1. A sample was purified by bulb-to-bulb distillation at a reduced pressure (0.01 Torr, 25 °C). A pure sample of 1 could be obtained via preparative GC (column temperature <100 °C, 20% OV101 on Chromosorb P column). ^{1}H NMR of 1: δ 6.2 (d, 1 H, J = 2.9 Hz), 6.05 (d, 1 H, J = 2.9 Hz), 4.51–4.46 (m, 2 H), 2.24 (s, 2 H) 2.20–1.96 (m, 2 H), 1.68–1.15 (m, 6 H); ^{13}C NMR δ 153.97, 143.33, 134.61, 104.89, 54.24, 42.95, 38.58, 33.59, 27.82, 24.63; HRMS for $C_{10}H_{14}$ found 134.1087, calcd 134.1096.

1-Methylene-2-allylidenecyclohexane (2). Method A. The reaction of 2-methylenecyclohexanone (8)[19] with the anion derived from NaH and diethyl (cyanomethyl)phosphonate gave a mixture of Z and E nitriles 9. The crude nitrile mixture 9 was reduced with diisobutylaluminum hydride followed by acid hydrolysis to give a mixture of aldehydes 10.[20] Bulb-to-bulb distillation under vacuum (0.01 Torr, 20 °C) led to a 1:1 mixture of Z and E aldehydes 10 along with some impurities. ^{1}H NMR analysis of this mixture showed 2 doublets (~1:1 ratio) at ~10.0 ppm which correspond to the E and Z aldehyde protons. One of these aldehydes goes away quickly. The aldehyde mixture was treated with ylide derived from methyltriphenylphosphonium bromide and n-butyllithium in diethyl ether for 8 h. Standard workup and solvent removal revealed only one triene. This triene was purified by silica gel flash chromatography and was assigned structure 2.

Method B. (E)-2-Acetoxycyclohexanone (12)[21] was treated with the ylide derived from allyltriphenylphosphonium chloride and potassium hexamethyldisilazide (Li-free condition)[21] gave a low yield (~10%) of diene 13. It was purified by silica gel flash chromatography (8% ethyl acetate in hexanes). The ester 13 was reduced with lithium aluminum hydride in diethyl ether to afford alcohol 14, which without further purification was oxidized with PDC[22] in methylene chloride (8 h, room temperature) to the ketone 15E. It was purified by flash chromatography (8% ethyl acetate in hexanes). Wittig reaction of ketone 15E with the ylide derived from triphenylphosphonium bromide and n-butyllithium in diethyl ether gave triene 2 in good yield. Bulb-to-bulb distillation under vacuum (0.01 Torr, room temperature) afforded pure triene 2.

12: ^{1}H NMR δ 5.20–5.13 (m, 1 H), 2.56–2.25 (m, 4 H), 2.16 (s, 3 H), 2.10–1.60 (m, 4 H).

13: ^{1}H NMR δ 6.60–6.54 (apparent td, 1 H, J = 10, 10.8, and 16.5 Hz), 6.00 (d, 1 H, J = 10.8 Hz), 5.30–5.20 (m, 2 H), 5.11 (d, 1 H, J = 10 Hz), 2.58–2.20 (m, 2 H), 2.09 (s, 3 H), 2.01–1.50 (m, 6 H); HRMS for $C_{11}H_{16}O_2$ found 180.1134, calcd 180.1150.

14: ^{1}H NMR δ 6.69–6.58 (dt, 1 H, J = 10.0 and 16.8 Hz), 6.08 (bd, 1 H, J = 10.8 Hz), 5.23 (bd, 1 H, J = 17 Hz), 5.08 (bd, 1 H, J = 10.0 Hz); HRMS for $C_9H_{14}O$ found 138.1040, calcd 138.1044.

15E: ^{1}H NMR (400 MHz) δ 7.02 (d, 1 H, J = 12 Hz), 6.64–6.54 (ddd, 1 H, J = 10.8, 12 and 18.4 Hz), 5.63 (bd, 1 H, J = 18.4 Hz), 5.52 (bd, 1 H, J = 10.8 Hz), 2.66–2.62 (dt, 2 H), 2.48–2.44 (bt, 2 H, J = 6.4 Hz), 1.90–1.74 (m, 4 H); ^{13}C NMR δ 201.23, 135.73, 135.08, 131.38, 125.89, 40.22, 26.90, 23.43, 23.20; MS 136 (M^+, 3), 119 (6), 105 (100), 91 (45), 79 (30); HRMS for $C_9H_{12}O$ found 136.0888, calcd 136.0882.

2: ^{1}H NMR (500 MHz) δ 6.67–6.59 (ddd, 1 H, J = 10.1, 11.1, and 16.8 Hz), 6.12 (d, 1 H, J = 11.1 Hz), 5.25–5.21 (dd, 1 H, J = 1.8 and 16.8 Hz), 5.10–5.07 (dd, 1 H, J = 1.7 and 10.1 Hz), 4.91 (bs, 1 H), 4.65 (bs, 1 H), 2.40–2.37 (bt, 2 H), 2.28–2.26 (bt, 2 H), 1.67–1.63 (m, 4 H); ^{13}C NMR δ 150.57, 142.67, 132.69, 123.44, 116.82 108.24, 35.36, 28.92, 26.85, 26.07; MS 134 (M^+, 82), 119 (53), 106 (28), 105 (37), 92 (49), 91 (100), 79 (30), 77 (21); HRMS for $C_{10}H_{14}$ found 134.1103, calcd 134.1096.

