Chromium(II)-Mediated Stereodivergent Additions of Allylic Phosphates and Halides to Aldehydes

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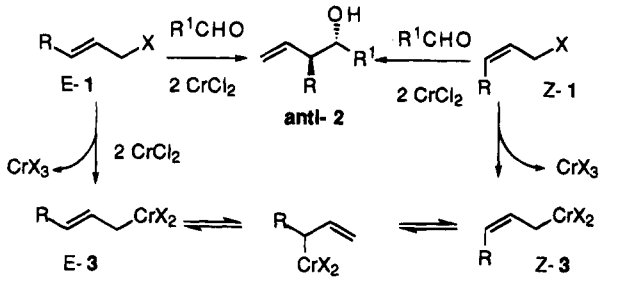
The addition of γ-disubstituted allylchromium(III) reagents to aldehydes proceeds in a stereodivergent manner, in contrast to the case of γ-monosubstituted allylchromium(III) species. The method allows the preparation of a variety of homoallylic alcohols bearing a quaternary center of defined relative configuration in the α-position. The preparation of both stereomeric homoallylic alcohols **13** is possible by using either of the two (*E*)- or (*Z*)-allylic precursors. The reaction has been extended to a γ-monosubstituted β-(trimethylsilyl)allylic system. The intermediate allylic chromium(III) reagents can be conveniently prepared from the corresponding phosphates (or chlorides) in DMPU or THF in the presence of catalytic amounts of LiI.

Introduction

The chromium(II)-mediated addition of allylic halides to aldehydes is a very mild and highly chemoselective method for the preparation of polyfunctional homoallylic alcohols.[1,2] γ-Substituted allylic halides of type **1** usually react regioselectively with aldehydes in the presence of Cr(II) salts from the most substituted end of the allylic system[1-3] and produce *anti*-homoallylic alcohols **2** with excellent stereoselectivity, *regardless* of the double bond stereochemistry of **1** (Scheme 1).[4] This stereochemical convergence can be rationalized by assuming that the intermediate allylic chromium(III) species (*E*)-**3** and (*Z*)-**3** are in rapid equilibrium.[4c] Recently, we have reported that this equilibrium is slow, compared to the rate of aldehyde addition, in the case of γ-disubstituted allylic chromium organometallics. This allows the stereodivergent allylation of aldehydes.[5] Herein, we report chromium(II)-mediated additions of γ-disubstituted and some β,γ-disubstituted allylic phosphates or halides to aldehydes which proceed with good to excellent diastereoselectivity. All of these reactions are stereodivergent and thus extend the scope of the Hiyama–Nozaki allylation reaction.[1,2] Solvent and salt effects will be discussed.

Scheme 1



Results and Discussion

The trisubstituted allylic alcohols **4a–c** (Scheme 2) used in this study were prepared according to the following procedures. 1-Hexyne was converted to 2-heptyn-1-ol (**5**) in 83% yield by successive deprotonation with BuLi (THF, −60 to 0°C) and formylation with solid paraformaldehyde (addition at −60 °C, then rt, 24 h).[6] A selective titanium-catalyzed hydromagnesiation, according to Sato's procedure[7] (*i*-BuMgCl (2.4 equiv), Cp_2TiCl_2 (10 mol %), ether, rt, 46 h) followed by iodolysis produces the (*E*)-allylic alcohol **6** in 64% yield (>98% *Z* by GC and ^{1}H-NMR analysis). Treatment of **6** with an excess of Me_2CuLi·LiCN[8] (Et_2O, −78 °C to rt) gives (*Z*)-3-methyl-2-hepten-1-ol (**4a**) in 92% yield (>98% Z by GC and ^{1}H-NMR analysis; Scheme 2). The stereospecific carbocupration of pentyne with *n*-BuCu·MgX_2 and hexyne with *n*-PrCu·$MgBr_2$ (Et_2O, −10 °C, 2.5 h)[9] provides, after iodolysis, the alkenyl iodides (*Z*)- and (*E*)-**7**, respectively, in excellent stereoisomeric purity (>99:1). An iodine–lithium exchange reaction using BuLi (Et_2O, −78 °C, 0.5 h)[10] followed by a formylation with paraformaldehyde (50 °C, 1 h) furnishes the isomeric alcohols (*Z*)- and (*E*)-**4b** in satisfactory yields (65–74%). Trisubstituted alcohols bearing a substituent in β- and in γ-position were also

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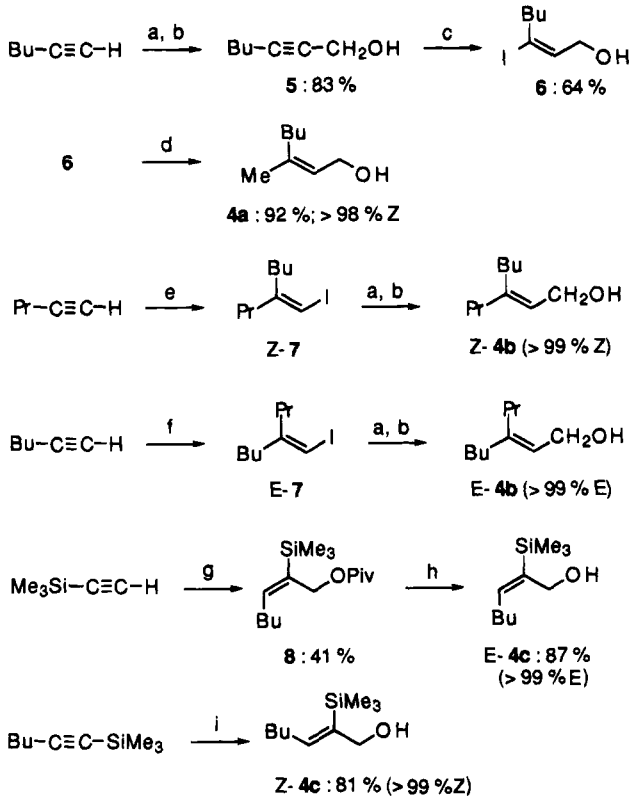
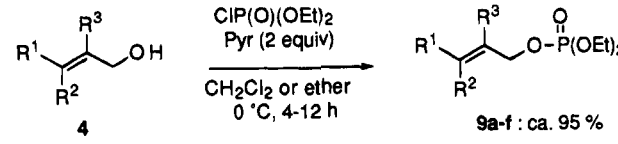
Scheme 2[a]



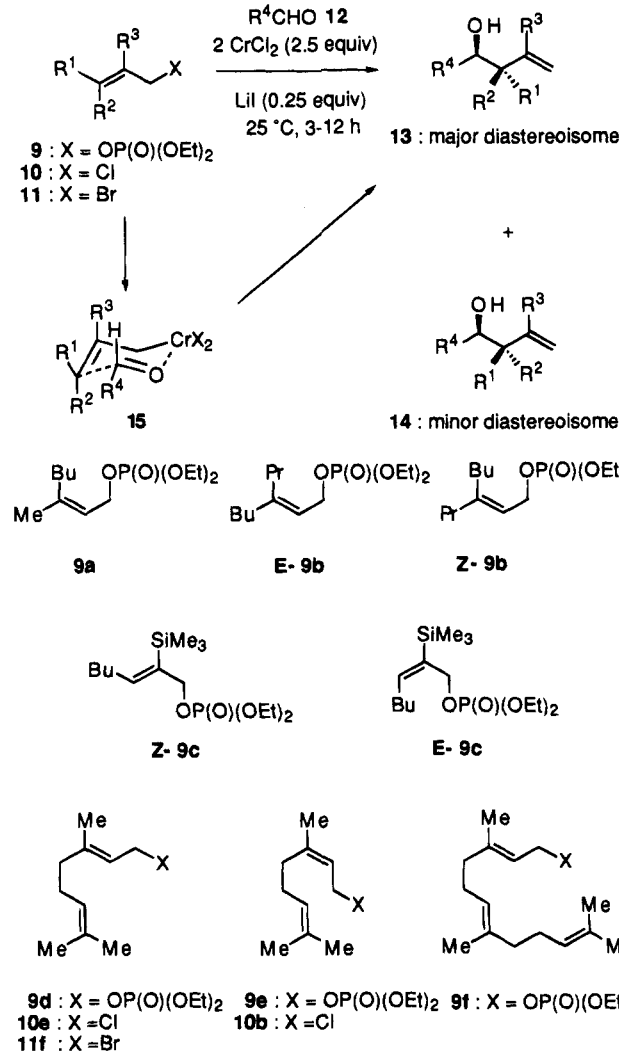
[a] Key: (a) BuLi, THF, −60 to 0 °C; (b) $(CH_2O)_n$, −60 to 25 °C (c): (i) *i*-BuMgCl, cat. Cp_2TiCl_2, ether; (ii) I_2; (d) $Me_2CuLi{\cdot}LiCN$ (excess), −78 to 25 °C; (e) (i) $BuCu{\cdot}MgX_2$, −30 to −10 °C, 2.5 h; (ii) I_2; (f) (i) $PrCu{\cdot}MgX_2$, −30 to −10 °C, 2.5 h; (ii) I_2; (g) (i) $BuCu{\cdot}MgBr_2$, ether, −30 to −10 °C, 2 h; (ii) $P(OEt)_3$, ICH_2OPiv; (h) MeLi (2.05 equiv), ether; (i) (i) DIBAL (1.1 equiv), ether, 25 °C, 21 h; (ii) BuLi (1.1 equiv); (iii) $(CH_2O)_n$ excess, −5 to 25 °C, 24 h.

prepared. The carbocupration of (trimethylsilyl)acetylene[11] with $BuCu{\cdot}MgBr_2$ (Et_2O, −30 to −10 °C, 2 h) produces stereospecifically a vinylcuprate which was trapped with iodomethyl pivalate[12] using trimethyl phosphite as a cosolvent ($P(OMe)_3$ (2 equiv), −50 to 25 °C, 12 h) and leads to the allylic pivalate **8** in 42% yield. The treatment of **8** with MeLi (2.05 equiv, Et_2O, −90 °C) provides stereospecifically the allylic alcohol (*E*)-**4c** in 87% yield (>99% *Z*). The hydroalumination of 1-(trimethylsilyl)-1-hexyne with DIBAL (1.1 equiv, Et_2O, rt, 21 h) furnishes an intermediate alkenylaluminum[13] which after the addition of BuLi (1.1 equiv, −15 to 5 °C, 1 h) was readily formylated with formaldehyde giving the alcohol (*Z*)-**4c** in 81% yield (>99% *Z*). The allylic alcohols of type **4** were easily converted to the corresponding phosphates **9a−f** by the reaction with $ClP(O)(OEt)_2$ (1.05 equiv), pyridine (2 equiv), CH_2Cl_2 or Et_2O, 0 °C, 4−12 h, 95% yield; Scheme 3).[14] These phosphates proved to be very convenient allylating reagents,[15] showing a better stability than the corresponding allylic bromides or even

Scheme 3



Scheme 4



chlorides. They were unstable to distillation and were used crude for all the chromium(II)-mediated reactions.

The trisubstituted organic phosphates **9a−f** and halides **10a−b,11** were treated with an aldehyde **12** and $CrCl_2$ (2.5 equiv) in *N,N'*-dimethylpropyleneurea (DMPU),[16] *N*-methylpyrrolidone (NMP), or THF in the presence of a catalytic amount of LiI (0.25 equiv) at rt for several hours (3−12 h), affording the homoallylic alcohols **13a−y** and **14** (Scheme 4 and Table 1).

