10-H). − ^{13}C NMR: δ = 138.5 (+, C-3), 114.7 (+, C-4), 96.8 (x, C-6), 78.0 (x, C-5), 51.8 (+, C-2), 49.0 (−, C-1), 30.6 (−, C-8), 21.9 (−, C-9), 19.0 (−, C-7), 13.5 (+, C-10). − IR: $\tilde{\nu}$ = 2956 cm^{-1} (s, C−H), 2214 (m, C≡C), 1633 (m, C=C). − MS: *m/z* (%) = 150 (16) [M$^+$], 135 (5) [M − CH$_3$], 108 (41), 79 (100). − $C_{10}H_{14}O$ (150.22): calcd. C 79.96, H 9.39; found C 80.19, H 9.37.

1-Methyl-1-(1-octen-3-yn-1-yl)oxirane (10b): According to the procedure given for **10a**, treatment of 6.40 g (42.0 mmol) of **3a** with 10.0 g (64.0 mmol) of trimethylsulfonium bromide, 16.9 g (0.26 mol) of K_2CO_3, and 0.20 g (11.0 mmol) of water furnished 5.60 g (81%) of **10b** as red oil after purification of the crude product by column chromatography (SiO_2, cyclohexane/diethyl ether, 10:1). − ^{1}H NMR: δ = 5.77 (d, *J* = 16.0 Hz, 1 H, 3-H), 5.73 (dt, *J* = 16.0/2.0 Hz, 1 H, 4-H), 2.79 (d, *J* = 5.2 Hz, 1 H, 1-H), 2.70 (dd, *J* = 5.2/0.5 Hz, 1 H, 1-H), 2.28 (td, *J* = 6.9/2.0 Hz, 2 H, 7-H), 1.60−1.24 (m, 4 H, 8/9-H), 1.41 (d, *J* = 0.5 Hz, 3 H, 2-CH$_3$), 0.89 (t, *J* = 7.2 Hz, 3 H, 10-H). − ^{13}C NMR: δ = 142.0 (+, C-3), 112.3 (+, C-4), 92.4 (x, C-6), 78.1 (x, C-5), 56.1 (−, C-1), 55.4 (x, C-2), 30.7 (−, C-8), 21.9 (−, C-9), 19.3 (+, 2-CH$_3$), 19.0 (−, C-7), 13.6 (+, C-10). − IR: $\tilde{\nu}$ = 2956 cm^{-1} (s, C−H), 2214 (m, C≡C), 1682 (m, C=C). − MS: *m/z* (%) = 164 (11) [M$^+$], 149 (4) [M − CH$_3$], 122 (62), 79 (100). − $C_{11}H_{16}O$ (164.25): calcd. C 80.44, H 9.82; found C 80.50, H 9.64.

General Procedure for the Preparation of Vinylallenes by 1,5-Substitution of Enyne Acetates and Oxiranes with Organocuprates: To a suspension of 1.5−2.0 equiv. of copper(I) iodide or copper(I) cyanide in diethyl ether 3.0−4.0 equiv. of the organolithium compound in diethyl ether (MeLi), hexane (*n*BuLi), or pentane (*t*BuLi) is added dropwise at −20 to −30°C under argon. After 15 min stirring at this temperature, the cuprate solution is cooled to −80°C, and 1.0 equiv. of the enyne in diethyl ether is added. The mixture is stirred at −60 to −80°C, and the reaction is monitored by GC and TLC. After complete consumption of the starting material (1−3 h), 5−10 mL of a saturated NH_4Cl solution is added, the mixture is warmed up to room temp. and filtered through Celite. The solvent is removed in vacuo, and the crude vinylallene is purified by column chromatography (SiO_2, cyclohexane).

6-Methyl-2,4,5-decatriene (11a): From 152 mg (1.0 mmol) of **2a** in 10 mL of diethyl ether, 381 mg (2.0 mmol) of CuI in 20 mL of diethyl ether and 2.5 mL (4.0 mmol) of *n*BuLi (1.6 M in hexane). Yield: 135 mg (90%) of **11a** (2:1 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − ^{1}H NMR: δ = 6.10−5.35 (m, 3 H, 2/3/4-H), 2.05−1.91 (m, 2 H, 7-H), 1.76−1.68 (m, 6 H, 1-H/6-CH$_3$), 1.47−1.31 (m, 4 H, 8/9-H), 0.89 (t, *J* = 6.9 Hz, 3 H, 10-H). − ^{13}C NMR: δ = 203.5 (x, C-5), 128.2*/126.1 (+, C-2), 126.0*/124.1 (+, C-3), 100.6*/ 100.5 (x, C-6), 93.2*/88.6 (+, C-4), 33.8 (−, C-7), 29.7 (−, C-8), 22.4 (−, C-9), 19.2*/19.0 (+, 6-CH$_3$), 13.1 (+, C-1), 14.0 (+, C-10). − IR: $\tilde{\nu}$ = 2925 cm^{-1} (s, C−H), 1948 (m, C=C=C), 1450 (m, C=C). − MS: *m/z* (%) = 150 (6) [M$^+$], 135 (4) [M − CH$_3$], 100 (48), 93 (100). − HRMS ($C_{11}H_{18}$): calcd. 150.1408; found 150.1406.