Kinetic Studies. Samples were prepared by dissolving 1 (7–8 μL) in $CDCl_3$ (0.5 mL) in an NMR tube. The samples were degassed, and the tubes were sealed under vacuum. Tubes were then immersed in constant boiling solvent baths (isobutyl alcohol, n-butyl alcohol, and xylene), and the ^{1}H NMR spectra were recorded at different periods of time. Ratios of integrals of olefinic protons of compounds 1–3 were measured and corrected to obtain mole fraction data (Table I).

Acknowledgment. We thank the Department of Energy for support of this work.

Supplementary Material Available: Complete experimental procedures for the preparation of 2 and ^{1}H NMR spectra of 1, 2, 9, 10, 13, 14, and 15E (10 pages). Ordering information is given on any current masthead page.

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Reactions between Tantalum- or Niobium–Alkyne Complexes and Carbonyl Compounds

Yasutaka Kataoka, Jiro Miyai, Koichiro Oshima, Kazuhiko Takai,* and Kiitiro Utimoto*

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan

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A variety of tantalum–alkyne complexes are generated in situ by treatment of alkynes with low-valent tantalum derived from $TaCl_5$ and zinc. These complexes add regioselectively to carbonyl compounds in a one-to-one fashion to yield (E)-allylic alcohols stereoselectively. Iodinolysis of the oxatantalacyclopentene, which is postulated as an intermediate of the reaction, gives a (Z)-3-iodo-2-propen-1-ol derivative. In contrast to tantalum–alkyne complexes, niobium–alkyne complexes, prepared with low-valent niobium derived from $NbCl_5$ and zinc, add in situ to aldehydes in a one-to-two fashion to give 1,3-diene derivatives. The dienes are produced through (i) addition of the alkyne complexes with 2 equiv of aldehydes at cis vicinal positions of the alkenes and (ii) deoxygenative elimination of 2,7-dioxanioba-4-cycloheptene complexes.

Since the discovery of transition metal–alkyne complexes, many reports on their structure and reactivities have appeared.[1-12] Recently, they received much attention as useful intermediates in organic synthesis. One of the

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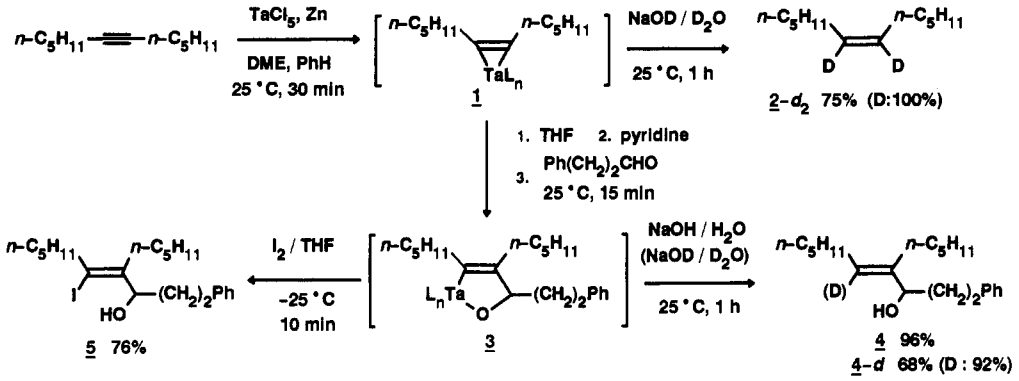
Scheme I



leaps in synthetic chemistry using metal–alkyne complexes is cyclotrimerization of alkynes with cobalt catalysis.[1a-c] Titanocene–[2] and zirconocene–alkyne complexes[3] are also employed in carbon–carbon bond formation. In contrast, group 5 metal–alkyne complexes have not been widely utilized in organic synthesis until quite recently.[4a-c,5] Low-valent tantalum complexes react with inactivated acetylenic triple bonds to form tantalum–alkyne complexes.[5-7] The isolated tantalum–alkyne complexes are sterically congested, and the only carbon–carbon bond-forming transformations which have been effected using these complexes are cyclotrimerizations[6] and coupling reactions with nitriles[7e] and isocyanide.[7f] We disclose in the first half of this paper that the tantalum–alkyne complexes, which are generated in situ by treatment of alkynes with low-valent tantalum, react stereoselectively with carbonyl compounds in a one-to-one fashion to yield (*E*)-allylic alcohols. Niobium–alkyne complexes are also produced by treatment of alkynes with a $NbCl_5$–zinc system. We have found that the niobium complexes react in situ with 2 equiv of simple aldehydes to give 1,3-diene derivatives through deoxygenative elimination of 2,7-dioxanioba-4-cycloheptene complexes. The niobium reaction is described in the second half of this paper.