All γ-disubstituted allylic phosphates react with excellent diastereoselectivity. The relative stereochemistry of the products **13** has been established by comparison with the ^{1}H-NMR spectra of product **13k** for which a detailed stereochemical study has been performed by Koreeda.[17] Especially impressive are the reactions of the two allylic phosphates (*E*)- and (*Z*)-**9b** having two γ-substituents which are only different by one CH_2− unit (butyl versus

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Table 1. Homoallylic Alcohols 13a–y Obtained by the Reaction of the Allylic Phosphates 9a–f, Chlorides 10a-b with Aldehydes and $CrCl_2$

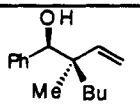
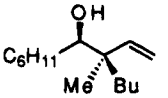
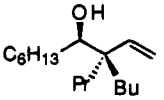
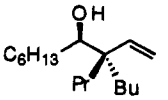
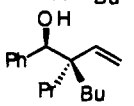
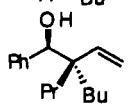
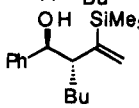
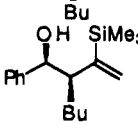
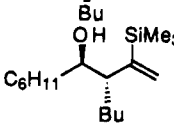
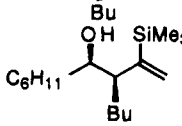
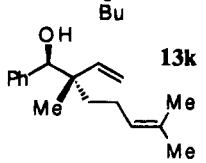
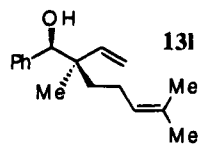
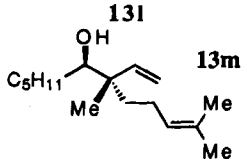
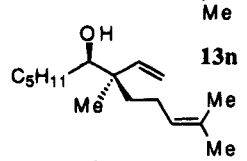
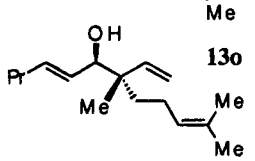
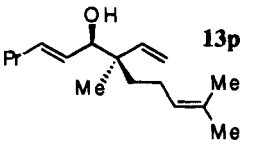
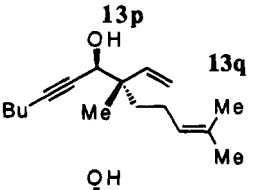
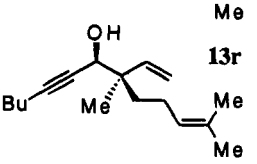
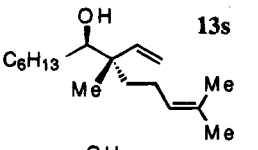
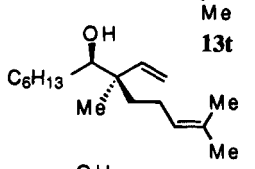
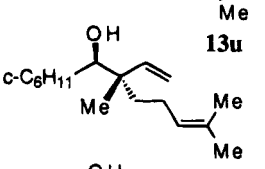
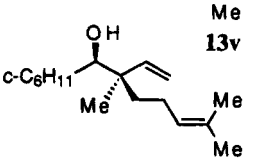
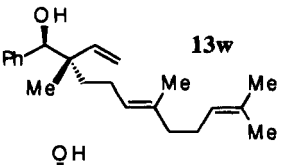
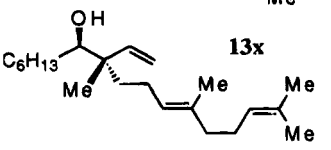
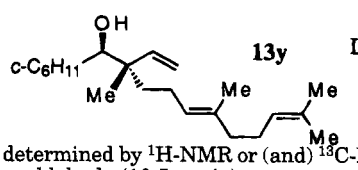
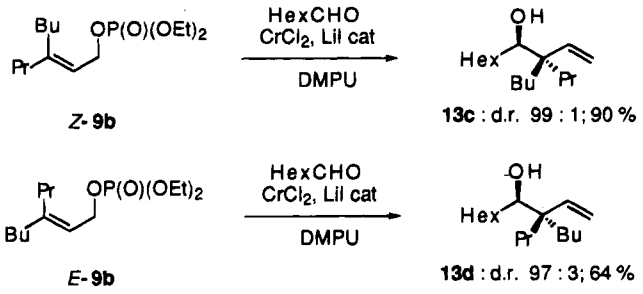
entry	allylic reagent 9 or 10	aldehyde 12 R^4	product 13	solvent	d.r.[a]	yield (%)[b]
1	**9a**	Ph	 **13a**	DMPU	97:3	95
2	**9a**	c-Hex	 **13b**	DMPU	90:10	89
3	*Z*-**9b**	Hex	 **13c**	DMPU	99:1	90
4	*E*-**9b**	Hex	 **13d**	DMPU	97:3	64
5	*Z*-**9b**	Ph	 **13e**	DMPU	99:1	66
6	*E*-**9b**	Ph	 **13f**	DMPU	97:3	75
7	*Z*-**9c**	Ph	 **13g**	DMPU	84:16	91
8	*E*-**9c**	Ph	 **13h**	DMPU	87:13	83
9	*Z*-**9c**	Hex	 **13i**	DMPU	68:32	69
10	*E*-**9c**	Hex	 **13j**	DMPU	87:13	67
11	**9d**	Ph	 **13k**	DMPU	97:3	94
12	**9d**	Ph	**13k**	THF	93:7	90
13	**9e**	Ph	 **13l**	DMPU	99:1	98
14	**9e**	Ph	**13l**	THF	93:7	91
15	**9d**	Pent	 **13m**	DMPU	94:6	93
16	**9e**	Pent	 **13n**	DMPU	99:1	94
17	**9d**	*E*-Pr-CH=CH-	 **13o**	DMPU	96:4	77

Table 1 (Continued)

entry	allylic reagent 9 or 10	aldehyde 12 R^4	product 13	solvent	d.r.[a]	yield (%)[b]
18	**9d**	*E*-Pr-CH=CH-	**13o**	THF	97:3	87
19	**9e**	*E*-Pr-CH=CH-	 **13p**	DMPU	97:3	84
20	**9e**	*E*-Pr-CH=CH-	**13p**	THF	96:4	92
21	**9d**	Bu-C≡C-	 **13q**	DMPU	99:1	86
22	**9e**	Bu-C≡C-	 **13r**	DMPU	98:2	89
23	**9d**	n-Hex	 **13s**	THF	97:3	72
24	**9e**	n-Hex	 **13t**	THF	98:2	71
25	**9d**	c-Hex	 **13u**	THF	96:4	66
26	**9e**	c-Hex	 **13v**	THF	94:6	73
27	**9e**	c-Hex	**13v**	NMP	89:11	68
28	**10a**	c-Hex	**13u**	DMPU	93:7	85
29	**10b**	c-Hex	**13v**	DMPU	83:17	84
30	**10b**	Ph	**13l**	THF	99:1	93
31	**10b**	*E*-Pr-CH=CH-	**13p**	DMPU	96:4	68
32	**10b**	Hex	**13t**	DMPU	96:4	68
33	**9f**	Ph	 **13w**	DMPU	95:5	84 (60)[c]
34	**9f**	n-Hex	 **13x**	DMPU	93:7	88
35	**9f**	c-Hex	 **13y**	DMPU	94:6	86

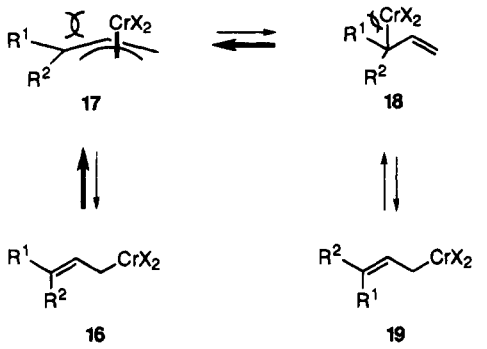
[a] Diastereomeric ratio between the products **13** and **14** determined by ^{1}H-NMR or (and) ^{13}C-NMR analysis. [b] Isolated yield of analytically pure products. [c] Yield obtained by using an excess of benzaldehyde (10,5 equiv).

Scheme 5



propyl). Their reaction with an aldehyde (benzaldehyde or hexanal) proceeds with excellent stereoselectivity (compare Scheme 4 and entries 3–6 of Table 1). The observed stereochemistry can be rationalized assuming a chair transition state such as **15** in which the R^4 substituent of the aldehyde occupies a pseudoequatorial position (Scheme 4).[2,8] Although DMF was not found to be a satisfactory solvent,[2] both DMPU and THF proved to be equally good (compare entries 11 and 12, 13 and 14, 17 and 18). On the other hand, NMP leads to lower yields and to a lower diastereoselectivity (compare entries 26 and 27). The reaction rate and the stereoselectivity depends on the nature of the aldehyde. Unsaturated aldehydes react faster and usually give the highest diastereoselectivities (compare entries 11, 15, 17, and 21). The use of an excess of the aldehyde lowers the reaction yield (entry 33). The presence of catalytic amounts of LiI is important and speeds up the allylation reaction. For example, in the absence of LiI, the slow reaction of benzaldehyde with geranyl phosphate provides the desired homoallylic alcohol **13k** in only 28% isolated yield (dr = 96:4). The role of LiI may be to form CrI_2 or CrICl *in situ* which would be more prone to undergo an oxidative addition.[10] It has been shown that lithium halides react rapidly with allylic phosphates in DMF leading to the corresponding allylic halide with retention of the double bond stereochemistry.[20] Therefore, it is also possible that LiI generates an allylic iodide via a substitution reaction which is also known to be a more reactive substrate for the Hiyama–Nozaki reaction.[1,2] Interestingly, the method allows a highly diastereoselective synthesis of very similar homoallylic alcohols bearing a quatenary center in β position. Thus, the homoallylic alcohol **13c** is obtained with 99:1 diastereomeric purity (90%) starting from the allylic phosphate (*Z*)-**9b**. By using (*E*)-**9b** as allylic phosphate, the diastereomeric alcohol **13d** is obtained (dr = 97:3; Scheme 5). This high diastereoselectivity is general (compare with entries 5 and 6). The ^{1}H-NMR spectra of **13c** and **13d** are very similar, but the corresponding ^{13}C-NMR spectra show different signals allowing a ratio determination (precision of the determination: ±1–2%). The high stereoselectivity observed in these allylation reactions is not due to the specific use of allylic *phosphates*, since the allylic chlorides (geranyl chloride **10a** and neryl chloride **10b**) react with similarly good diastereoselectivities (entries 28–32 of Table 1). The steric hindrance of the three double bond substituents may be responsible for the configurational stability of the double bond of the intermediate σ-allylchromium(III) **16**. The steric influences of the alkyl substituents may prevent the formation of the π-allylchromium complex **17** and of the isomeric σ-allylchromium species **18**, which, after rotation of the double bond, eventually leads to the isomerized allylic chromium reagent **19**. A similar steric hindrance should be observed for β,γ-disubstituted allylic phosphates or halides. We have prepared the two isomeric allylic phosphates (*E*)- and (*Z*)-**9c** and have observed a stereodivergent behavior in their addition to aldehydes. The trimethylsilyl group strongly decreases the reaction rate, especially for the (*E*)-isomer. These slow reactions consequently are less stereoselective[21] (reaction times of 5–7 days are required for **9c**); entries 7–10 of Table 1. Finally, attempts were made to use the elegant method of Wipf[22] for performing the Hiyama–Nozaki reaction using Ph_2Cr. This method allows the insertion of chromium into the allylic halide at low temperature which may give better stereoselectivities. Geranyl phosphate **9d** showed no reaction under these conditions, but geranyl bromide **11** adds under Wipf's conditions to cyclohexanecarboxaldehyde leading to the desired homoallylic alcohol **13u** in 36% yield and 92:8 diastereoselectivity (compare with entry 25). Similarly, the addition of **11** to heptanal under these conditions gives the alcohol **13s** in 53% yield and 96:4 stereoselectivity (see the Experimental Section).

Scheme 6



Conclusion

In summary, we have shown that γ-disubstituted allylic phosphates or chlorides and a β,γ-disubstituted allylic phosphate react in a stereodivergent fashion with aldehydes in the presence of $CrCl_2$. These results are in contrast with the well-known examples of γ-monosubstituted allylic halides which add in a stereoconvergent fashion to an aldehyde in the presence of $CrCl_2$. This difference of behavior is attributed to a very slow isomerization of the intermediate γ-disubstituted allylic chromium(III) species compared to the addition rate to the aldehyde. In the case of γ-monosubstituted allylic chromium reagents, this isomerization is fast.

Experimental Section

General Considerations. Unless otherwise indicated, all reactions were carried out under argon and solvents (THF, ether, toluene) were dried and freshly distilled from sodium/benzophenone. *N*-Methyl-2-pyrrolidone (NMP), 1,3-dimethyltetrahydro-2(1*H*)-propyleneurea (DMPU), and dichloromethane were freshly distilled over CaH_2. Reactions were

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monitored by gas–liquid-phase chromatography (GC) or thin-layer chromatography (TLC) analysis of hydrolyzed aliquots.