6,7,7-Trimethyl-2,4,5-octatriene (11b): From 152 mg (1.0 mmol) of **2a** in 10 mL of diethyl ether, 135 mg (1.5 mmol) of CuCN in 20 mL of diethyl ether and 2.0 mL (3.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 140 mg (93%) of **11b** (1:3 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − (*E*)-**11b**: ^{1}H NMR: δ = 5.82 (ddq, *J* = 15.5/10.3/1.7 Hz, 1 H, 3-H), 5.70 (dq, *J* = 10.3/2.9 Hz, 1 H, 4-H), 5.58 (dqd, *J* = 15.5/6.6/0.5 Hz, 1 H, 2-H), 1.76−1.70 (m, 6 H, 1-H/6-CH$_3$), 1.06 [s, 9 H, C(CH$_3$)$_3$]. − ^{13}C NMR: δ = 202.7 (x, C-5), 128.3 (+, C-2), 125.5 (+, C-3), 109.4

(x, C-6), 93.6 (+, C-4), 33.7 (x, C-7), 29.2 [+, C(CH_3)$_3$], 18.1 (+, 6-CH_3), 13.1 (+, C-1). − (*Z*)-**11b**: ^{1}H NMR: δ = 5.99 (dq, *J* = 10.8/1.2 Hz, 1 H, 4-H), 5.81 (ddq, *J* = 10.8/10.6/1.7 Hz, 1 H, 3-H), 5.38 (dqd, *J* = 10.6/7.1/1.2 Hz, 1 H, 2-H), 1.76−1.70 (m, 6 H, 1-H/6-CH_3), 1.07 [s, 9 H, C(CH_3)$_3$]. − ^{13}C NMR: δ = 204.3 (x, C-5), 126.3 (+, C-2), 123.7 (+, C-3), 109.2 (x, C-6), 89.1 (+, C-4), 33.7 (x, C-7), 29.2 [+, C(CH_3)$_3$], 18.1 (+, 6-CH_3), 15.0 (+, C-1). − IR: $\tilde{\nu}$ = 2962 cm^{-1} (s, C−H), 1944 (m, C=C=C), 1450 (m, C=C). − MS: *m/z* (%) = 150 (12) [M$^+$], 135 (5) [M − CH_3], 84 (54), 57 (100). − HRMS ($C_{11}H_{18}$): calcd. 150.1408; found 150.1410.

7,7-Dimethyl-6-phenyl-2,4,5-octatriene (11c): From 214 mg (1.0 mmol) of **2b** in 8 mL of diethyl ether, 135 mg (1.5 mmol) of CuCN in 20 mL of diethyl ether and 2.0 mL (3.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 170 mg (80%) of **11c** (1:1 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − (*E*)-**11c**: ^{1}H NMR: δ = 7.33−7.26 (m, 5 H, Phenyl-H), 6.24−5.41 (m, 3 H, 2/3/4-H), 1.75 (dd, *J* = 6.9/1.7 Hz, 3 H, 1-H), 1.19 [s, 9 H, C(CH_3)$_3$]. − ^{13}C NMR: δ = 204.2 (x, C-5), 137.8 (x, Phenyl), 129.5/127.8/126.6/125.6/124.9 (5+, C-2/3/Phenyl), 116.9 (x, C-6), 94.7 (+, C-4), 34.7 (x, C-7), 29.9 [+, C(CH_3)$_3$], 13.3 (+, C-1). − (*Z*)-**11c**: ^{1}H NMR: δ = 7.33−7.26 (m, 5 H, Phenyl-H), 6.24−5.41 (m, 3 H, 2/3/4-H), 1.78 (dd, *J* = 6.4/1.5 Hz, 3 H, 1-H), 1.18 [s, 9 H, C(CH_3)$_3$]. − ^{13}C NMR: δ = 205.6 (x, C-5), 137.8 (x, Phenyl), 129.5/127.8/126.6/ 125.6/124.9 (5+, C-2/3/Phenyl), 116.9 (x, C-6), 90.1 (+, C-4), 34.7 (x, C-7), 29.9 [+, C(CH_3)$_3$], 18.2 (+, C-1). − IR: $\tilde{\nu}$ = 2962 cm^{-1} (s, C−H), 1939 (m, C=C=C), 1597 (m), 1450 (m, C=C). − MS: *m/z* (%) = 212 (2) [M$^+$], 197 (2) [M − CH_3], 84 (42), 57 (100). − HRMS ($C_{16}H_{20}$): calcd. 212.1565; found 212.1564.