Regio- and Stereoselective Synthesis of Allylic Alcohols Mediated by Tantalum–Alkyne Complexes.[5c] A variety of tantalum–alkyne complexes have been generated in situ by treatment of alkynes with low-valent tantalum derived from $TaCl_5$ and zinc in a mixed solvent of 1,2-dimethoxyethane (DME) and benzene.[5a] Although the structure of the tantalum–alkyne complexes is not characterized, treatment of the complexes with a NaOD–D_2O solution gave the corresponding cis vicinal dideuterated alkenes. The result prompted us to examine the use of the tantalum–alkyne complexes as a cis vicinal alkene dianion synthon.[4c,5] Treatment of tantalum-6-dodecyne complex 1 with 3-phenylpropanal at 25 °C for 20 min afforded the allylic alcohol 4 in 96% yield after aqueous alkaline workup (Scheme I). (*E*)-Allylic alcohol was produced exclusively,[13] as expected from the insertion of a carbonyl group into the tantalum–carbon bond of the complex 1.

The results of the preparation of allylic alcohols from alkynes and carbonyl compounds are summarized in Table I. Yields of allylic alcohols depended on additives prior to addition of an aldehyde. Coupling reactions between tantalum–alkyne complexes and aldehydes without ad-

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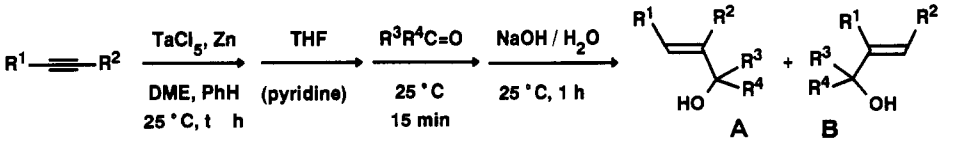
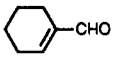
Table I. Synthesis of Allylic Alcohols from Alkynes and Carbonyl Compounds[a]



run	R^1	R^2	R^3	R^4	t/h	yield[b]/%	A/B[c]
1	n-C_5H_{11}	n-C_5H_{11}	n-C_8H_{17}	H	0.5	94	
2			c-C_6H_{11}	H	0.5	87	
3			t-Bu	H	0.5	82	
4			$-(CH_2)_5-$		0.5	87	
5			c-C_6H_{11}	n-C_6H_{13}	0.5	41[d]	
6			c-C_6H_{11}	c-C_6H_{11}	0.5	trace[e]	
7			CH_2=CH	H	0.5	78[f]	
8			CH_2=CH	Me	0.5	76[f]	
9	n-$C_{10}H_{21}$	H	n-C_8H_{17}	H	0.7	48[g]	>99/<1
10			$-(CH_2)_5-$		0.7	45[g]	>99/<1
11	c-C_6H_{11}	n-C_6H_{13}	$Ph(CH_2)_2$	H	1.5	80	65/35
12			$-(CH_2)_5-$		1.5	83	76/24
13	t-Bu	n-C_7H_{15} (6)	$Ph(CH_2)_2$	H	4.5	67[h,i]	>99/<1
14			$-(CH_2)_5-$		4.5	<5[h,j]	
15	n-C_6H_{13}	Ph (7)	$Ph(CH_2)_2$	H	1	73	83/17
16			$-(CH_2)_5-$		1	80	79/21
17			CH_2=CH	H	1.5	75[f]	71/29
18	Me_3Si	n-$C_{10}H_{21}$	$Ph(CH_2)_2$	H	1.5	77[k]	89/11
19			$-(CH_2)_5-$		1.5	85[k]	>99/<1
20			CH_2=CH	H	2	82[f,l]	97/3
21			CH_2=CH	Me	2	85[f,l]	>99/<1
22					2	81[f,l]	>99/<1
23	t-$BuMe_2Si$	n-$C_{10}H_{21}$	$Ph(CH_2)_2$	H	3	68[h,k]	>99/<1
24			$-(CH_2)_5-$		3	71[h,k]	>99/<1
25			CH_2=CH	H	4	75[f,m]	>99/<1

[a] $TaCl_5$ (2.0 equiv), zinc (3.0 equiv), and pyridine (4.0 equiv) were employed. A tantalum–alkyne complex was treated with a carbonyl compound (1.2 equiv) at 25 °C for 15 min unless otherwise noted. [b] Isolated yields. [c] The isomer ratios were determined by ^1H NMR analysis. [d] Unreacted 6-dodecene was recovered in 46% yield. [e] 6-Dodecene was recovered in 91% yield. [f] The tantalum–alkyne complex was treated with an α,β-unsaturated carbonyl compound (2.0 equiv) at 0 °C for 30 min. [g] $TaCl_5$ (1.0 equiv), zinc (1.5 equiv), and pyridine (2.0 equiv) were employed. Tantalum-1-dodecyne complex was treated with a carbonyl compound (1.2 equiv) at 25 °C for 45 min. [h] $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (8.0 equiv) were employed. [i] (Z)-2,2-Dimethyl-3-undecene was obtained in 24% yield. [j] The unreacted olefin was recovered in 81% yield. Cyclohexanone was recovered in 32% yield, and the pinacol-type 1,2-diol of cyclohexanone was produced in 45% yield. [k] The reaction was conducted without addition of pyridine. [l] $TaCl_5$ (2.0 equiv), zinc (3.0 equiv), and pyridine (2.0 equiv) were employed. [m] $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (4.0 equiv) were employed.