Starting Materials. 1-(Trimethylsilyl)hexyne.[23] 1-(Trimethylsilylhexyne) was obtained as described in the literature.[23] ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 2.08 (t, 2H, J = 7.0 Hz), 1.33–1.28 (m, 4H), 0.77 (t, 3H, J = 7.0 Hz), 0.00 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 107.5, 84.0, 30.6, 21.8, 19.4, 13.4, 0.2.

Iodomethyl 2,2-Dimethylpropionate.[12a,24] A solution of sodium iodide (73 g, 0.49 mol) and chloromethyl 2,2-dimethylpropionate (26.7 g, 177 mmol) in acetone (150 mL) was refluxed for 1 h. Aqueous workup and distillation through a helix-packed column (bp_{12} 87–91 °C) gave the desired product in 58% yield (24.7 g, 102 mmol). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.86 (s, 2H), 1.12 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 176.1, 38.7, 31.3, 26.4.

(*Z*)-3-Methyl-2-heptenol (4a).[25,26] Lithium dimethylcopper(I) (115.5 mmol) was prepared from copper(I) cyanide (10.35 g, 115.5 mmol) in ether (100 mL) and methyllithium (232 mmol, 145 mmol of a 1.6 M etheral solution) at −60 °C for 30 min and at −10 °C for 10 min. To this vigorously stirred cuprate suspension was carefully added the iodide **6** (5.50 g, 23 mmol) in ether (30 mL) at −78 °C. The reaction mixture was stirred at −70 °C for 1 h, warmed gradually to rt, stirred for an additional 2 h, and worked up by pouring into a saturated aqueous NH_4Cl solution (100 mL). The product was isolated by extraction with hexanes. The combined organic layer was washed with water (50 mL) and brine (50 mL) and dried ($MgSO_4$), and the solvents were evaporated in vacuo. The alcohol **4a** was obtained as a colorless liquid (2.72 g, 21.2 mmol, 92% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.33 (dt, 1H, J = 6.95, 0.63 Hz), 4.05 (dd, 2H, J = 7.2, 0.72 Hz), 2.00 (t, 2H, J = 7.7 Hz), 1.66 (d, 3H, J = 1.2 Hz), 1.52 (s, 1H), 1.34–1.18 (m, 4H), 0.83 (t, 3H, J = 7.2 Hz).

(*E*)-3-Propyl-2-hepten-1-ol ((*E*)-4b). To a stirred solution of (*Z*)-**7** (0.64 g, 2.54 mmol) in ether (20 mL) was added dropwise *n*-butyllithium (3.18 mmol, 2.1 mL of a 1.5 M solution in hexane) within 5 min at −78 °C. After the mixture was stirred at −78 °C for 1 h, gaseous formaldehyde (0.76 g, 25.3 mmol) obtained by heating paraformaldehyde in the presence of a trace of concd H_2SO_4 was introduced into the reaction mixture at such a rate that the temperature was kept below −45 °C. The reaction mixture was stirred for an additional hour and then worked up with saturated aqueous NH_4Cl solution (100 mL), and the aqueous phase was extracted with ether. The combined organic phase was washed with brine and dried (Na_2SO_4), and the solvents were evaporated. Purification of the residue by chromatography (hexane:ether = 4:1) afforded the desired alcohol as a colorless oil (0.26 g, 1.66 mmol, 65% yield). IR (neat): 3330 (br), 2935 (s), 1667 (m), 1461 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.30 (t, 1H, J = 6.9 Hz), 4.07 (d, 2H, J = 6.9 Hz), 1.97 (t, 2H, J = 7.3 Hz), 1.92 (t, 2H, J = 8.3 Hz), 1.64 (s, 1H), 1.43–1.19 (m, 6H), 0.831 (t, 3H, J = 6.9 Hz), 0.826 (t, 3H, J = 7.4 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.9, 123.5, 59.1, 38.9, 31.0, 30.1, 22.7, 21.0, 13.9, 13.8. MS-EI (70 eV): 156 (2) [M$^+$], 113 (16), 99 (25), 95 (26). Anal. Calcd for $C_{10}H_{20}O$ (156.26): C, 76.87; H, 12.89. Found: C, 76.95; H, 12.65.

(*Z*)-3-Propyl-2-hepten-1-ol ((*Z*)-4b) was prepared in a manner similar to that of the (*E*)-isomer (see above) by treating (*Z*)-**7** (2.50 g, 9.9 mmol) dissolved in ether (30 mL) with *n*-butyllithium (12.5 mmol, 8.3 mL of a 1.5 M solution in hexane) at −78 °C for 1 h, adding paraformaldehyde (2.98 g, 99.23 mmol) at −78 to −40 °C, and stirring for 1 h. Usual workup and purification by chromatography afforded the desired alcohol as a colorless oil (1.15 g, 7.36 mmol, 74% yield). IR (neat): 3335 (br), 2938 (s), 1668 (m), 1470 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.33 (t, 1H, 7.0 Hz), 4.08 (d, 2H, J = 7.0 Hz), 1.97 (t, 2H, J = 7.7 Hz), 1.94 (t, 2H, J = 8.2 Hz), 1.36–1.19 (m, 7H), 0.83 (t, 3H, J = 7.1 Hz), 0.82 (t, 3H, J = 7.4 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.0, 123.4, 59.0, 36.3, 32.2, 30.0, 22.3, 21.7, 13.9, 13.8. MS-EI (70 eV): 156 (4.) [M$^+$], 113 (32), 99 (48), 96 (15). Anal. Calcd for $C_{10}H_{20}O$ (156.26): C, 76.87; H, 12.89. Found: C, 76.61; H, 13.07.

(*E*)-2-(Trimethylsilyl)-2-hepten-1-ol ((*E*)-4c). A solution of (*E*)-2-(trimethylsilyl)-2-heptenyl pivalate (2.16 g, 8.0 mmol) in ether (30 mL) was treated with methyllithium (16.4 mmol, 10.25 mL of a 1.6 M etheral solution) at -80 °C. The solution was stirred at −80 °C for 1 h and then warmed to 0 °C within 2 h. The reaction mixture was worked up with saturated aqueous NH_4Cl solution. The organic layer was washed with water and brine, and dried ($MgSO_4$), and the solvents were evaporated. Chromatographical purification (hexanes:ether = 95:5) provided the desired alcohol as a colorless oil (1.29 g, 6.92 mmol, 87%). IR (neat): 3345 (s, br), 2955 (s), 1640 (m), 1465 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.77 (tt, 1H, J = 7.1, 1.1 Hz), 4.21 (s, 2H), 2.07 (q, 2H, J = 7.1 Hz), 1.38 (s, br, 1H), 1.34–1.17 (m, 4H), 0.82 (t, 3H, J = 7.0 Hz), 0.02 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.0, 140.5, 60.7, 31.7, 28.3, 22.4, 13.9, −1.1. MS EI (70 eV): 171 (2), 129 (15). Anal. Calcd for $C_{10}H_{22}OSi$ (186.36): C, 64.45; H, 11.89. Found: C, 64.30; H, 11.70.

(*Z*)-2-(Trimethylsilyl)-2-hepten-1-ol ((*Z*)-4c). To a stirred solution of diisobutylaluminum hydride (4.06 g, 28.6 mmol) in ether (50 mL) was added 1-(trimethylsilyl)hexyne (4.00 g, 25.9 mmol) at rt. The mixture was stirred for 21 h. The resulting alkenylaluminum derivative was treated with *n*-butyllithium (29 mmol, 18.1 mL of a 1.6 M solution in hexane) at 0 °C, stirred for 30 min, and then treated with an excess of paraformaldehyde (2.34 g, 77.9 mmol). The reaction mixture was stirred for 20 h at rt and was then poured onto crushed ice (concd HCl:H_2O 3:1). The aqueous phase was extracted with ether. The combined organic phase was washed sequentially with saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$), and the solvents were evaporated. Purification by chromatography on silica gel (eluent hexanes:ether 95:5) affords the desired product (3.87 g, 21 mmol, 81% yield) as a colorless oil. IR (neat): 3335 (br), 2963 (s), 1623 (m), 1470 (m), 1462 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.20 (t, 1H, J = 7.5 Hz), 4.14 (s, 2H), 2.17 (q, 2H, J = 7.0 Hz), 1.43–1.30 (m, 5H), 1.00–0.91 (m, 3H), 0.20 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.8, 138.9, 69.2, 32.0, 31.5, 22.4, 14.0, 0.0. MS-EI (70 eV): 130 (17), 75 (100). Anal. Calcd for $C_{10}H_{22}OSi$ (186.36): C, 64.45; H, 11.89. Found: C, 64.47; H, 11.69.

2-Heptynol (5).[6,28] To a stirred solution of 1-hexyne (62 g, 0.75 mol) in THF (400 mL) was added *n*-butyllithium (500 mL of a 1.5 M solution in hexane) between −60 and −40 °C within 2.5 h. The solution was stirred at −30 °C for 1 h and at 5 °C for 3 h, and was cooled back to −78 °C. After addition of paraformaldehyde (22.6 g, 0.75 mol) in small portions at −78 °C, the resulting suspension was allowed to warm to rt and was stirred for 24 h. After hydrolysis with saturated aqueous NH_4Cl solution (300 mL), the organic layer was separated and the aqueous layer was extracted twice with ether (200 mL). The combined organic phase was washed with saturated aqueous NaCl solution (200 mL) and dried ($MgSO_4$). After evaporation of the solvents, the remaining residue was distilled ($bp_{0.5}$ 84–86 °C), furnishing the desired alcohol (69.8 g, 0.62 mol, 83% yield) as a clear colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.25 (m, 2H), 2.21 (m, 2H), 1,71 (t, 1H, J = 4.9 Hz), 1.52–1.37 (m, 4H), 0.91 (t, 3H, J = 7.2 Hz).

(*E*)-3-Iodo-2-hepten-1-ol (6).[25,27] To a solution of isobutylmagnesium chloride (0.126 mol, 90 mL of a 1.4 M etheral solution) was added dicyclopentadienyltitanium dichloride (1.25 g, 5.0 mmol) at −7 °C. After the solution was stirred at this temperature for 15 min, a solution of 2-heptynol (5.89 g, 52.5 mmol) in ether (150 mL) was added dropwise within 30 min. The solution was allowed to warm to rt and was stirred for 2 d. After the solution was cooled to −70 °C, a solution of iodine (25.1 g, 100 mmol) in THF (80 mL) was added. The

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reaction mixture was stirred at −60 °C for 15 min and was then allowed to warm to rt in 1 h. The reaction mixture was diluted with dilute aqueous HCl (500 mL), and the aqueous layer was extracted with ether (7 × 200 mL). The combined organic phase was washed with a saturated aqueous Na_2CO_3 solution and brine and dried ($MgSO_4$), and the solvent was evaporated. Distillation ($bp_{0.5}$ 108−110 °C) afforded the alcohol as a clear oil (8.06 g, 33.6 mmol, 64% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.34 (t, 1H, J = 7.6 Hz), 4.02 (d, 2H, J = 6.9 Hz), 2.34 (t, 2H, J = 7.1 Hz), 1.99 (s, 1H), 1.46 (m, 2H), 1.25 (m, 2H), 0.85 (t, 3H, J = 7.2 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 139.7, 108.2, 60.0, 38.8, 31.4, 21.5, 13.9.

(*E*)-1-Iodo-2-propyl-1-hexene ((*E*)-7). To a suspension of *n*-butylcopper prepared from *n*-butylmagnesium bromide (50 mmol, 38.5 mL of 1.3 M etheral solution) and copper iodide (9.53 g, 50 mmol) at −30 to −20 °C was added 1-pentyne (3.41 g, 50 mmol) at −30 °C. The mixture was gradually warmed to −10 °C, and stirring was continued for 2.5 h. After the mixture was cooled to −25 °C, a solution of iodine (25.4 g, 100 mmol) in THF (50 mL) was added within 30 min. The reaction mixture was stirred at −20 °C for 15 min, at 0 °C for 30 min, and at rt for 30 min. The mixture was hydrolyzed with aqueous sodium thiosulfate solution (150 mL), the organic layer was dried ($MgSO_4$), and the solvents were evaporated. The crude residue was purified by distillation (bp_{13} 121 °C) and afforded the product as a colorless oil (10.0 g, 39.8 mmol, 80% yield). IR (neat): 3060 (w), 2958 (s), 1611 (w), 1458 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.79 (s, 1H), 2.15 (dt, 2H, J = 7.6 , 1.0 Hz), 2.13 (dt, 2H, J = 7.5, 1.1 Hz), 1.52−1.33 (m, 6H), 0.90 (t, 3H, J = 7.0 Hz), 0.86 (t, 3H, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 151.6, 74.1, 39.1, 36.7, 29.3, 22.5, 20.9, 13.9, 13.5. MS-EI (70 eV): 253 (2.3) [M$^+$ + 1], 252 (25.0) [M$^+$], 210 (12). Anal. Calcd for $C_9H_{17}I$ (252.13): C, 42.88; H, 6.79. Found: C, 43.3; H, 7.03.