6-Trimethylsilyl-2,4,5-decatriene (11d): From 210 mg (1.0 mmol) of **2c** in 8 mL of diethyl ether, 135 mg (1.5 mmol) of CuCN in 20 mL of diethyl ether and 1.9 mL (3.0 mmol) of *n*BuLi (1.6 M in hexane). Yield: 167 mg (80%) of **11d** (3:2 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − ^{1}H NMR: δ = 5.86−5.24 (m, 3 H, 2/3/4-H), 1.99−1.92 (m, 2 H, 7-H), 1.74−1.69 (m, 3 H, 1-H), 1.40−1.30 (m, 4 H, 8/9-H), 0.89 (m, 3 H, 10-H), 0.10/0.09* [s, 9 H, Si(CH_3)$_3$]. − ^{13}C NMR: δ = 208.1/207.1* (x, C-5), 127.5*//125.7/124.4*/122.1 (+, C-2/3), 97.9*/97.3 (x, C-6), 89.2*/84.7 (+, C-4), 31.8*/31.3 (−, C-7), 29.1/29.0 (−, C-8), 22.6/22.4* (−, C-9), 14.0 (+, C-1), 13.9 (+, C-10), 1.5 [+, Si(CH_3)$_3$]. − IR: $\tilde{\nu}$ = 2958 cm^{-1} (s, C−H), 1916 (m, C=C=C), 1250 (s). − MS: *m/z* (%) = 208 (4) [M$^+$], 193 (2) [M − CH_3], 137 (65), 56 (100). − HRMS ($C_{13}H_{24}Si$): calcd. 208.1647; found 208.1639.

7,7-Dimethyl-6-trimethylsilyl-2,4,5-octatriene (11e): From 210 mg (1.0 mmol) of **2c** in 8 mL of diethyl ether, 135 mg (1.5 mmol) of CuCN in 20 mL of diethyl ether and 2.0 mL (3.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 200 mg (96%) of **11e** (2:3 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − (*E*)-**11e**: ^{1}H NMR: δ = 5.84−5.25 (m, 3 H, 2/3/4-H), 1.73 (dd, *J* = 6.6/1.7 Hz, 3 H, 1-H), 1.12 [s, 9 H, C(CH_3)$_3$], 0.16 [s, 9 H, Si(CH_3)$_3$]. − ^{13}C NMR: δ = 207.1 (x, C-5), 127.6 (+, C-2), 123.8 (+, C-3), 108.8 (x, C-6), 90.2 (+, C-4), 35.3 (x, C-7), 31.4 [+, C(CH_3)$_3$], 13.3 (+, C-1), 1.2 [+, Si(CH_3)$_3$]. − (*Z*)-**11e**: ^{1}H NMR: δ = 5.84−5.25 (m, 3 H, 2/3/4-H), 1.71 (dd, *J* = 6.9/1.7 Hz, 3 H, 1-H), 1.11 [s, 9 H, C(CH_3)$_3$], 0.17 [s, 9 H, Si(CH_3)$_3$]. − ^{13}C NMR: δ = 208.3 (x, C-5), 125.9 (+, C-2), 122.1 (+, C-3), 108.3 (x, C-6), 85.8 (+, C-4), 35.3 (x, C-7), 31.4 [+, C(CH_3)$_3$], 18.2 (+, C-1), 1.2 [+, Si(CH_3)$_3$]. − IR: $\tilde{\nu}$ = 2959 cm^{-1} (s, C−H), 1922 (s, C=C=C), 1450 (m, C=C). − MS: *m/z* (%) = 208 (3) [M$^+$], 193 (1) [M − CH_3], 168 (2), 152 (5), 57 (100). − HRMS ($C_{13}H_{24}Si$): calcd. 208.1647; found 208.1651.

6-(1,1-Dimethylethyl)-2,4,5-decatriene (11f): From 388 mg (2.0 mmol) of **4a** in 20 mL of diethyl ether, 270 mg (3.0 mmol) of CuCN in 40 mL of diethyl ether and 4.0 mL (6.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 300 mg (78%) of **11f** (1:2 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − ^{1}H NMR: δ = 6.18−5.30 (m, 3 H, 2/3/4-H), 2.10−1.96 (m, 2 H, 7-H), 1.75 (d, *J* = 6.9 Hz, 3 H, 1-H), 1.42−1.34 (m, 4 H, 8/9-H), 1.07 [s, 9 H, C(CH_3)$_3$], 0.92 (m, 3 H, 10-H). − ^{13}C NMR: δ = 203.8*/202.3 (x, C-5), 128.5/126.6* (+, C-2), 125.2/123.4* (+, C-3), 114.8/114.6* (x, C-6), 96.3/91.7* (+, C-4), 33.9 [x, *C*(CH_3)$_3$], 30.5 (−, C-7), 29.4 [+, C(CH_3)$_3$], 27.5 (−, C-8), 26.9 (−, C-9), 18.1/13.1* (+, C-1), 14.1 (+, C-10). − IR: $\tilde{\nu}$ = 2960 cm^{-1} (s, C−H), 1936 (m, C=C=C), 1463 (m, C=C). − MS: *m/z* (%) = 192 (1) [M$^+$], 177 (1) [M − CH_3], 150 (16), 57 (100). − HRMS ($C_{14}H_{24}$): calcd. 192.1878; found 192.1884.