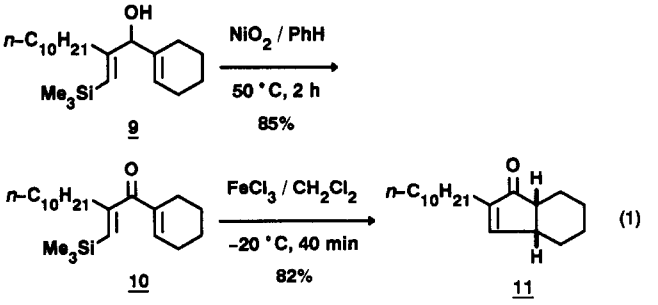
dition of THF was marginal, and many byproducts appeared. Pretreatment of the complexes with pyridine was essential to suppress the formation of 1,3-dienes through dehydration of the allylic alcohols, especially in the case of ketones. Tantalum–6-dodecyne complex 1 reacted with pivalaldehyde (run 3), whereas sterically hindered dicyclohexyl ketone did not react with 1, and unreacted 6-dodecene was recovered in 91% yield (run 6).

In the case of unsymmetrical alkynes, two regioisomeric adducts could be produced. The regioselectivities (A/B) of the reactions with the tantalum–alkyne complexes are higher than those observed with zirconocene–alkyne complexes.[3b,3f] Bulkiness of the substituents R^1, R^2, R^3, and R^4 influences the regiochemistry of the products. Thus, as R^1, R^3, or R^4 become bigger, or as R^2 becomes smaller, higher regioselectivities (A/B) are obtained (except runs 15–17). In the case of the sterically crowded 2,2-dimethyl-3-undecyne (6), both reactions, reduction of the acetylenic bond and addition of the tantalum–alkyne complex to carbonyl compounds, were retarded (runs 13 and 14). The results of the reactions between 1-phenyl-1-octyne (7) and carbonyl compounds reveal that electronic effects are also directing factors of the regiochemistry (runs 15–17). In the case of terminal alkynes, significant amounts (ca. 40% yield) of polymeric products were obtained as byproducts, but this did not involve cyclotrimerized aromatic compounds (runs 9 and 10).[4b,6]

Reaction of tantalum–6-dodecyne complex 1 with acrolein at 25 °C for 15 min produced (E)-4-pentyl-1,4-decadien-3-ol (8) in 60% yield along with a regioisomeric mixture of trienes derived by dehydration of the dienol 8 in 12% yield. The yield of 8 was improved when reaction was conducted at 0 °C and 2.0 equiv of acrolein was employed.

As shown in Scheme I, quenching of the reaction mixture with $NaOD/D_2O$ gave monodeuterated alcohol 4-d in 68% yield. This observation suggests the formation of an oxatantalacyclopentene 3 as an intermediate. The oxatantalacyclopentene 3 could be trapped with I_2 at −25 °C to give iodo alcohol 5 in 76% yield (Scheme I).

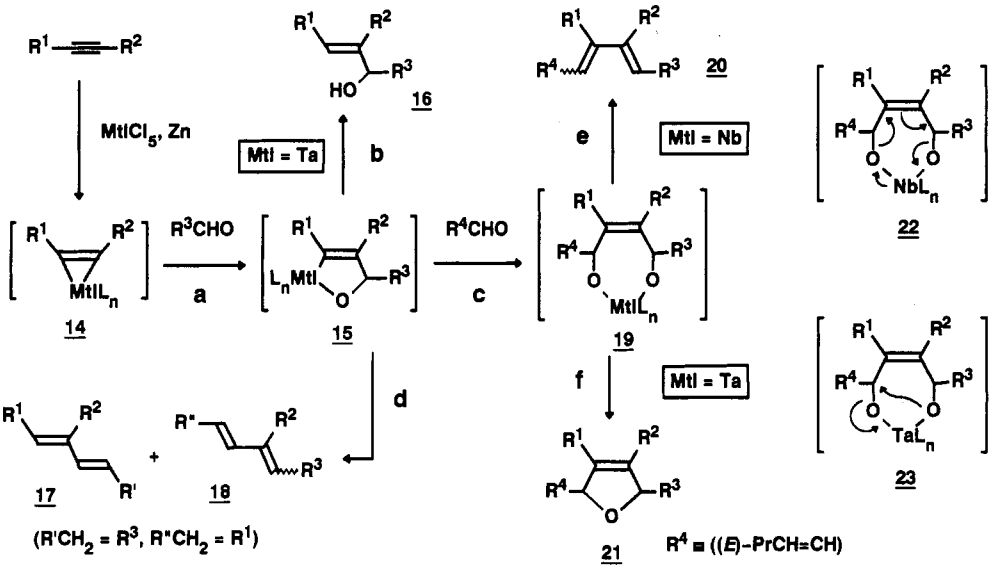
1-Trimethylsilyl-substituted 1,4-dien-3-ol is a useful precursor for silicon-directed Nazarov cyclization (eq 1).[14]