(*Z*)-1-Iodo-2-propyl-1-hexene ((*Z*)-7) was prepared in a manner similar to that for (*E*)-**7** (see above) from *n*-propylmagnesium bromide (50 mmol, 36 mL of 1.4 M etheral solution), copper iodide (9.53 g, 50 mmol), and 1-hexyne (4.11 g, 50 mmol). The resulting cuprate was treated with a solution of iodine (25.4 g, 100 mmol) in THF (50 mL) at −45 °C and stirred at −30 °C for 2 h and at rt for 12.5 h. The usual workup and distillation (bp_{13} 119−121 °C) gave (*Z*)-**7** as a colorless oil (6.34 g, 25.2 mmol, 50%). IR (neat): 3060 (w), 2960 (s), 1612 (w), 1467 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.82 (t, 1H, J = 1.2 Hz), 2.15 (dt, 2H, J = 6.3, 1.5 Hz), 2.146 (dt, 2H, J = 6.9, 2.1 Hz), 1.51−1.52 (m, 6H), 0.90 (t, 3H, J = 7.3 Hz), 0.87 (t, 3H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 151.8, 74.4, 39.1, 36.9, 30.1, 22.3, 20.6, 14.0, 13.9. MS-EI (70 eV): 253 (3) [M$^+$ + 1], 252 (29) [M$^+$], 210 (16), 83 (96). Anal. Calcd for $C_9H_{17}I$ (252.13): C, 42.88; H, 6.79. Found: C, 43.13; H, 6.81.

(*E*)-2-(Trimethylsilyl)-2-heptenyl Pivalate (8). To a suspension of *n*-butylcopper prepared from *n*-butylmagnesium bromide (31.6 mmol, 19.75 mL of 1.60 M etheral solution) and copper bromide (4.98 g, 34.7 mmol) at −20 °C for 40 min was added (trimethylsilyl)acetylene (4.34 g, 44.2 mmol) and then triethyl phosphite (5.76 g, 34.7 mmol). The mixture was gradually warmed to −10 °C, and stirring was continued for 2 h. After the mixture was cooled to −50 °C, triethyl phosphite (5.76 g, 34.7 mmol) and iodomethyl 2,2-dimethylpropionate (8.40 g, 34.7 mmol) in DMPU (20 mL) was added. The mixture was kept at this temperature for 1 h and gradually allowed to warm to rt overnight. The reaction mixture was worked up with a saturated aqueous NH_4Cl solution (150 mL), the organic layer was washed with saturated aqueous NH_4Cl and brine and dried ($MgSO_4$), and the solvents were evaporated. The crude residue obtained was purified by chromatography (hexanes) affording the desired product as a colorless oil (3.54 g, 13.1 mmol, 42% yield). IR (neat): 2950 (s), 1753 (m), 1720 (s), 1610 (w), 1475 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.90 (m, 1H), 4.66 (s, 2H), 2.11 (q, 2H, J = 7.1 Hz), 1.33−1.25 (m, 4H), 1.16 (s, 9H), 0.85 (t, 3H, J = 6.9 Hz), 0.57 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 178.5, 145.3, 135.2, 62.8, 38.6, 31.5, 28.5, 27.2, 22.3, 13.8, −1.2. MS-EI (70 eV): 255 (1), 160 (9), 159 (72). Anal. Calcd for $C_{15}H_{30}O_2Si$ (270.47): C, 66.61; H, 11.17. Found: C, 66.60; H, 11.26.

Diethyl 3-Methylhept-2(*Z*)-enyl Phosphate (9a). Obtained as an oil (2.89 g, 10.9 mmol, 62% yield) prepared from the alcohol **4a** (2.27 g, 17.7 mmol), pyridine (4 g, 50 mmol), and diethyl chlorophosphate (4.35 g, 25.2 mmol). Reaction conditions: −10 °C, 30 min, then rt, 40 h. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.32 (t, 1H, J = 7.2 Hz), 4.47 (dd, 2H, $^3J_{HP}$ = J = 7.6 Hz), 4.05 (qd, 4H, $^3J_{HP}$ = J = 7.3 Hz), 2.02 (t, 2H, J = 7.0 Hz), 1.68 (s, 3H), 1.36−1.20 (m, 4H), 1.26 (t, 6H, J = 7.1 Hz), 0.83 (t, 3H, J = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 143.1, 119.5 (d, $^3J_{CP}$ = 6.8 Hz), 63.6 (d, $^2J_{CP}$ = 5.6 Hz), 63.4 (d, $^2J_{CP}$ = 5.8 Hz), 31.7, 30.2, 23.3, 22.4, 16.0 (d, $^3J_{CP}$ = 6.7 Hz), 13.8. The product was used crude for the next step.

(2*E*)-Diethyl 3-(*n*-Propyl)heptenyl Phosphate ((*E*)-9b). Obtained as an oil (8.66 g, 29.6 mmol, 90% yield) from (*E*)-**4b** (5.16 g, 33.0 mmol), pyridine (5.70 g, 72 mmol), and diethyl chlorophosphate (8.50 g, 49.3 mmol) in CH_2Cl_2 (20 mL). Reaction conditions: 0 °C, 15 min, then rt, 5 h. This compound was used crude in the next step.

(2*Z*)-Diethyl 3-(*n*-Propyl)-2-heptenyl Phosphate ((*Z*)-9b). Obtained as an oil (4.23 g, 14.5 mmol, 79% yield) prepared from (2*Z*)-3-(*n*-propyl)-2-hepten-1-ol (Z)-**4b** (2.87 g, 18.4 mmol), pyridine (2.93 g, 37.0 mmol), and diethyl chlorophosphate (3.33 g, 19.3 mmol) in CH_2Cl_2 (18.5 mL). Reaction conditions: 0 °C, 15 min, then rt, 12 h. It was used crude for the next step.

(2*E*)-Diethyl 2-(Trimethylsilyl)-2-heptenyl Phosphate ((*E*)-9c). Obtained as an oil (0.58 g, 1.8 mmol, 73% yield) prepared from (*E*)-**4c** (0.46 g, 2.5 mmol), pyridine (0.41 g, 5.2 mmol), and diethyl chlorophosphate (0.45 g, 2.61 mmol) in CH_2Cl_2 (10 mL). Reaction conditions: −10 °C, 10 min, then rt for 2 d. IR (neat): 2968 (s), 1620 (m), 1463 (m), 1400 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.80 (m, 1H), 4.62 (dd, 2H, $^3J_{HP}$ = 4.8 Hz, J = 1Hz), 4.01 (dq, 4H, $^3J_{HP}$ = 7.03 Hz, J = 7.1 Hz), 2.04 (q, 2H, J = 7.0 Hz), 1.44−1.02 (m, 4H), 1.23 (dt, 6H, J = 7.2 Hz, $^4J_{HP}$ = 1Hz), 0.78 (t, 3H, J = 6.9 Hz), 0.01 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.6, 136.1 (d, $^3J_{CP}$ = 9.5 Hz), 65.7 (d, $^2J_{CP}$ = 5.6 Hz), 63.5 (d, $^2J_{CP}$ = 5.9 Hz), 31.4, 28.5, 22.3, 16.1 (d, $^3J_{CP}$ = 6.7 Hz), 13.8, −1.2. MS EI (70 eV): 307 (1), 227 (10), 211 (11), 168 (10), 155 (88), 153 (10), 127 (9). This product was used crude for the next reaction step.

(2*Z*)-Diethyl 2-(Trimethylsilyl)-2-heptenyl Phosphate ((*Z*)-9c). Oil (3.93 g, 12.2 mmol, 76% yield) obtained from (*Z*)-**4c** (3.00 g, 16.1 mmol), pyridine (2.67 g, 33.8 mmol), and diethyl chlorophosphate (4.72 g, 27.4 mmol) in CH_2Cl_2 (20 mL). Reaction conditions: −10 °C, 15 min, rt, 1 d. IR (neat): 2965 (s), 1620 (m), 1475 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.22 (t, 1H, J = 7.5 Hz), 4.46 (dd, 2H, $^3J_{HP}$ = 6.5 Hz, J = 0.8 Hz), 4.03 (dq, 4H, $^3J_{HP}$ = 7.1 Hz, J = 7.1 Hz), 2.09 (q, 2H, J = 7.2 Hz), 1.31−1.23 (m, 4H), 1.26 (dt, 6H J = 7.0 Hz, $^4J_{HP}$ = 1Hz), 0.87−0.81 (m, 3H), 0.11 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 147.6, 133.9 (d, $^3J_{CP}$ = 7.0 Hz), 73.3 (d, $^2J_{CP}$ = 5.9 Hz), 63.3 (d, $^2J_{CP}$ = 5.9 Hz), 31.5, 31.3, 22.2, 15.9 (d, $^3J_{CP}$ = 6.7 Hz), 13.7, −0.3. MS EI (70 eV): 307 (2) [M$^+$ − 15], 227 (16), 211 (19), 183 (14), 168 (15), 156 (11), 155 (99), 153 (15), 127 (17), 99 (19), 77 (21), 75 (38), 74 (13), 73 (100), 59 (17), 45 (13). Anal. Calcd for $C_{14}H_{31}O_4PSi$ (322.443): C, 52.15; H, 9.69. Found: C, 52.05; H, 9.78.

(2*E*)-Diethyl 3,7-Dimethyl-2,6-octadienyl Phosphate (Geranyl Phosphate) (9d). Obtained as an oil (16.65 g, 57.3 mmol, 82% yield) from geraniol (10.8 g, 70.1 mol), pyridine (12.2 g, 154 mmol), and diethyl chlorophosphate (14.7 g, 85.1 mmol). Reaction conditions: −10 °C, 30 min, then rt, 2 d. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.34 (tq, 1H, J = 7.1, 1.2 Hz), 5.02 (m, 1H), 4.50 (dd, 2H, $^3J_{HP}$ = 7.8, 7.8 Hz), 4.04 (qd, 4H, $^3J_{HP}$ = 7.7 Hz, J = 7.1 Hz), 2.05−1.95 (m, 4H), 1.64 (d, ^{3}H, J = 0.8 Hz), 1.61 (d, 3H, J = 0.66 Hz), 1.53 (s, 3H), 1.27 (td, 6H, J = 7.01 Hz, $^4J_{HP}$ = 1 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.5, 131.7, 123.5, 118.9 (d, $^3J_{CP}$ = 6,6Hz), 63,9 (d, $^2J_{CP}$ = 5.6 Hz), 63,4 (d, $^2J_{CP}$ = 5,8 Hz), 39.3, 26.1, 25.5, 17.5, 16.3, 15.9 (d, $^3J_{CP}$ = 6.8 Hz). The product was used crude for the next step.

Diethyl 3,7-Dimethyloctadi-2(*Z*),6-enyl Phosphate (Neryl Phosphate) (9e). Oil (17.25 g, 59.4 mmol, 84% yield) prepared from nerol (10.85 g, 70.4 mmol), pyridine (12.2 g, 154 mmol), and diethyl chlorophosphate (15.5 g, 90 mmol). Reaction conditions: −10 °C, 30 min then rt, 2 d. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.39 (m, 1H), 5.06 (m, 1H), 4.52 (dd, 2H, $^3J_{HP}$ = 7,3 Hz, J = 7.3 Hz), 4.09 (qd, 4H, $^3J_{HP}$ = 7 Hz, J = 7 Hz),

2.13–2.03 (m, 4H), 1.75 (d, 3H, J = 0.1 Hz), 1.66 (s, 3H), 1.58 (s, 3H), 1.31 (td, 6H, J = 7.0, $^4J_{HP}$ = 1 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.5, 132.1, 123.4, 119.9 (d, $^3J_{CP}$ = 6.8 Hz), 63.7 (d, $^2J_{CP}$ = 5.5 Hz), 63.5 (d, $^2J_{CP}$ = 5.8 Hz), 32.0, 26.5, 25.6, 23.4, 17.5, 16.0 (d, $^3J_{CP}$ = 6.7 Hz). The product was used crude for the next step.