(*E*)-2,2,7-Trimethyl-3,5,6-undecatriene (11g): From 473 mg (2.0 mmol) of **4b** in 15 mL of diethyl ether, 762 mg (4.0 mmol) of CuI in 30 mL of diethyl ether and 5.0 mL (8.0 mmol) of MeLi (1.6 M in diethyl ether). Yield: 354 mg (92%) of **11g** as a colorless liquid. − ^{1}H NMR: δ = 5.76 (dd, *J* = 15.0/10.0 Hz, 1 H, 4-H), 5.69 (dq, *J* = 10.0/2.5 Hz, 1 H, 5-H), 5.61 (d, *J* = 15.0 Hz, 1 H, 3-H), 1.97 (m, 2 H, 8-H), 1.70 (d, *J* = 2.5 Hz, 3 H, 7-CH_3), 1.42−1.30 (m, 4 H, 9/10-H), 1.04 (s, 9 H, C(CH_3)$_3$), 0.91 (t, *J* = 7.1 Hz, 3 H, 11-H). − ^{13}C NMR: δ = 203.8 (x, C-6), 142.5 (+, C-3), 121.8 (+, C-4), 100.5 (x, C-7), 93.5 (+, C-5), 33.9 (−, C-8), 33.2 (x, C-2), 29.6 [+, C(CH_3)$_3$], 29.6 (−, C-9), 22.4 (−, C-10), 19.1 (+, 7-CH_3), 14.0 (+, C-11). − IR: $\tilde{\nu}$ = 2956 cm^{-1} (s, C−H), 1948 (m, C=C=C), 1461 (m, C=C). − MS: *m/z* (%) = 192 (4) [M$^+$], 177 (2) [M − CH_3], 150 (32), 107 (100). − HRMS ($C_{14}H_{24}$): calcd. 192.1878; found 192.1881.

2,2-Dimethyl-7-(1,1-dimethylethyl)-3,5,6-undecatriene (11h): From 473 mg (2.0 mmol) of **4b** in 10 mL of diethyl ether, 270 mg (3.0 mmol) of CuCN in 30 mL of diethyl ether and 4.0 mL (6.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 445 mg (95%) of **11h** (3:2 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − (*E*)-**11h**: ^{1}H NMR: δ = 5.80 (dt, *J* = 10.0/3.2 Hz, 1 H, 5-H), 5.72 (dd, *J* = 15.0/10.0 Hz, 1 H, 4-H), 5.60 (d, *J* = 15.0 Hz, 1 H, 3-H), 2.02−1.94 (m, 2 H, 8-H), 1.40−1.34 (m, 4 H, 9/10-H), 1.06 [s, 9 H, C(CH_3)$_3$], 1.04 [s, 9 H, C(CH_3)$_3$], 0.91 (m, 3 H, 11-H). − ^{13}C NMR: δ = 202.5 (x, C-6), 141.9 (+, C-3), 122.1 (+, C-4), 114.8 (x, C-7), 96.6 (+, C-5), 34.0 [x, *C*(CH_3)$_3$], 33.4 [x, *C*(CH_3)$_3$], 30.5 [+, C(CH_3)$_3$], 29.8 (-, C-8), 29.3 [+, C(CH_3)$_3$], 27.0 (-, C-9), 22.6 (-, C-10), 14.1 (+, C-11). − (*Z*)-**11h**: ^{1}H NMR: δ = 6.29 (dm, *J* = 11.6 Hz, 1 H, 5-H), 5.62 (dd, *J* = 11.8/11.6 Hz, 1 H, 4-H), 5.26 (d, *J* = 11.8 Hz, 1 H, 3-H), 2.02−1.94 (m, 2 H, 8-H), 1.40−1−34 (m, 4 H, 9/10-H), 1.18 [s, 9 H, C(CH_3)$_3$], 1.05 [s, 9 H, C(CH_3)$_3$], 0.91 (m, 3 H, 11-H). − ^{13}C NMR: δ = 203.8 (x, C-6), 139.2 (+, C-3), 124.1 (+, C-4), 114.3 (x, C-7), 93.2 (+, C-5), 34.0 [x, *C*(CH_3)$_3$], 33.4 [x, *C*(CH_3)$_3$], 30.5 [+,C(CH_3)$_3$], 29.8 (−, C-8), 29.7 [+, C(CH_3)$_3$], 27.0 (−, C-9), 22.6 (−, C-10), 14.1 (+, C-11). − IR: $\tilde{\nu}$ = 2957 cm^{-1} (s, C−H), 1935 (m, C=C=C), 1462 (m, C=C). − MS: *m/z* (%) = 234 (<1) [M$^+$], 192 (11), 149 (13), 57 (100). − HRMS ($C_{17}H_{30}$): calcd. 234.2347; found 234.2342.