Oxidation of dienol 9, derived by reaction of a tanta-

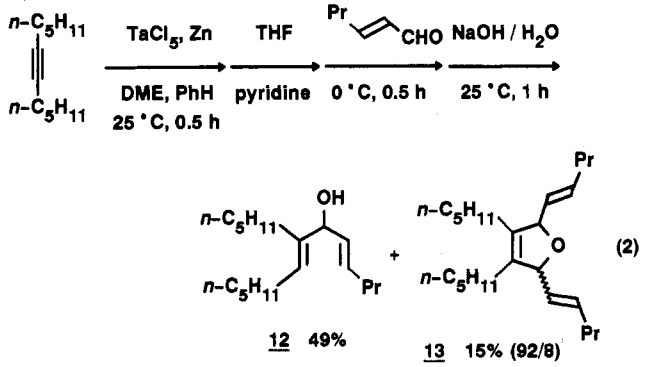
(14) Denmark, S. E.; Jones, T. K. J. Am. Chem. Soc. 1982, 104, 2642.

Scheme II



lum–(1-(trimethylsilyl)-1-dodecyne) complex and 1-cyclohexenylcarbaldehyde (Table I, run 22), was performed with nickel peroxide.[15] Nazarov cyclization of divinyl ketone **10** at −20 °C with $FeCl_3$ afforded bicyclo[4.3.0]nonene derivative **11** in 82% yield.[14]

It is interesting to note that considerable amounts of one-to-two addition products of tantalum–alkyne complexes and aldehydes were produced in the case of α,β-unsaturated aldehydes having one β-substituent. For example, treatment of a tantalum–6-dodecyne complex with (*E*)-2-hexenal at 0 °C for 30 min produced the allylic alcohol **12** in 49% yield and two stereoisomers of 2,5-dihydrofuran derivatives **13** in 15% yield (eq 2).



One-to-Two Addition Reaction of Niobium–Alkyne Complexes to Aldehydes and Sequential Deoxygenation Leading to 1,3-Dienes. Insertion of carbonyl groups into metal–carbon bonds of such alkyne complexes of zirconium,[3] niobium,[4,5b] and tantalum,[5,7c,e,f] takes place, and oxametalacyclopentene complexes are produced. Thus, one terminus of the metal–alkyne complex is employed as an alkene anion equivalent. Although the other metal–carbon bond of the complex still exists, it has not been employed as a nucleophilic center until recently. Pedersen[4c] and we[5b] have reported independently that niobium–alkyne complexes are produced by treating alkynes with low-valent niobium such as $NbCl_3$(DME) and $NbCl_5$–Zn and that reaction of the niobium–alkyne complexes with phthalaldehyde, which has two formyl groups at the suitable positions for cyclization, gave 1-naphthols. We have found that the reactivity of niobium–alkyne complexes, prepared by $NbCl_5$–Zn, toward simple aldehydes is different from that of the complexes prepared from $NbCl_3$(DME) and that the former niobium–alkyne complexes add to 2 equiv of aldehydes at the cis vicinal alkene carbons to give 1,3-diene derivatives.

When niobium–1-dodecyne complex,[5a,18] derived from 1-dodecyne and a $NbCl_5$-Zn system, was treated with excess 3-phenylpropanal at 25 °C, 1,3-diene **20a** was produced after 30 min of stirring (Table II, run 2). New carbon–carbon bonds were formed at vicinal positions of the alkyne. Other results are shown in Table II. While trisubstituted ethene moieties were produced as mixtures of *E* and *Z*, disubstituted ones had *E* configuration (runs 1–3). In the case of an internal alkyne, dehydration products **17b** and **18b**, derived from one-to-one adduct, were produced as byproducts (run 4). Treatment of a niobium–1-dodecyne complex with cyclohexanone in DMF–benzene–THF (1:1:1) gave the analogous dehydration product **17c** in 60% yield (run 5).

Formation of 1,3-dienes with the $NbCl_5$–Zn system and 2,5-dihydrofuran **13** with the $TaCl_5$–Zn system could be explained by the following mechanism shown in Scheme II. (1) Treatment of alkynes with the low-valent tantalum or niobium forms the corresponding metal–alkyne complex **14**. (2) Addition of metal–alkyne complex **14** to an aldehyde affords oxametalacyclopentene **15**. (3) In the case of niobium, insertion of another aldehyde into **15** takes place smoothly to give a niobium salt of 2-butene-1,4-diol, **19** (path c). Deoxygenative elimination of two oxygen groups from niobium salt **22** gives 1,3-diene **20** (path e). (4) In the case of tantalum, the second insertion path c does not occur, and allylic alcohol **16** is obtained after workup except 2-hexenal is employed as the second alcohol (R^4CHO). When 2-hexenal is used, 2,5-dihydrofuran **21** is produced through uptake of one oxygen from **23** (path f).