Typical Procedure for the Preparation of Allylic Diethyl Phosphates. (2*E*,6*E*)-Diethyl 3,7,11-Trimethyl-2,6,10-dodecatrienyl Phosphate (9f). To a solution of (*E*,*E*)-farnesol (2.20 g, 10 mmol) in ether (10 mL) was added dry pyridine (1.90 g, 24 mmol) followed by diethyl chlorophosphate (2.09 g, 12.1 mmol). The resulting colorless suspension was allowed to warm to rt and was stirred for 1.5–2 d. The reaction mixture was diluted with ether and was washed successively with saturated aqueous NH_4Cl (20 mL), $NaHCO_3$ (3 × 20 mL), and NaCl solution (20 mL). The organic layer was dried ($MgSO_4$). Removal of the solvent in vacuo furnished **9f** as a colorless oil (3.49 g, 9.74 mmol, 97% yield). The ^{1}H-NMR spectrum indicates a purity of over 95%. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.35 (m, 1H), 5.03–4.98 (m, 2H), 4.50 (dd, 2H, $^3J_{HP}$ = 7.6 Hz, J = 7.6 Hz), 4.03 (qd, 4H, $^3J_{HP}$ = 7.6 Hz, J = 7.1 Hz), 2.06–1.95 (m, 8H), 1.64 (s, 3H), 1.61 (s, 3H), 1.53 (s, 6H), 1.26 (td, 6H, J = 7.1, $^4J_{HP}$ = 0.8 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.4, 135.3, 131.1, 124.1, 123.4, 118.8 (d, $^3J_{CP}$ = 6.7 Hz), 63.9 (d, $^2J_{CP}$ = 5.6 Hz), 63.4 (d, $^2J_{CP}$ = 5.7 Hz), 39.5, 39.3, 26.5, 26.0, 25.5, 17.5, 16.3, 15.9 (d, $^3J_{CP}$ = 4.1 Hz), 15.8. The product was used crude for the next step.

(2*E*)-1-Chloro-3,7-dimethyl-2,6-octadiene (Geranyl Chloride) (10a).[20] To a solution of *N*-chlorosuccinimide (12.0 g, 90 mmol) in CH_2Cl_2 (100 mL) was added under stirring at −10 °C dimethyl sulfide (8.8 mL, 123.9 mmol) over a period of 30 min. The resulting suspension was cooled to −50 °C, and geraniol (10 g, 58.4 mmol) was added dropwise over a period of 30 min. The reaction mixture was warmed to 0 °C, stirred for 2.5 h, and poured into water (300 mL). The aqueous phase was extracted twice with CH_2Cl_2 (50 mL). The combined organic phase was washed with cold brine and dried ($MgSO_4$), and the solvent was evaporated. The resulting crude product was purified by distillation ($bp_{0.02}$ 35 °C) furnishing geranyl chloride as a colorless oil (7.50 g, 43.4 mmol, 74%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.40 (tq, 1H, J = 8, 1.2 Hz), 5.05 (m, 1H), 4.05 (d, 2H, J = 8 Hz), 2.04 (m, 4H), 1.68 (d, 3H, J = 1.2 Hz), 1.64 (d, 3H, J = 0.7 Hz), 1.56 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.7, 131.9, 123.7, 120.4, 41.1, 39.5, 26.3, 25.7, 17.7, 16.1.

(2*Z*)-1-Chloro-3,7-dimethyl-2,6-octadiene (Neryl Chloride) (10b).[20] It was prepared as geranyl chloride (see above) from *N*-chlorosuccinimide (6.50 g, 48.7 mmol), dimethyl sulfide (4.25 g, 68.4 mmol) in CH_2Cl_2 (60 mL), and nerol (5 g, 32.4 mmol). Usual workup and purification by distillation ($bp_{0.02}$ 38–42 °C) provided neryl chloride as a colorless oil (4.12 g, 23.86 mmol, 74% yield). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.45 (dt, 1H, J = 8.1, 1.2 Hz), 5.12 (m, 1H), 4.08 (dd, 2H, J = 8.1, 0.6 Hz), 2.19–2.06 (m, 4H), 1.78 (m, 3H), 1.70 (s, 3H), 1.62 (d, 3H, J = 0.6 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.6, 132.3, 123.5, 121.2, 40.9, 31.9, 26.5, 25.6, 23.4, 17.6.

Typical Procedure for the Preparation of Homoallylic Alcohols of Type 13. Preparation of (1*S,2*S**)-2,6-Dimethyl-2-ethenyl-1-phenyl-5-hepten-1-ol (13k) (ds = 93:7).** A 20 mL flask equipped with an argon inlet, a stirring bar, and a septum cap was charged with lithium iodide (0.18 g, 1.38 mmol) which had been dried at 150 °C in vacuum (0.1 mmHg) for 2 h. After the mixture was cooled to rt, chromium(II) chloride (1.37 g, 11.2 mmol) and THF (10 mL) were successively added. After the resulting suspension was stirred for 15 min at rt, a solution of the phosphate **10a** (1.53 g, 5.26 mmol) and benzaldehyde (0.49 g, 4.66 mmol) in THF (4 mL) was added. The reaction mixture was stirred at rt for 20 h and was quenched with a saturated aqueous NH_4Cl solution (200 mL). The organic phase was washed with saturated aqueous NH_4Cl solution (4 × 100 mL), and the aqueous phase was extracted with ether (3 × 100 mL). The combined organic phase was dried ($MgSO_4$). After filtration and evaporation of the solvents, the residual oil was purified by flash chromatography (eluent hexanes:ether 95:5) leading to the pure homoallylic alcohol **13k** as a colorless oil (1.02 g, 4.17 mmol, 90% yield).

Analytical Data of the Products 13a–y of Table 1. (1*S,2*R**)-2-Ethenyl-2-methyl-1-phenylhexan-1-ol (13a) (ds = 97:3).** A total of 0.92 g (95% yield) of a clear oil was obtained from (*Z*)-**9c** (1.38 g, 5.2 mmol) and benzaldehyde (0.47 g, 4.4 mmol). Purification by flash chromatography (hexanes:ether 93:7). IR (neat): 3448 (s, br), 3085 (m), 3033 (m), 2958 (s), 2873 (s), 1638 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.32–7.22 (m, 5H), 5.77 (dd, 1H, J = 17.6, 10.9 Hz), 5.17 (dd, 1H, J = 10.9, 1.4 Hz), 4.99 (dd, 1H, J = 17.6, 1.4 Hz), 4.44 (d, 1H, J = 2.0 Hz), 2.03 (d, 1H, J = 4.5 Hz), 1.33 (m, 2H), 1.26–1.15 (m, 4H), 1.06 (s, 3H), 0.85 (t, 3H, J = 6.7 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.0, 141.4, 127.9, 127.5, 127.3, 114.9, 80.8, 45.3, 36.2, 26.3, 23.5, 19.0, 14.2. MS-EI (70 eV): 200 (1), 128 (1), 112 (41), 107 (100). Anal. Calcd for $C_{15}H_{22}O$ (218.34): C, 82.52; H, 10.16. Found: C, 82.57; H, 10.18.

(1*R,2*R**)-1-Cyclohexyl-2-ethenyl-2-methylhexan-1-ol (13b) (ds = 90:10).** Obtained as a clear oil (0.86 g, 89% yield) from the phosphate (*Z*)-**9c** (1.23 g, 4.7 mmol) and cyclohexanecarboxaldehyde (0.48 g, 4.3 mmol). Purification by flash chromatography (hexanes:ether 93:7). IR (neat): 3464 (s, br), 3082 (w), 2929 (s), 2854 (s), 1636 (w), 1468 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.86 (dd, 1H, J = 17.6, 10.9 Hz), 5.10 (dd, 1H, J = 10.9, 1.5 Hz), 4.99 (dd, 1H, J = 17.6, 1.5 Hz), 3.10 (d, 1H, J = 5.4 Hz), 1.72–1.09 (m, 18H), 1.01 (s, 3H), 0.88 (t, 3H, J = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.2, 113.8, 81.8, 45.5, 39.2, 38.1, 33.4, 27.5, 26.7, 26.3, 26.2, 26.1, 23.5, 19.0, 14.0. MS-EI (70 eV): 113 (7), 112 (39). Anal. Calcd for $C_{15}H_{28}O$ (224.3890): C, 80.29; H, 12.58. Found: C, 80.30; H, 12.60.

(5*R,6*R**)-5-Ethenyl-5-propyldodecan-6-ol (13c) (ds = 99:1).** Obtained as a clear oil (0.91 g, 90% yield) from the phosphate (*Z*)-**9c** (1.46 g, 5 mmol) and heptanal (0.46 g, 4 mmol). Purification by flash chromatography (3% ether in hexanes). The diastereoselectivity was determined by ^{13}C-NMR spectroscopy (signal at 34.8 ppm). IR (neat): 3442 (s, br), 2962 (s), 2940 (s), 1645 (m), 1486 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.66 (1H, dd, J = 17.8, 11.1 Hz), 5.13 (1H, d, J = 11.1 Hz), 4.95 (1H, d, J = 17.8 Hz), 3.33 (1H, d, J = 9.9 Hz), 1.53–1.44 (4H, m), 1.37–1.07 (20H, m), 0.87–0.80 (6H, m). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.1, 114.8, 75.9, 46.8, 34.8, 32.6, 32.0, 31.9, 29.4, 29.1, 27.0, 25.7, 23.7, 22.7, 15.0, 14.1, 14.0; MS-EI (70 eV): 140 (32) 98 (100). Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47. Found: C, 80.04; H, 13.34.

(5*S,6*R**)-5-Ethenyl-5-propyldodecan-6-ol (13d) (ds = 97:3).** Obtained as a clear oil (0.65 g, 64% yield) from the phosphate (*Z*)-**9c** (1.46 g, 5 mmol) and heptanal (0.46 g, 4 mmol). Purification by flash chromatography (3% ether in hexanes). The diastereoselectivity was determined by ^{13}C-NMR spectroscopy (signal at 35.3 ppm). IR (neat): 3452 (s, br), 2970 (s), 1482 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.65 (1H, dd, J = 17.8, 11.1 Hz), 5.11 (1H, d, J = 11.1 Hz), 4.93 (1H, d, J = 17.8 Hz), 3.33 (1H, d, J = 10.4 Hz), 1.48–1.09 (24H, m), 0.87–0.80 (6H, m). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.1, 114.9, 75.9, 46.8, 35.3, 32.7, 32.1, 32.0, 29.4, 27.0, 25.6, 23.7, 22.7, 16.8, 15.1, 14.2, 14.1. MS-EI (70 eV): 140 (47), 98 (100). Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47. Found: C, 79.92; H, 13.12.

(1*S,2*R**)-2-Ethenyl-1-phenyl-2-propylhexan-1-ol (13e) (ds = 99:1).** Obtained as a clear oil (0.65 g, 66% yield) from the phosphate (*Z*)-**9c** (1.46 g, 5 mmol) and benzaldehyde (0.42 g, 4 mmol). Flash chromatography (3% ether in hexanes). The diastereoselectivity was determined by ^{13}C-NMR spectroscopy (signal at 34.2 ppm). IR (neat): 3466 (s, br), 2957 (s), 1643 (m), 1450 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.27–7.17 (5H, m), 5.64 (1H, dd, J = 17.8, 11.1 Hz), 5.19 (1H, d, J = 11.1 Hz), 4.90 (1H, d, J = 17.8 Hz), 4.52 (1H, s), 1.97 (1H, s), 1.65–1.53 (2H, m), 1.48–0.77 (14H, m). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.4, 141.7, 128.0, 127.5, 127.4, 115.6, 78.1, 47.3, 34.2, 32.9, 25.8, 23.6, 16.6, 15.0, 14.1. MS-EI (70 eV): 98 (80), 107 (100), 140 (44). Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Observed: C, 82.50; H, 10.68.