(*E*)-5-Methyl-1-phenyl-1,3,4-nonatriene (11i): From 513 mg (2.0 mmol) of **4c** in 15 mL of diethyl ether, 762 mg (4.0 mmol) of CuI in 30 mL of diethyl ether and 5.0 mL (8.0 mmol) of MeLi (1.6 M in diethyl ether). Yield: 280 mg (66%) of **11i** as a colorless liquid. − ^{1}H NMR: δ = 7.41−7.18 (m, 5 H, Phenyl-H), 6.61 (ddd, *J* = 15.8/10.1/1.0 Hz, 1 H, 2-H), 6.48 (d, *J* = 15.8 Hz, 1 H, 1-H), 5.92 (m, 1 H, 3-H), 2.03 (m, 2 H, 6-H), 1.77 (d, *J* = 2.7 Hz, 3 H, 5-CH_3), 1.78−1.32 (m, 4 H, 7/8-H), 0.93 (t, *J* = 7.1 Hz, 3 H, 9-H). − ^{13}C NMR: δ = 205.8 (x, C-4), 137.6 (x, Phenyl), 129.2/128.6/127.1/126.6/ 126.1 (5+, C-1/2/Phenyl), 101.3 (x, C-5), 94.0 (+, C-3), 33.8 (−, C-6), 29.8 (−, C-7), 22.4 (−, C-8), 19.1 (+, 5-CH_3),

14.0 (+, C-9). − IR: $\tilde{\nu}$ = 2956 cm^{-1} (s, C−H), 1944 (m, C=C=C), 1594 (m), 1497 (m), 1447 (m, C=C). − MS: *m/z* (%) = 212 (18) [M^+], 192 (6), 170 (78), 155 (100). − HRMS ($C_{16}H_{20}$): calcd. 212.1565; found 212.1565.

5-(1,1-Dimethylethyl)-1-phenyl-1,3,4-nonatriene (11j): From 513 mg (2.0 mmol) of **4c** in 10 mL of diethyl ether, 270 mg (3.0 mmol) of CuCN in 30 mL of diethyl ether and 4.0 mL (6.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 480 mg (94%) of **11j** (2:3 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − ^{1}H NMR: (*E*)-**11j**: δ = 7.44−7.19 (m, 5 H, Phenyl-H), 6.62 (dd, *J* = 15.8/10.1 Hz, 1 H, 2-H), 6.50 (d, *J* = 15.8 Hz, 1 H, 1-H), 6.06 (dt, *J* = 10.1/3.2 Hz, 1 H, 3-H), 2.10−1.97 (m, 2 H, 6-H), 1.45−1.38 (m, 4 H, 7/8-H), 1.12 [s, 9 H, $C(CH_3)_3$], 0.94 (m, 3 H, 9-H). − (*Z*)-**11j**: δ = 7.44−7.19 (m, 5 H, Phenyl-H), 6.47 (dm, *J* = 11.1 Hz, 1 H, 3-H), 6.34 (d, *J* = 11.3 Hz, 1 H, 1-H), 6.12 (dd, *J* = 11.3/11.1 Hz, 1 H, 2-H), 2.10−1.97 (m, 2 H, 6-H), 1.45−1.38 (m, 4 H, 7/8-H), 1.11 [s, 9 H, $C(CH_3)_3$], 0.94 (m, 3 H, 9-H). − ^{13}C NMR: δ = 205.8*/204.7 (x, C-4), 137.7 (x, Phenyl), 128.9/128.7/128.6/128.3/127.9/127.3/127.1/ 127.0/126.7/126.0 (10+, C-1/2/Phenyl), 115.6/115.2 (x, C-5), 97.1/93.2* (+, C-3), 34.1 (x, *C*$(CH_3)_3$), 30.5 (-, C-6), 29.4 [+, C(*C*$H_3)_3$], 27.0 (−, C-7), 22.7 (−, C-8), 14.2 (+, C-9). − IR: $\tilde{\nu}$ = 2958 cm^{-1} (s, C−H), 1934 (m, C=C=C), 1598 (m), 1491 (m), 1447 (m, C=C). − MS: *m/z* (%) = 254 (9) [M^+], 239 (2) [M − CH_3], 197 (78), 57 (100). − HRMS ($C_{19}H_{26}$): calcd. 254.2034; found 254.2033.

1-(1-Cyclohexen-1-yl)-3-methyl-1,2-heptadiene (11k): From 234 mg (1.0 mmol) of **6** in 10 mL of diethyl ether, 381 mg (2.0 mmol) of CuI in 20 mL of diethyl ether and 2.5 mL (4.0 mmol) of MeLi (1.6 M in diethyl ether). Yield: 158 mg (83%) of **11k** as a colorless liquid. − ^{1}H NMR: δ = 5.72 (q, *J* = 2.8 Hz, 1 H, 1-H), 5.60 (t, *J* = 3.7 Hz, 1 H, 2′-H), 2.10−1.92 (m, 6 H, 3′/6′/4-H), 1.70 (d, *J* = 2.8 Hz, 3 H, 3-CH_3), 1.68−1.55 (m, 4 H, 4′/5′-H), 1.45−1.25 (m, 4 H, 5/6-H), 0.89 (t, *J* = 7.1 Hz, 3 H, 7-H). − ^{13}C NMR: δ = 201.5 (x, C-2), 133.5 (x, C-1′), 124.7 (+, C-2′), 102.5 (x, C-3), 96.9 (+, C-1), 34.1 (−, C-4), 29.9 (−, C-5), 25.8 (−, C-3′/6′), 22.7 (−, C-4′/5′), 22.6 (-, C-6), 19.4 (+, 3-CH_3), 14.0 (+, C-7). − IR: $\tilde{\nu}$ = 2924 cm^{-1} (s, C−H), 1945 (w, C=C=C), 1446 (m, C=C). − MS: *m/z* (%) = 190 (19) [M^+], 175 (3) [M − CH_3], 148 (75), 105 (100). − HRMS ($C_{14}H_{22}$): calcd. 190.1722; found 190.1726.