At the early stage of a reaction between niobium–1-dodecyne complex and 3-phenylpropanal, allylic alcohol **16a**, hydrolyzed product of the one-to-one adduct **15a** (a: R^1 = n-$C_{10}H_{21}$, R^2 = H, R^3 = $Ph(CH_2)_2$), was observed by TLC. The opposite regioisomer, 2-decyl-5-phenyl-1-penten-3-ol, was not obtained as in the case of tantalum–alkyne complexes.[5c] As reaction time went by, 1,3-diene **20a** increased gradually with decreasing allylic alcohol **16a**. When a NaOD/D_2O solution (15%) was added to the re-

(15) Nakagawa, K.; Konaka, R.; Nakata, T. *J. Org. Chem.* **1962**, *27*, 1597.

Scheme III

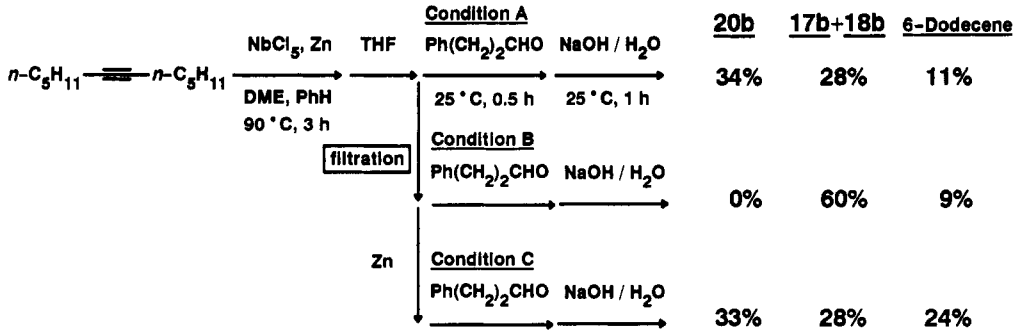
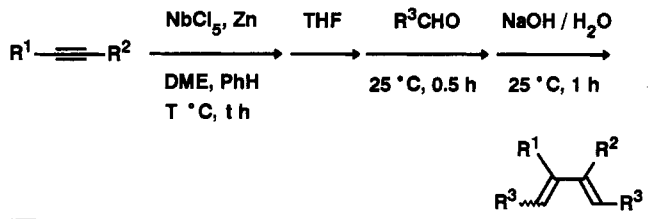
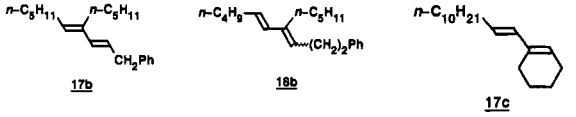


Table II. Preparation of Substituted 1,3-Butadienes from Alkynes and Aldehdyes[a]

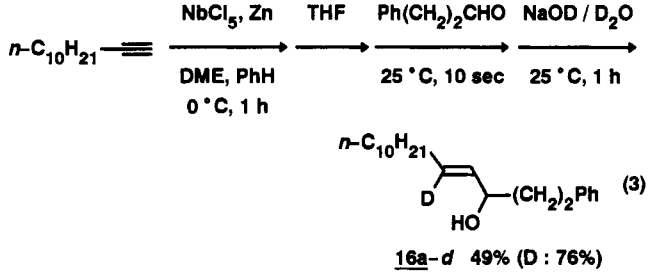


run	R^1	R^2	R^3	T/°C	t/h	yield[b]/%	E/Z[c]
1	n-$C_{10}H_{21}$	H	Ph	0	1	41	75/25
2			$Ph(CH_2)_2$	0	1	74 (**20a**)	63/37
3	Ph	H	n-C_8H_{17}	0	1	58	43/57
4	n-C_5H_{11}	n-C_5H_{11}	$Ph(CH_2)_2$	25	8	59[d] (**20b**)	68/32[e]
5	n-$C_{10}H_{21}$	H	(cyclohexanone)	0	1	0[f]	

[a] See Experimental Section. [b] Isolated yields. [c] The isomer ratios were determined by ^1H NMR analysis. [d] 1,3-Dienes (**17b** and **18b**) were obtained in 26% combined yields. [e] The E/Z ratio indicates (3*E*,5*E*)/(3*E*,5*Z*). [f] 1,3-Diene **17c** was produced in 60% yield.



action mixture after 10 s of the addition of 3-phenylpropanal, deuterated allylic alcohol **16a**-*d* was obtained in 49% yield (content of deuterium: 76%, eq 3). Hydrolyzed



(3)

16a-*d* 49% (D : 76%)

product of the niobium–diol complex **19a** was not observed throughout the reaction. These results suggest that the second insertion process **15** → **19** (path c) is almost as fast as the first insertion **14** → **15** (path a) and that sequential deoxygenation **19** → **20** (path e) proceeds very fast. It is reported that deoxygenative elimination of 2-butene-1,4-diols to 1,3-butadienes using low-valent titanium requires heating at reflux (THF solution) to complete the reaction.[16] Thus, strong oxophilicity of niobium facilitates the deoxygenative elimination under milder conditions.