(1*R,2*R**)-2-Ethenyl-1-phenyl-2-propylhexan-1-ol (13f) (ds = 97:3).** Obtained as a clear oil (0.74 g, 75% yield) from 1.46 g (5 mmol) of the phosphate (*E*)-**9c** and benzaldehyde (0.46 g, 4 mmol). Purification by flash chromatography (3% ether in hexanes). The diastereoselectivity was determined by ^{13}C-NMR spectroscopy (signal at 35.5 ppm). IR (neat): 3453 (s,

br), 2976 (s), 1459 (m), 1012 (m) cm^{-1}. ^1H-NMR ($CDCl_3$, 300 MHz): δ 7.31−7.21 (5H, m), 5.67 (1H, dd, J = 17.8, 11.1 Hz), 5.25 (1H, d, J = 11.1 Hz), 4.97 (1H, d, J = 17.8 Hz), 4.54 (1H, s), 2.00 (1H, s), 1.78−1.66 (2H, m), 1.42−0.77 (14H, m). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.3, 141.7, 128.0, 127.5, 127.4, 115.7, 78.0, 47.4, 35.5, 31.5, 25.6, 23.7, 16.9, 14.9, 14.3. MS-EI (70 eV): 98 (72), 107 (100), 140 (59), 205 (5). Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.54; H, 10.64.

(1*S,2*R**)-1-Phenyl-2-[(1-trimethylsilyl)ethenyl]hexan-1-ol (13g) (ds = 84:16).** The phosphate (*Z*)-**4c** (0.90 g, 2.8 mmol) and benzaldehyde (0.27 g, 2.54 mmol) were added to a suspension of LiI (0.07 g, 0.52 mmol) and $CrCl_2$ (0.79 g, 6.43 mmol) in DMPU (5 mL). After 6 d at rt, the reaction was worked up as usual. Purification of the crude product by chromatography (hexanes:ether 93:7) yielded **13g** as a clear oil (0.64 g, 2.32 mmol, 91% yield). IR (neat): 3465 (br), 3040 (m), 2965 (s), 1610 (w), 1495 (w) 1460 (m) cm^{-1}. ^1H-NMR ($CDCl_3$, 300 MHz): δ 7.30−7.18 (m, 5H), 5.82 (d, 1H, J = 2.6 Hz), 5.68 (d, 1H, J = 6.2 Hz), 4.46 (dd, 1H, J = 9.0, 1.9 Hz), 2.48 (dt, 1H, J = 10.4, 3.0 Hz), 2.09 (d, 1H, J = 1.9 Hz), 1.62−0.85 (m, 6H), 0.71 (t, 3H, J = 6.7 Hz), 0.12 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 153.8, 143.1, 128.9, 128.2, 127.7, ,127.3, 77.3, 55.4, 31.1, 29.8, 22.7, 14.0, -0.3. MS-EI (70 eV): 155 (38), 128 (8), 107 (67), 96 (31). Anal. Calcd for $C_{17}H_{28}OSi$ (276.48): C, 73.85; H, 10.20. Found: C, 73.74; H, 10.42.

(1*S,2*S**)-1-Phenyl-2-[(1-trimethylsilyl)ethenyl]hexan-1-ol (13h) (ds = 87:13).** The phosphate (*E*)-**4c** (0.20 g, 6.20 mmol) and benzaldehyde (0.06 g, 0.57 mmol) were added to a suspension of LiI (0.08 g, 0.60 mmol) and $CrCl_2$ (0.16 g, 1.30 mmol) in DMPU (3 mL). After 5 d at rt, the reaction was worked up as usual. Purification by chromatography (hexanes: ether 95:5) yielded **13h** as an oil (0.13 g, 0.47 mmol, 83% yield). IR (neat): 3440 (br), 3035 (w), 2965 (s), 1610 (w), 1495 (w), 1460 (m) cm^{-1}. ^1H-NMR ($CDCl_3$, 300 MHz): δ 7.30−7.17 (m, 5H), 5.73 (d, 1H, J = 2.1 Hz), 5.59 (d, 1H, J = 2.3 Hz), 4.58 (d, 1H, J = 4.75 Hz), 2.55 (dt, 1H, J = 10.8, 4.0 Hz), 2.02 (s, 1H), 1.60−1.36 (m, 2H), 1.27−0.84 (m, 4H), 0.75 (t, 3H, J = 7.1 Hz), 0.00 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 153.6, 143.3, 128.1, 127.0, 126.5, 126.1, 75.4, 50.9, 29.8, 27.1, 23.0, 14.0, −1.2. MS-EI (70 eV): 278 (1) [M^+ + 1], 277 (1) [M^+], 179 (31), 170 (43), 156 (35), 155 (94), 128 (37), 115 (15), 114 (17), 113 (26), 108 (27), 107 (100). Anal. Calcd for $C_{17}H_{28}OSi$ (276.48): C, 73.85; H, 10.20. Found: C, 73.57; H 10.50.

(6*R,5*R**)-5-[(1-Trimethylsilyl)ethenyl]dodecan-6-ol (13i) (ds = 68:32).** The phosphate (*Z*)-**4c** (0.90 g, 2.8 mmol) and heptanal (0.29 g, 2.54 mmol) were added to a suspension of LiI (0.07 g, 0.52 mmol) and $CrCl_2$ (0.79 g, 6.43 mmol) in DMPU (5 mL). After 7d at 25 °C the reaction was worked up as usual. Purification by chromatography (hexanes:ether 95:5) furnished **13i** as a clear oil (0.50 g, 1.75 mmol, 69% yield). IR (neat): 3430 (br), 3055 (w), 2935 (s), 1475 (m) cm^{-1}. ^1H-NMR ($CDCl_3$, 300 MHz): δ 5.67 (dd, 1H, J = 2.6, 0.6 Hz), 5.56 (d, 1H, J = 2.7 Hz), 3.46 (m, 1H), 2.17 (m, 1H), 1.55−1.03 (m, 17H), 0.83 (t, 3H, J = 6.9 Hz), 0.82 (t, 3H, J = 7.0 Hz), 0.05 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 153.8, 125.5, 73.5, 53.0, 34.5, 31.8, 30.7, 29.9, 29.4, 25.8, 22.9, 22.5, 14.0, 13.95, −0.5. MS-EI (70 eV): 156 (10), 155 (59), 128 (9), 96 (37). Anal. Calcd for $C_{17}H_{36}OSi$ (284.54): C, 71.76; H 12.75. Found: C, 71.65; H, 12.66.

(6*R,5*S**) 5-[(1-Trimethylsilyl)ethenyl]dodecan-6-ol (13j) (ds = 87:13).** The phosphate (*E*)-**4c** (0.27 g, 0.84 mmol) and heptanal (90 mg, 0.79 mmol) were added to a suspension of LiI (0.11 g, 0.82 mmol) and $CrCl_2$ (0.21 g, 1.71 mmol) in DMPU (3 mL). Reaction conditions: 25 °C, 6 d. Purification by flash chromatography (hexanes:ether 97:3) furnished **13j** as a clear oil (0.15 g, 0.53 mmol, 67% yield). IR (neat): 3455 (br), 3045 (w), 2940 (s), 1473 (m), 1412 (m) cm^{-1}. ^1H-NMR ($CDCl_3$, 300 MHz): δ 5.60 (dd, 1H, J = 2.6, 0.6 Hz), 5.50 (d, 1H, J = 2.6 Hz), 3.36 (m, 1H), 2.20 (dt, 1H, J = 10.7, 4.5 Hz), 1.60 (s, 1H), 1.54−0.96 (m, 16H), 0.81 (t, 3H, J = 6.8 Hz), 0.80 (t, 3H, J = 7.2 Hz), 0.02 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 153.7, 125.5, 73.2, 50.3, 35.0, 31.7, 29.8, 29.3, 27.3, 26.2, 22.9, 22.5, 14.0, 13.9, −1.1. MS-EI (70 eV): 285 (1) [M^+], 155 (60), 97 (13), 96 (28). Anal. Calcd for $C_{17}H_{36}OSi$ (284.54): C, 71.76; H, 12.75. Found: C, 71.58; H, 12.95.

(1*S,2*S**)-2,6-Dimethyl-2-ethenyl-1-phenyl-5-hepten-1-ol (13k). (a) Preparation of 13k from the Phosphate 9d in THF (ds = 93:7). See typical procedure above.**

(b) Preparation from the Phosphate 9d in DMPU (ds = 97:3). Obtained as an oil (0.80 g, 94% yield) from the phosphate **9e** (1.45 g, 5.0 mmol) and benzaldehyde (0.37 g, 3.5 mmol). Reaction conditions: 25 °C, 3 h. Purified by flash chromatography (hexanes:ether 16:1). IR (neat): 3458 (m), 2969 (s), 2925 (s), 2857 (m), 1638 (w) cm^{-1}. ^1H-NMR (500 MHz, $CDCl_3$): δ 7.31−7.26 (m, 5H), 5.86 (dd, 1H, J = 17.6, 10.8 Hz), 5.28 (dd, 1H, J = 10.9, 1.4 Hz), 5.09 (dd, 1H, J = 17.6, 1.4 Hz), 5.04 (m, 1H), 4.42 (s, 1H), 2.04 (s, 1H), 1.85 (m, 2H), 1.65 (d, 3H, J = 0.9 Hz), 1.55 (s, 3H), 1.51−1.26 (m, 2H), 0.92 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.8, 140.4, 131.1, 128.0 (2C), 127.4 (2C), 127.3, 124.7, 115.7, 80.0, 45.8, 37.5, 25.6, 22.7, 17.5, 16.2. MS-EI (70 eV): 244 (1) [M^+], 158 (2), 138 (20), 123 (26), 107 (88), 95 (57). Anal. Calcd for $C_{17}H_{24}O$ (244.36): C, 83.56; H, 9.89. Found: C, 83.49; H, 10.03.

(1*S,2*S**)-2,6-Dimethyl-2-ethenyl-1-phenyl-5-hepten-1-ol (13l) (ds = 99:1). (a) Preparation of 13l from the Phosphate (9e) in DMPU.** Obtained as a clear oil (0.96 g, 98% yield) from the phosphate **9e** (1.45 g, 5 mmol), benzaldehyde (0.42 g, 4 mmol), LiI (0.13 g, 1 mmol), and $CrCl_2$ (1.23 g, 10 mmol) in DMPU (6 mL). Reaction conditions: 25 °C, 3 h. Purified by flash chromatography (hexanes:ether 16:1).

(b) Preparation of 13l from the Phosphate (9e) in THF (ds = 93:7). Obtained as a clear oil (0.93 g, 3.81 mmol, 91% yield) from the phosphate **9e** and benzaldehyde (0.44 g, 4.18 mmol), LiI (0.20 g, 1.49 mmol), and $CrCl_2$ (1.42 g, 11.6 mmol) in THF (4 mL). Reaction conditions: 25 °C, 17 h. Purified by flash chromatography (hexanes:ether 95:5).

(c) Preparation of 13l from Neryl Chloride in THF (ds = 99:1). Obtained from the addition of neryl chloride (0.70 g, 4.05 mmol) and benzaldehyde (0.49 g, 4.62 mmol) to a suspension LiI (0.11 g, 8.22 mmol) and $CrCl_2$ (1.03 g, 8.38 mmol) in THF (14 mL) (reaction conditions: rt, 3 d). The purification by flash chromatography (hexanes:ether 95:5) furnished **13l** as an oil (0.92 g, 3.77 mmol, 93% yield). IR (neat): 3456 (m), 2969 (s), 2926 (s), 1638 (w) cm^{-1}. ^1H-NMR ($CDCl_3$, 200 MHz): δ 7.30 (m, 5H), 5.81 (dd, 1H, J = 17.7, 8.7 Hz), 5.20 (d, 1H, J = 11.8 Hz), 5.02 (m, 2H), 4.44 (d, 1H, J = 3.9 Hz), 2.16 (d, 1H, J = 3.9 Hz), 1.88 (m, 2H), 1.66 (s, 3H), 1.56 (s, 3H), 1.35 (m, 2H), 1.07 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 142.8, 141.3, 130.7, 127.7, 127.2, 127.1, 124.9, 114.5, 80.5, 45.0, 36.3, 25.4, 22.7, 18.5, 17.4. MS (CI, NH_4^+, 34): 244 (19), 227 (100), 136 (72). Anal. Calcd for $C_{17}H_{24}ONH_4^+$: 262.2171. Found: 262.2169.