1-(1-Cyclohexen-1-yl)-3-(1,1-dimethylethyl)-1,2-heptadiene (11l): From 234 mg (1.0 mmol) of **6** in 10 mL of diethyl ether, 135 mg (1.5 mmol) of CuCN in 20 mL of diethyl ether and 2.0 mL (3.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 197 mg (85%) of **11l** as a colorless liquid. − ^{1}H NMR: δ = 5.85 (t, *J* = 3.3 Hz, 1 H, 1-H), 5.60 (t, *J* = 3.8 Hz, 1 H, 2′-H), 2.12−1.90 (m, 6 H, 3′/6′/4-H), 1.71−1.55 (m, 4 H, 4′/5′-H), 1.43−1.26 (m, 4 H, 5/6-H), 1.05 [s, 9 H, $C(CH_3)_3$], 0.90 (t, *J* = 7.1 Hz, 3 H, 7-H). − ^{13}C NMR: δ = 200.1 (x, C-2), 133.7 (x, C-1′), 124.1 (+, C-2′), 116.6 (x, C-3), 99.9 (+, C-1), 34.0 [x, *C*$(CH_3)_3$], 30.8 (−, C-4), 29.5 [+, C(*C*$H_3)_3$], 27.2 (−, C-5), 25.8 (−, C-3′/6′), 22.8 (−, C-6), 22.7 (−, C-4′/5′), 14.1 (+, C-7). − IR: $\tilde{\nu}$ = 2959 cm^{-1} (s, C−H), 1936 (w, C=C=C), 1459 (m, C=C). − MS: *m/z* (%) = 232 (3) [M^+], 217 (4) [M − CH_3], 190 (20), 175 (36), 57 (100). − HRMS ($C_{17}H_{28}$): calcd. 232.2190; found 232.2192.

***(E)*-4,7,7-Trimethyl-2,4,5-octatriene** (**11m**): From 304 mg (2.0 mmol) of **8** in 15 mL of diethyl ether, 270 mg (3.0 mmol) of CuCN in 30 mL of diethyl ether and 4.0 mL (6.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 249 mg (83%) of **11m** as a colorless liquid. − ^{1}H NMR: δ = 6.00 (dm, *J* = 15.5 Hz, 1 H, 3-H), 5.52 (dqd, *J* = 15.5/6.7/1.2 Hz, 1 H, 2-H), 5.17 (m, 1 H, 6-H), 1.80−1.76 (m, 6 H, 1-H, 4-CH_3), 1.03 [s, 9 H, $C(CH_3)_3$]. − ^{13}C NMR: δ = 203.2 (x, C-5), 130.3 (+, C-2), 123.2 (+, C-3), 102.3 (+, C-6), 101.6 (x, C-4), 33.8 (x, C-7), 30.2 [+, C(*C*$H_3)_3$], 18.3 (+, 4-CH_3), 15.9 (+, C-1). − IR: $\tilde{\nu}$ = 2958 cm^{-1} (s, C−H), 1945 (w, C=C=C), 1463 (m, C=C). − MS: *m/z* (%) = 150 (11) [M^+], 135 (10) [M − CH_3], 84 (48), 57 (100). − HRMS ($C_{11}H_{18}$): calcd. 150.1409; found 150.1418.

(E)-6-(1,1-Dimethylethyl)-2,4,5-decatrien-1-ol (12a): From 300 mg (2.0 mmol) of **10a** in 10 mL of diethyl ether, 270 mg (3.0 mmol) of CuCN in 20 mL of diethyl ether and 4.0 mL (6.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 300 mg (72%) of **12a** as a colorless liquid. − ^{1}H NMR: δ = 6.00 (ddt, *J* = 15.3/10.3/1.2 Hz, 1 H, 3-H), 5.80 (dt, *J* = 10.3/3.2 Hz, 1 H, 4-H), 5.70 (dt, *J* = 15.3/5.9 Hz, 1 H, 2-H), 4.10 (dd, *J* = 5.9/1.2 Hz, 2 H, 1-H), 2.30 (s, 1 H, OH), 2.00−1.90 (m, 2 H, 7-H), 1.34−1.28 (m, 4 H, 8/9-H), 1.01 [s, 9 H, $C(CH_3)_3$], 0.86 (t, *J* = 7.2 Hz, 3 H, 10-H). − ^{13}C NMR: δ = 203.9 (x, C-5), 129.4 (+, C-2), 128.4 (+, C-3), 115.3 (x, C-6), 95.6 (+, C-4), 70.2 (−, C-1), 33.9 [x, *C*$(CH_3)_3$], 30.4 (−, C-7), 29.3 [+, C(*C*$H_3)_3$], 26.8 (−, C-8), 22.5 (−, C-9), 13.6 (+, C-10). − IR: $\tilde{\nu}$ = 3600−3200 cm^{-1} (s, OH), 2960 (s, C−H), 1937 (m, C=C=C). − MS: *m/z* (%) = 208 (1) [M^+], 166 (27), 105 (39), 57 (100). − HRMS ($C_{14}H_{24}O$): calcd. 208.1827; found 208.1822.