Considerable difference between the $NbCl_5$–Zn system[5a,b] and $NbCl_3$(DME)[4b] was observed. In contrast to the $NbCl_5$–Zn system, treatment of the niobium–6-dodecyne complex derived from the alkyne and $NbCl_3$(DME) with 3-phenylpropanal did not afford 1,3-diene **20b**.[4a] To examine the effect of the excess amounts of zinc in the $NbCl_5$–Zn system, the experiments in Scheme III were conducted. Although the reaction with 4 mol of niobium per mol of alkyne gave the best results, the amounts of the niobium could be reduced to 1.2 mol in the case of internal alkynes.[5h] Treatment of the reaction mixture of a niobium–6-dodecyne complex, derived from 1.0 equiv of 6-dodecyne, 1.2 equiv of $NbCl_5$, and 1.8 equiv of zinc in DME–benzene–THF (1:1:1), with 3-phenylpropanal at 25 °C gave 1,3-diene **20b** in 34% yield after alkaline workup along with dehydrated one-to-one products **17b** and **18b** in 28% combined yields and 6-dodecene in 11% yield (condition A). The same reaction mixture of a niobium–6-dodecyne complex was filtered, and the filtrate was divided into two parts. Zinc dust (1.8 mol) was added to one of the filtrates (condition C), and then 3-phenylpropanal was introduced into both mixtures. The desired 1,3-diene **20b** was not detected without zinc, and a mixture of **17b** and **18b** was obtained in 60% yield (condition B), while **20b** was produced in 33% yield (E/Z = 88/12) in the presence of additional zinc (condition C). These results suggest that the presence of zinc in the reaction mixture is indispensable for the second insertion of aldehydes into the niobium complex **15** (Scheme II, **15** → **19**). Reduction of niobium complex **19** with zinc takes place also for promoting deoxygenation (**19** → **20**).[16]

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Benzene, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone just before use. Zinc dust (GR grade) purchased from Wako Pure Chemical Industries, Ltd., was activated by washing several times with 5% hydrochloric acid, washing in turn with water, methanol, and ether, and drying in vacuo according to Fieser and Fieser.[19] Internal alkynes were prepared according to the standard procedure described in ref 20. Distillation of small amounts of products was performed with a Büchi Kugelrohr, and boiling points are indicated by an air bath temperature without correction. IR spectra were determined with a JASCO IR-810 spectrometer. Mass spectra were obtained with on a Hitachi M-80 mass spectrometer. ^1H and ^{13}C NMR spectra were determined with a Varian XL-200 spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane using the δ scale. Column chromatography was done with silica gel (200 mesh). Elemental analyses were performed by the staff at the Elemental Analyses Center of Kyoto University.

(16) Walborsky, H. M.; Wust, H. H. *J. Am. Chem. Soc.* **1982**, *104*, 5807.

(17) For reviews, see: (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Bennet, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296.

(18) Fourfold excess of low-valent niobium was required in the case of terminal alkynes because undesirable side reactions such as dimerization of the alkynes took place.

(19) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 1276.

(20) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: New York, 1988 and see also ref 5h.

General Procedure for the Synthesis of Allylic Alcohols from Alkynes and Carbonyl Compounds. In a 50-mL reaction flask was placed $TaCl_5$ (0.72 g, 2.0 mmol) under an argon atmosphere. To the salt was added at 25 °C benzene (5 mL) and DME (5 mL) successively. Zinc (0.20 g, 3.0 mmol) was added at 25 °C to a stirred pale yellow solution of $TaCl_5$, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned to greenish dark blue with slightly exothermic process. To the mixture was added at 25 °C a solution of an alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 25 °C. After consumption of the alkyne was confirmed by TLC, THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added to the mixture; the resulting mixture was stirred at 25 °C for an additional 15 min. A carbonyl compound (1.2 mmol) was added to the mixture at 25 °C, and the mixture was stirred at 25 °C for 15 min. In the case of an α,β-unsaturated carbonyl compound, 2.0 mmol of the carbonyl compound was used and the reaction was conducted at 0 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed well with ethyl acetate (3 × 5 mL). Organic extracts were concentrated in vacuo and diluted with hexane (10 mL), dried over $MgSO_4$, and concentrated again in vacuo. Purification of the crude product by column chromatography on silica gel gave the desired allylic alcohol.

(*E*)-4-Pentyl-1-phenyl-4-decen-3-ol (4): bp 140–143 °C (bath temp, 0.20 Torr); IR (neat) 3348, 2952, 2924, 2856, 1604, 1496, 1456, 1048, 746, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.2–1.5 (m, 13 H), 1.85 (ddd, J = 6.7, 7.9, 7.9 Hz, 2 H), 1.9–2.2 (m, 4 H), 2.60 (dt, J = 14.0, 7.9 Hz, 1 H), 2.73 (dt, J = 14.0, 7.9 Hz, 1 H), 4.0–4.1 (m, 1 H), 5.40 (t, J = 7.3 Hz, 1 H), 7.2–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 14.9, 23.3, 23.4, 28.3, 30.4, 30.5, 32.5, 33.1, 33.2, 38.2, 76.8, 126.5, 127.8, 129.1, 129.2, 142.6, 143.0; MS m/z (rel intensity) 302 (M^+, 65), 231 (99), 197 (100), 71 (9). Anal. Calcd for $C_{21}H_{34}O$: C, 83.38; H, 11.33. Found: C, 83.12; H, 11.46.