(6*R,7*S**)-7,11-Dimethyl-7-ethenyl-10-dodecen-6-ol (13m) (ds = 94:6).** Obtained as an oil (0.77 g, 93% yield) prepared from the phosphate **9e** (1.45 g, 5.0 mmol) and hexanal (0.35 g, 3.5 mmol). Reaction conditions: rt, 3 h. Purified by flash chromatography (hexanes:ether 16:1). IR (neat): 3446 (m), 2926 (s), 2858 (s), 1635 (w) cm^{-1}. ^1H-NMR ($CDCl_3$, 200 MHz): δ 5.76 (dd, 1H, J = 17.5, 10.9 Hz), 5.20 (dd, 1H, J = 10.9, 1.5 Hz), 5.07 (m, 2H), 3.26 (d, 1H, J = 9.8 Hz), 1.88 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.47 (m, 11H), 0.96 (s, 3H), 0.89 (t, 3H, J = 6.6 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 144.3, 131.0, 124.8, 114.6, 77.1, 44.9, 37.3, 31.8, 30.9, 26.6, 25.4, 22.7, 22.5, 17.4, 16.8, 13.8. MS-EI (70 eV): 238 (3), 123 (43), 109 (17), 95 (76). Anal. Calcd for $C_{16}H_{30}O$: 238.2297. Found: 238.2286.

(6*R,7*R**)-7,11-Dimethyl-7-ethenyl-10-dodecen-6-ol (13n) (ds = 99:1).** Obtained as a clear oil (0.78 g, 94% yield) from the phosphate **9d** (1.45 g, 5.0 mmol) and hexanal (0.35 g, 3.5 mmol). Reaction conditions: 25 °C, 3 h. Purified by flash chromatography (hexanes:ether 16:1). IR (neat): 3392 (m), 3388 (m), 2961 (s), 2939 (s), 1637 (w) cm^{-1}. ^1H-NMR ($CDCl_3$, 200 MHz): δ 5.72 (dd, 1H, J = 17.5, 10.9 Hz), 5.06 (m, 3H), 3.28 (d, 1H, J = 10.0 Hz), 1.87 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.35 (m, 11H), 1.00 (s, 3H), 0.88 (t, 3H, J = 7.4 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 143.7, 130.9, 124.9, 114.0, 77.9, 44.7, 37.3, 31.7, 26.6, 25.4, 22.6, 22.5, 17.6, 17.3, 13.8. MS-EI (70 eV): 238 (4), 123 (61), 109 (31), 95 (95). Anal. Calcd for $C_{16}H_{30}O$: 238.2297. Found: 238.2289.

(6*S,7*R**)-2,6-Dimethyl-6-ethenyl-2,8(*E*)-dodecadien-7-ol (13o) (ds = 96:4). (a) Preparation of 13o from the Phosphate 9d in DMPU.** Obtained as a clear oil (0.73 g,

77% yield) from **9d** (1.45 g, 5 mmol) and (*E*)-2-hexenal (0.39 g, 4 mmol). Flash chromatography purification (2% ether in hexanes).

(b) Preparation of 13o from Phosphate 9d in THF (ds = 97:3). Obtained by the addition of **9d** (2.19 g, 7.53 mmol) and (*E*)-2-hexenal (0.63 g, 6.46 mmol) to a suspension of LiI (0.20 g, 1.52 mmol) and $CrCl_2$ (2.16 g, 17.6 mmol) in THF (16 mL) (reaction conditions: 25 °C, 16 h). Purification by flash chromatography furnishes the alcohol **13o** as a clear oil (1.32 g, 5.59 mmol, 87% yield). IR (neat): 3445 (br), 2960 (s), 2938 (s), 1725 (m), 1452 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.79 (1H, dd, J = 17.6 Hz, 10.1 Hz), 5.69–6.61 (1 H, m), 5.48–5.40 (1 H, m), 5.21 (1H, d, J = 10.8 Hz), 5.10–5.03 (2H, m), 3.75 (1H, d, J = 7.7 Hz), 2.02 (2H, m), 1.89–1.66 (2H, m), 1.57–1.30 (11H, m), 1.02–0.87 (6H, m). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.9, 134.4, 131.1, 128.6, 124.8, 115.0, 78.5, 44.7, 37.5, 34.4, 25.5, 22.6, 22.2, 17.5, 16.8, 13.6. MS-EI (70 eV): 95 (49), 123 (20), 175 (10). Anal. Calcd for $C_{16}H_{28}O$: C, 81.28; H, 11.95. Found: C, 81.44; H, 11.62.

(6*S,7*S**)-2,6-Dimethyl-6-ethenyl-2,8(*E*)-dodecadien-7-ol (13p) (ds = 97:3). (a) Preparation of 13p from the Phosphate 9e in DMPU.** Obtained as a clear oil (0.79 g, 84% yield) from **9e** (1.45 g, 5 mmol) and (*E*)-2-hexenal (0.39 g, 4 mmol). Purification by flash chromatography (2% ether in hexanes).

(b) Preparation of 13p from the Phosphate 9e in THF (ds = 96:4). Obtained as a clear oil (1.10 g, 4.65 mmol, 92% yield) from **9e** (1.78 g, 6.13 mmol), (*E*)-2-hexenal (0.50 g, 5.04 mmol), LiI (0.14 g, 1.08 mmol), and $CrCl_2$ (1.53 g, 12.5 mmol) in THF (16 mL). Reaction conditions: 25 °C, 16 h; purified by flash chromatography (hexanes:ether 95:5).

(c) Preparation of 13p from Neryl Chloride in DMPU (ds = 96:4). Obtained as a clear oil (0.84 g, 3.55 mmol, 68% yield) from neryl chloride (1.00 g, 5.79 mmol), (*E*)-2-hexenal (0.51 g, 5.2 mmol), LiI (0.16 g, 1.2 mmol), and $CrCl_2$ (1.50 g, 12.2 mmol) in DMPU (10 mL). Reaction conditions: 25 °C, 4 d. Purified by flash chromatography (hexanes:ether 95:5). IR (neat): 3453 (br), 2962 (s), 2937 (s), 1729 (m), 1469 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.80 (1H, dd, J = 17.5 Hz, 10.9 Hz), 5.71–5.47 (2H, m), 5.27–5.04 (3H, m), 3.81 (1H, t, J = 6.3 Hz), 2.04 (2H, m), 1.95–1.88 (2H, m), 1.70 (3H, s), 1.60–1.34 (8H, m), 1.06 (3H, s), 0.90 (3H, t, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.2, 133.5, 131.2, 129.4, 125.0, 114.7, 79.1, 44.6, 37.0, 34.5, 25.7, 22.7, 22.4, 18.8, 17.6, 13.7. MS EI (70 eV): 95 (50), 99 (42), 123 (21). Anal. Calcd for $C_{16}H_{28}O$ (236.39): C, 81.28; H, 11.95. Found: C, 81.02; H, 12.14.

(6*S,7*S**)-2,6-Dimethyl-6-ethenyldodec-2-en-8-yn-7-ol (13q) (ds = 99:1).** Obtained as a clear oil (0.85 g, 86% yield) from the phosphate **9d** (1.45 g, 5 mmol) and 2-heptynal (0.44 g, 4 mmol). Purification by flash chromatography (2% ether in hexanes). IR (neat): 3449 (vb), 2969 (s), 2940 (s), 1456 (m), 1382 (m), 1003 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (1H, dd, J = 17.6, 10.8 Hz), 5.19–4.98 (3H, m), 4.06 (1H, s), 2.19–2.15 (2H, m), 1.85–1.77 (2H, m), 1.53–1.22 (13H, m), 1.03 (3H, s), 0.83 (3H, t, J = 1.3 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.8, 131.3, 124.6, 115.5, 86.8, 78.6, 69.3, 45.4, 36.7, 30.7, 25.6, 22.7, 22.5, 21.9, 18.3, 17.5, 13.5. MS-EI (70 eV): 41 (92), 69 (100), 81 (19), 95 (29), 111 (15), 123 (15). Anal. Calcd for $C_{17}H_{28}O$ (248.40): C 82.20, H 11.36. Found: C, 82.26; H, 11.39.

(6*S,7*R**)-2,6-Dimethyl-6-ethenyldodec-2-en-8-yn-7-ol (13r) (ds = 98:2).** Obtained as a clear oil (0.88 g, 89% yield) from the phosphate **9e** (1.45 g, 5 mmol) and 2-heptynal (0.44 g, 4 mmol). Purification by flash chromatography (2% ether in hexanes). IR (neat): 3455 (br), 2987 (s), 2944 (s), 1475 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.83 (1 H, dd, J = 17.6, 10.9 Hz), 5.18–4.93 (3H, m), 3.99 (1H, s), 2.18–2.13 (2H, m), 1.87–1.75 (2H, m), 1.60–1.30 (13H, m), 1.02 (3H, s), 0.84 (3H, t, J = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.1, 131.3, 124.7, 115.6, 86.9, 79.1, 69.7, 45.3, 37.0, 30.7, 25.6, 22.6, 22.1, 18.4, 18.3, 17.5, 13.5. MS-EI (70 eV): 95 (34), 111 (11), 123 (13). Anal. Calcd for $C_{17}H_{28}O$ (248.40): C, 82.20; H, 11.36. Found: C, 81.90; H, 11.44.

(6*S,7*R**)-6-Ethenyl-2,6-dimethyltridec-11-en-7ol (13s) (ds = 97:3). (a) Preparation of 13s from the Phosphate 9d in DMPU.** Obtained as a clear oil (0.95 g, 3.76 mmol, 72% yield) from the phosphate **9d** (1.76 g, 6.1 mmol), heptanal (0.60 g, 5.25 mmol), LiI (0.16 g, 1.23 mmol), and $CrCl_2$ (1.67 g, 13.6 mmol) in THF (19 mL). Reaction conditions: 25 °C, 23 h. Purified by flash chromatography (hexanes:ether 97:3).

(b) Preparation of 13s Using Ph_2Cr (ds = 96:4). To a suspension of $CrCl_2$ (1.47 g, 11.96 mmol) in THF (12 mL) was added TMEDA (1.40 g, 1.8 mL, 12.8 mmol). After 1 h, the blue suspension was treated with PhMgBr (23.1 mmol, 21 mL of a 1.1 M solution in THF) at −30 °C for 20 min. After the solution cooled to −60 °C for 1 h, geranyl bromide (1.24 g, 5.71 mmol) was added dropwise over a period of 45 min followed by the addition of heptanal (0.57 g, 5.0 mmol) at −70 °C. Typical workup and purification by flash chromatography (hexanes:ether 95:5) furnished **13s** as an oil (0.67 g, 2.65 mmol, 53% yield). IR (neat): 3427 (s, br), 3081 (m), 2925 (s), 1636 (s), 1456 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.75 (dd, 1H, J = 17.6, 10.9 Hz), 5.20 (dd, 1H, J = 10.8, 1.5 Hz), 5.09 (m,1H), 5.05 (dd, 1H, J = 17.6, 1.5 Hz), 3.26 (m, 1H), 1.91–1.75 (m, 2H), 1.66 (s, 3H), 1.57 (s, 3H), 1.47–1.24 (m, 13 H), 0.95 (s, 3H), 0.87 (t, 3H, J = 6.4 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.3, 131.2, 124.8, 114.8, 77.1, 45.0, 37.3, 31.8, 30.9, 29.4, 27.0, 25.6, 22.7, 22.6, 17.5, 16.6, 14.0. MS-EI (70 eV): 252 (1) [M^+]. Anal. Calcd for $C_{17}H_{32}O$ (252.44): C, 80.89; H, 12.77. Found: C, 79.98; H, 13.16.

(6*R,7*R**)-6-Ethenyl-2,6-dimethyltridec-11-en-7ol (13t) (ds = 98:2). (a) Preparation of 13t from the Phosphate 9e in DMPU.** Obtained as a clear oil (1.01 g, 4.0 mmol, 71% yield) from **9e** (0.39 g, 4 mmol), heptanal (0.64 g, 5.61 mmol), LiI (0.19 g, 1.41 mmol), and $CrCl_2$ (1.96 g, 16.0 mmol) in THF (19 mL). Reaction conditions: rt, 1 d. Purification by flash chromatography (hexanes:ether 97:3).