6-(1,1-Dimethylethyl)-2-methyl-2,4,5-decatrien-1-ol (12b): From 164 mg (1.0 mmol) of **10b** in 5 mL of diethyl ether, 135 mg (1.5 mmol) of CuCN in 15 mL of diethyl ether and 2.0 mL (3.0 mmol) of *t*BuLi (1.5 M in pentane). Yield: 135 mg (61%) of **12b** (4:1 mixture of (*E*/*Z*)-isomers according to GC analysis) as a colorless liquid. − (*E*)-**12b**: ^{1}H NMR: δ = 5.99 (dt, *J* = 10.8/3.2 Hz, 1 H, 4-H), 5.80 (dt, *J* = 10.8/1.2 Hz, 1 H, 3-H), 4.02 (s, 2 H, 1-H), 2.09 (s, 1 H, OH), 2.00−1.90 (m, 2 H, 7-H), 1.74 (d, *J* = 1.2 Hz, 3 H, 2-CH_3), 1.40−1.30 (m, 4 H, 8/9-H), 1.02 [s, 9 H, $C(CH_3)_3$], 0.87 (t, *J* = 7.2 Hz, 3 H, 10-H). − ^{13}C NMR: δ = 204.2 (x, C-5), 134.2 (x, C-2), 122.4 (+, C-3), 114.8 (x, C-6), 92.7 (+, C-4), 68.7 (−, C-1), 33.9 [x, *C*$(CH_3)_3$], 30.5 (−, C-7), 29.4 [+, C(*C*$H_3)_3$], 27.2 (+, 2-CH_3), 26.9 (−, C-8), 22.6 (−, C-9), 13.6 (+, C-10). − ^{1}H{^{1}H}-NOE difference spectra (irradiation at → intensity enhancement at): δ = 1.74 (2-CH_3) → δ = 5.99 (4-H), 4.02 (1-H); δ = 4.02 (1-H) → δ = 5.80 (3-H), 1.74 (2-CH_3); δ = 5.80 (3-H) → δ = 4.02 (1-H); δ = 5.99 (4-H) → δ = 1.74 (2′-H). − IR: $\tilde{\nu}$ = 3600−3200 cm^{-1} (s, OH), 2960 (s, C−H), 1934 (m, C=C=C). − MS: *m/z* (%) = 222 (1) [M^+], 191 (12), 180 (40), 57 (100). − HRMS ($C_{15}H_{26}O$): calcd. 222.1983; found 222.1967.

(*E*)-2-Methyl-2,4,5-decatrien-1-ol (13): From 164 mg (1.0 mmol) of **10b** in 10 mL of diethyl ether, 381 mg (2.0 mmol) of CuI in 20 mL of diethyl ether and 2.5 mL (4.0 mmol) of MeLi (1.6 M in diethyl ether). Yield: 90 mg (54%) of **13** as a colorless liquid. − ^{1}H NMR: δ = 6.00−5.93 (m, 1 H, 4-H), 5.86 (d, *J* = 10.8 Hz, 1 H, 3-H), 5.29 (q, *J* = 6.7 Hz, 1 H, 6-H), 4.04 (s, 2 H, 1-H), 2.13 (s, 1 H, OH), 2.05−1.98 (m, 2 H, 7-H), 1.75 (s, 3 H, 2-CH_3), 1.47−1.28 (m, 4 H, 8/9-H), 0.88 (t, *J* = 7.1 Hz, 3 H, 10-H). − ^{13}C NMR: δ = 208.0 (x, C-5), 135.6 (x, C-2), 121.0 (+, C-3), 92.1/89.1 (2+, C-4/6), 68.7 (−, C-1), 31.2 (−, C-7), 28.5 (−, C-8), 26.9 (−, C-9), 22.1 (+, 2-CH_3), 13.6 (+, C-10). − IR: $\tilde{\nu}$ = 3600−3200 cm^{-1} (s, OH), 2957 (s, C−H), 1942 (m, C=C=C). − MS: *m/z* (%) = 166 (11) [M^+], 149 (15), 124 (74), 91 (94), 79 (100). − HRMS ($C_{11}H_{18}O$): calcd. 166.1358; found 166.1358.

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[1] [1a] S. Patai (Ed.), *The Chemistry of Ketenes, Allenes and Related Compounds*, Wiley, New York, **1980**. − [1b] S. R. Landor (Ed.),

The Chemistry of the Allenes, Academic Press, London, **1982**. – [1c] H. F. Schuster, G. M. Coppola, *Allenes in Organic Synthesis*, Wiley, New York, **1984**.

[2] [2a] M. Hohmann, N. Krause, *Chem. Ber.* **1995**, *128*, 851–860. – [2b] N. Krause, A. Gerold, *Angew. Chem.* **1997**, *109*, 194–213; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 186–204.

[3] Reviews: [3a] A. Alexakis, P. Mangeney, A. Ghribi, I. Marek, R. Sedrani, C. Guir, J. F. Normant, *Pure Appl. Chem.* **1988**, *60*, 49–56. – [3b] A. Alexakis, *Pure Appl. Chem.* **1992**, *64*, 387–392. – [3c] C. J. Elsevier, in: *Methods of Organic Chemistry (Houben-Weyl)*, Ed.: G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann, Thieme, Stuttgart, **1995**, Vol. E 21, pp. 537–566.

[4] [4a] Enantioselective reduction: V. K. Singh, *Synthesis* **1992**, 605–617. – [4b] Enzymatic deracemization: C.-H. Wong, G. M. Whitesides, *Enzymes in Synthetic Organic Chemistry*, Elsevier, New York, **1994**. – [4c] K. Drauz, H. Waldmann (Ed.), *Enzyme Catalysis in Organic Synthesis*, VCH, Weinheim, **1995**.

[5] [5a] J. Gore, J. P. Dulcere, *Chem. Commun.* **1972**, 866–867. – [5b] J. P. Dulcere, J. Gore, M. L. Roumestant, *Bull. Soc. Chim. Fr.* **1974**, 1119–1123. – [5c] M. Bertrand, J. P. Dulcere, G. Gil, M. L. Roumestant, *Tetrahedron Lett.* **1979**, 1845–1846.

[6] S_N' and S_N'' substitutions of chiral dienyl acetals: H. Rakotoarisoa, R. G. Perez, P. Mangeney, A. Alexakis, *Organometallics* **1996**, *8*, 1957–1959.

[7] U. Koop, G. Handke, N. Krause, *Liebigs Ann.* **1996**, 1487–1499, and literature cited therein.

[8] Previous examples of remote stereocontrol in organocopper chemistry: [8a] S. E. Denmark, L. K. Marble, *J. Org. Chem.* **1990**, *55*, 1984–1986. – [8b] L. F. Captain, X. Xia, D. C. Liotta, *Tetrahedron Lett.* **1996**, *37*, 4293–4296. – [8c] V. Caló, A. Nacci, V. Fiandanese, *Tetrahedron* **1996**, *52*, 10799–10810. – [8d] B. Breit, *Angew. Chem.* **1998**, *110*, 535–538; *Angew. Chem. Int. Ed.* **1998**, *37*, 525–527.

[9] [9a] E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.* **1965**, *87*, 1353–1364. – [9b] Y. G. Gololobov, A. N. Nesmeyanov, V. P. Lysenko, I. E. Boldeskul, *Tetrahedron* **1987**, *43*, 2609–2651.

[10] Structure of cyanocuprates in the solid state: [10a] G. Boche, F. Bosold, M. Marsch, K. Harms, *Angew. Chem.* **1998**, *110*, 1779–1781; *Angew. Chem. Int. Ed.* **1998**, *37*, 1684–1686. – [10b] C. M. P. Kronenburg, J. T. B. H. Jastrzebski, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1998**, *120*, 9688–9689. – See also: [10c] S. H. Bertz, K. Nilsson, Ö. Davidsson, J. P. Snyder, *Angew. Chem.* **1998**, *110*, 327–331; *Angew. Chem. Int. Ed.* **1998**, *37*, 314–317. – [10d] T. A. Mobley, F. Müller, S. Berger, *J. Am. Chem. Soc.* **1998**, *120*, 1333–1334.

[11] [11a] H. O. House, *Acc. Chem. Res.* **1976**, *9*, 59–67. – [11b] A. Alexakis, D. Jachiet, J. F. Normant, *Tetrahedron* **1986**, *42*, 5607–5619. – [11c] A. Alexakis, I. Marek, P. Mangeney, J. F. Normant, *Tetrahedron* **1991**, *47*, 1677–1696. – [11d] T. R. Barbee, K. F. Albizati, *J. Org. Chem.* **1991**, *56*, 6764–6773. – [11e] N. Krause, G. Handke, *Tetrahedron Lett.* **1991**, *32*, 7229–7232. – [11f] M. H. Nantz, D. M. Bender, S. Janaki, *Synthesis* **1993**, 577–578. – [11g] Y. Chounan, T. Ibuka, Y. Yamamoto, *J. Chem. Soc., Chem. Commun* **1994**, 2003–2004.

[12] W. G. Kofron, L. M. Baclawski, *J. Org. Chem.* **1976**, *41*, 1879–1880.

[13] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 2nd Ed., **1988**, p. 102.

[14] M. Bellassoued, A. Majidi, *J. Org. Chem.* **1993**, *58*, 2517–2522.

[15] [15a] F. Mathey, P. Savignac, *Synth. Commun.* **1976**, 766–767. – [15b] F. Mathey, P. Savignac, *Tetrahedron* **1978**, *34*, 649–654.

[16] J. Villieras, M. Rambaud, *Synth. Commun.* **1983**, 300–303.

[17] T. Mukaiyama, K. Banno, K. Narasaka, *J. Am. Chem. Soc.* **1974**, *96*, 7503–7508.

[18] [18a] P. Mosset, R. Grée, *Synth. Commun.* **1985**, *15*, 749–757. – [18b] H. Bouda, M. E. Borredon, M. Delmas, A. Gaset, *Synth. Commun.* **1987**, *17*, 503–513.

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