(b) Preparation of 13t from Neryl Chloride in DMPU (ds = 96:4). Obtained by the addition of neryl chloride (1.00 g, 5.79 mmol) and heptanal (0.59 g, 5.17 mmol) to a suspension of LiI (0.16 g, 1.20 mmol) and $CrCl_2$ (1.50 g, 12.21 mmol) in DMPU (10 mL) (reaction conditions: rt, 16 h). Purification by flash chromatography (hexanes:ether 97:3) furnished the desired alcohol as an clear oil (0.88 g, 3.49 mmol, 68% yield). IR (neat): 3390 (s, br), 3083 (m), (2927 s, sh), 1638 (m), 1456 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.71 (dd, 1H, J = 17.6, 10.9 Hz), 5.14 (dd, 1H, J = 10.9, 1.5 Hz), 5.09 (m, 1H), 5.01 (dd, 1H, J = 17.6, 1.6 Hz), 3.27 (m, 1H), 1.88–1.87 (m, 2H), 1.66 (d, 3H, J = 0.9 Hz), 1.58 (s, 3H), 1.49–1.46 (m, 2H), 1.37–1.31 (m, 2H), 1.25–1.10 (m, 9H), 1.00 (s, 3H), 0.87 (t, 3H, J = 6.6 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.8, 131.2, 125.0, 114.4, 78.1, 44.9, 37.5, 32.0, 31.9, 29.5, 27.2, 25.7, 22.8, 22.7, 17.9, 17.6, 14.1. MS-EI (70 eV): 252 (1) [M^+], 123 (30), 109 (16), 95 (70), 82 (18). Anal. Calcd for $C_{17}H_{32}O$ (252.44): C, 80.89; H, 12.77. Found: C, 80.76; H, 12.86.

(1*S,2*R**)-1-Cyclohexyl-2-ethenyl-2,6-dimethylhept-5-en-1-ol (13u). (a) Preparation of 13u from the Phosphate 9d in THF (ds = 96:4).** Obtained as a clear oil (0.72 g, 2.9 mmol, 66% yield) from the phosphate **9d** (1.83 g, 6.29 mmol) and cyclohexanecarboxaldehyde (0.51 g, 4.41 mmol), LiI (0.14 g, 1.10 mmol), and $CrCl_2$ (1.65 g, 13.43 mmol) in THF (29 mL). Reaction conditions: rt, 17 h. Purified by flash chromatography (hexanes:ether 95:5).

(b) Preparation of 13u in DMPU from Geranyl Chloride (ds = 93:7). Geranyl chloride (0.57 g, 3.3 mmol) and cyclohexanecarboxaldehyde (0.36 g, 3.17 mmol) were added to a suspension of $CrCl_2$ (1.37 g, 11.2 mmol) and LiI (0.17 g, 1.27 mmol) in DMPU (14 mL). After being stirred at rt for 14 h, the reaction mixture was worked up as usual. Purification by flash chromatography (hexanes:ether 95:5) furnished **13u** as a clear oil (0.68 g, 2.70 mmol, 85% yield).

(c) Preparation of 13u Using Ph_2Cr (ds = 92:8). To a suspension of $CrCl_2$ (1.46 g, 11.9 mmol) in THF (12 mL) was added TMEDA (1.40 g, 1.8 mL, 12.1 mmol). After 1 h, the resulting blue suspension was treated with PhMgBr (23.1 mmol, 21 mL of a 1.1 M solution in THF) at −30 °C for 20 min. After the mixture was cooled to −60 °C a solution of geranyl bromide (1.23 g, 5.66 mmol) was added dropwise over a period of 45 min, followed by the addition of cyclohexanecarboxaldehyde (0.57 g, 5.9 mmol). GC analysis indicated the end of the reaction after 20 min. Usual workup and purification by flash chromatography (hexanes:ether 95:5) furnished **13u** as a colorless oil (0.45 g, 1.80 mmol, 36% yield). IR (neat): 3491 (m,br), 3082 (w), 2925 (s), 2854 (s), 1634 (w), 1451

(s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.82 (dd, 1H, J = 17.7, 10.9 Hz), 5.14 (dd, 1H, J = 10.8, 1.4 Hz), 5.09 (m, 1H), 5.01 (dd, 1H, J = 17.7, 1.4 Hz), 3.10 (d, 1H, J = 1.6 Hz), 1.84 (m, 2H), 1.76–1.68 (m, 3H), 1.66 (s, 3H) 1.57 (s, 3H), 1.51–1.04 (m, 11H), 1.00 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.6, 131.3, 125.0, 114.2, 81.5, 45.7, 39.1, 38.2, 33.9, 27.4, 27.1, 26.5, 26.5, 25.7, 22.9, 18.1, 17.7. MS-EI (70 eV): 250 (1) [M^+], 123 (33), 96 (13), 95 (97). Anal. Calcd for $C_{17}H_{30}O$ (250,41): C, 81.54; H, 12.07. Found: C, 81.78; H, 12.16.

(1*S,2*S**)-1-Cyclohexyl-2-ethenyl-2,6-dimethylhept-5-en-1-ol (13v). (a) Preparation of 13v from the Phosphate 9e in THF (ds = 94:6).** Obtained as a clear oil (1.09 g, 4.35 mmol, 73% yield) prepared from the phosphate **9e** (2.21 g, 7.61 mmol), cyclohexanecarboxaldehyde (0.67 g, 6 mmol), LiI (0.19 g, 1.42 mmol), and $CrCl_2$ (2.68 g, 21.8 mmol) in THF (29 mL). Reaction conditions: rt, 17 h. Purified by flash chromatography (hexanes:ether 97:3).

(b) Preparation of 13v from Phosphate 9e in *N*-methyl-2-pyrrolidone (NMP) (ds = 89:11). Clear oil (0.75 g, 3.00 mmol, 68% yield) obtained from **9e** (1.46 g, 5.00 mmol), cyclohexanecarboxaldehyde (0.49 g, 4.40 mmol), LiI (0.15 g, 1.12 mmol), and $CrCl_2$ (1.45 g, 11.80 mmol) in NMP (10 mL). Reaction conditions: 25 °C, 20 h. Purification by flash chromatography (hexanes:ether 97:3).

(c) Preparation of 13v from Neryl Chloride in DMPU (ds = 83:17). Obtained as a clear oil (0.94 g, 3.75 mmol, 84% yield) from neryl chloride (0.83 g, 4.81 mmol), cyclohexanecarboxaldehyde (0.50 g, 4.46 mmol), LiI (0.13 g, 0.97 mmol), and $CrCl_2$ (1.20 g, 9.76 mmol) in DMPU (30 mL). Reaction conditions: 25 °C, 3 d. Purification by flash chromatography (hexanes:ether 97:3). IR (neat): 3485 (m, br), 3058 (w), 2921 (s), 2854 (s), 1636 (w), 1449 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.79 (dd, 1H, J = 17.6, 10.9 Hz), 5.13 (dd, 1H, J = 10.9, 1.5 Hz), 5.09 (m, 1H), 5.01 (dd, 1H, J = 17.6, 1.4 Hz), 3.11 (d, 1H, J = 2.1 Hz), 1.88 (m, 2H), 1.72–1.01 (m, 14 H), 1.67 (s, 3H), 1.58 (s, 3H), 1.04 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144, 131.2, 124.9, 114.1, 81.8, 45.6, 39.3, 38.4, 33.5, 27.6, 26.8, 26.3 (2C), 25.6, 22.7, 19.1, 17.5. MS-EI (70 eV): 250 (1) [M^+], 167 (2), 123 (28), 109 (13), 96 (13). Anal. Calcd for $C_{17}H_{30}O$ (250.41): C, 81.54; H, 12.07. Found: C, 81.30; H, 12.15.

(1*R,2*R**)-2-Ethenyl-1-phenyl-2,6,10-trimethyl-5(*E*),9-undecadien-1-ol (13w) (ds = 95:5).** Obtained as a clear oil (1.18 g, 84% yield) from the phosphate **9f** (1.80 g, 5.0 mmol) and benzaldehyde (0.48, 4.5 mmol). Reaction conditions: rt, 18 h. Purification by flash chromatography (ether:hexanes 93:7). IR (neat): 3463 (s,br), 3083 (w), 3031 (m), 2925 (s), 1453 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.31–7.25 (m, 5H), 5.87 (dd, 1H, J = 17.6, 10.8 Hz), 5.28 (dd, 1H, J = 10.8, 1.3 Hz), 5.09 (dd, 1H, J = 17.6, 1.3 Hz), 5.07 (tt, 1H, J = 9.5, 1.3 Hz), 5.05 (tt, 1H, J = 9.9, 1.2 Hz), 4.43 (s, 1H), 2.06–2.02 (m, 3H), 1.95–1.93 (m, 2H), 1.89–1.84 (m, 2H), 1.67 (d, 3H, J = 1.1 Hz), 1.59 (s, 3H), 1.54 (s, 3H), 1.44–1.27 (m, 2H), 0.92 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 143.9, 140.6, 134.8, 131.2, 128.1, 127.5, 127.4, 124.7, 124.4, 115.7, 80.1, 45.9, 39.7, 37.5, 26.7, 25.7, 22.8, 17.7, 16.5, 16.0. MS-FD (70 eV): 312 (58) [M^+], 107 (89), 106 (100). Anal. Calcd for $C_{22}H_{32}O$ (312.4988): C, 84.56; H, 10.32. Found: C, 84.5; H, 10.29.

(7*S,8*R**)-8-Ethenyl-8,12,16-trimethyl-11(*E*),15-heptadecadien-7-ol (13x) (ds = 93:7).** Obtained as a clear oil (1.12 g, 88% yield) from the phosphate **9f** (1.82 g, 5.1 mmol) and heptanal (0.46 g, 4.0 mmol). Purification by flash chromatography (hexanes:ether 93:7). IR (neat): 3450 (brs), 3081 (w), 2927 (s), 1636 (w), 1457 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.75 (dd, 1H, J = 17.6, 10.8 Hz), 5.20 (dd, 1H, J = 10.8, 1.3 Hz), 5.09 (tt, 1H, J = 6.1, 1.2 Hz), 5.08 (tt, 1H, J = 6.5, 1.3 Hz), 5.05 (dd, 1H, J = 17.6, 1.4 Hz), 3.26 (d, 1H, J = 9.5 Hz), 2.06–1.94 (m, 7H), 1.67 (d, 3H, J = 0.9 Hz), 1.59 (s, 3H), 1.57 (s, 3H), 1.50–1.20 (m, 12H), 0.96 (s, 3H), 0.87 (t, 3H, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.3, 134.8, 131.1, 124.6, 124.3, 114.8, 77.1, 45.0, 39.6, 37.3, 31.8, 30.9, 29.3, 27.0, 26.6, 25.6, 22.6, 22.5, 17.5, 16.6, 15.8, 14.0. MS-EI (70 eV): 177 (3), 137 (20), 95 (20), 81 (47). Anal. Calcd for $C_{22}H_{40}O$ (320.5623): C, 82.43; H, 12.58. Found: C, 82.33; H, 12.50.

(1*S,2*R**)-1-Cyclohexyl-2-ethenyl-2,6,10-trimethyl-5(E),9-undecadien-1-ol (13y) (ds = 94:6).** Obtained as a clear oil (1.29 g, 86% yield) from the phosphate **9f** (1.81 g, 5.1 mmol) and cyclohexanecarboxaldehyde (0.53 g, 4.7 mmol). Purification by flash chromatography (hexanes:ether 93:7). IR (neat): 3469 (brs), 3081 (w), 2925 (s), 2854 (s), 1634 (m), 1451 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 5.82 (dd, 1H, J = 17.6, 10.9 Hz), 5.14 (dd, 1H, J = 10.9, 1.5 Hz), 5.10 (tt, 1H, J = 6.7, 1.2 Hz), 5.08 (tt, 1H, J = 6.9, 1.4 Hz), 5.01 (dd, 1H, J = 17.6, 1.5 Hz), 3.11 (s, 1H), 2.06–2.03 (m, 2H), 1.97–1.94 (m, 2H), 1.87–1.70 (m, 7H), 1.67 (d, 3H, J = 1.4 Hz), 1.59 (s, 3H), 1.57 (s, 3H), 1.45–1.11 (m, 9H), 1.01 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.6, 134.8, 131.2, 124.8, 124.4, 114.1, 81.5, 45.6, 39.7, 39.0, 38.1, 33.9, 27.3, 27.0, 26.7, 26.5, 26.4, 25.7, 22.7, 18.1, 17.7, 16.0. MS-EI (70 eV): 318 (2), 137 (17), 95 (51). Anal. Calcd for $C_{22}H_{38}O$ (318.5464): C, 82.95; H, 12.03. Found: C, 82.93, H, 12.08.

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Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra for compounds listed in the Experimental Section (105 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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