(*E*)-7-Pentyl-6-hexadecen-8-ol: bp 113–115 °C (bath temp, 0.12 Torr); IR (neat) 3340, 2954, 2924, 2852, 1466, 1379, 1052, 1013, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.1 (m, 9 H), 1.2–1.5 (m, 25 H), 1.4–1.6 (m, 2 H), 1.9–2.1 (m, 4 H), 3.9–4.1 (m, 1 H), 5.37 (t, J = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 22.6, 22.7, 26.0, 27.5, 29.3, 29.5, 29.6, 29.8, 31.6, 31.9, 32.4, 35.7, 76.9, 126.8, 140.1; MS m/z (rel intensity) 310 (M^+, 4), 239 (69), 197 (100), 71 (61), 43 (44). Anal. Calcd for $C_{21}H_{42}O$: C, 81.22; H, 13.63. Found: C, 81.02; H, 13.87.

(*E*)-1-Cyclohexyl-2-pentyl-2-octen-1-ol: bp 127–129 °C (bath temp, 0.14 Torr); IR (neat) 3382, 2922, 2850, 1658, 1466, 1450, 1382, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.1 (m, 6 H), 1.0–1.6 (m, 20 H), 1.6–1.9 (m, 4 H), 1.9–2.2 (m, 4 H), 3.6–3.8 (m, 1 H), 5.32 (t, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.5, 23.2, 26.8, 26.9, 27.3, 28.2, 28.5, 29.5, 30.3, 30.6, 30.8, 32.4, 33.2, 42.0, 82.9, 128.7, 141.6; MS m/z (rel intensity) 280 (M^+, 2), 209 (9), 197 (100), 83 (23), 71 (56). Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.20; H, 13.16.

(*E*)-2,2-Dimethyl-4-pentyl-4-decen-3-ol: bp 103–105 °C (bath temp, 0.34 Torr); IR (neat) 3482, 2954, 2926, 2858, 1466, 1362, 1002 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 0.91 (s, 9 H), 1.2–1.5 (m, 13 H), 1.7–1.9 (m, 1 H), 1.9–2.2 (m, 2 H), 2.1–2.4 (m, 1 H), 3.75 (d, J = 2.2 Hz, 1 H), 5.39 (t, J = 7.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 26.4, 27.6, 29.6, 29.8, 30.6, 31.6, 32.3, 35.9, 82.6, 127.9, 141.8; MS m/z (rel intensity) 254 (M^+, 0.4), 197 (100), 71 (76), 57 (39). Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47. Found: C, 80.10; H, 13.42.

(*E*)-1-(1-Pentyl-1-heptenyl)cyclohexanol: bp 122–124 °C (bath temp, 0.14 Torr); IR (neat) 3402, 2926, 2854, 1467, 1459, 1449, 1378, 1149, 955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.1–1.5 (m, 13 H), 1.5–1.8 (m, 10 H), 1.9–2.1 (m, 4 H), 5.47 (t, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.8, 22.9, 23.2, 23.4, 26.4, 28.5, 28.7, 30.4, 31.3, 32.3, 32.4, 33.4, 37.2, 78.4, 124.8, 146.7; MS m/z (rel intensity) 266 (M^+, 15), 223 (13), 195 (100), 55 (30), 43 (27). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.23; H, 13.11.

(*E*)-7-Cyclohexyl-8-pentyl-8-tetradecen-7-ol: bp 137–139 °C (bath temp, 0.20 Torr); IR (neat) 3500, 2922, 2852, 1466, 1340, 1270, 1120, 1071, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.1 (m, 9 H), 1.0–1.6 (m, 28 H), 1.4–1.9 (m, 4 H), 1.7–2.0 (m, 4 H), 2.0–2.2 (m, 2 H), 5.26 (t, J = 7.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.5, 22.7, 23.7, 26.7, 26.8, 27.0, 27.4, 27.9, 28.6, 29.3, 29.8, 29.9, 31.7, 31.9, 32.8, 36.7, 45.1, 80.2, 125.4, 141.6; MS m/z (rel intensity) 281 ($M^+ - C_6H_{11}$, 100), 113 (7), 83 (12), 71 (3). Anal. Calcd for $C_{25}H_{48}O$: C, 82.34; H, 13.27. Found: C, 82.04; H, 13.27.

(*E*)-4-Pentyl-1,4-decadien-3-ol (8): bp 97–98 °C (bath temp, 0.18 Torr); IR (neat) 3334, 2926, 2856, 1726, 1648, 1466, 1378, 989, 919 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.2–1.6 (m, 12 H), 1.49 (d, J = 3.9 Hz, 1 H), 1.9–2.2 (m, 4 H), 4.5–4.6 (m, 1 H), 5.14 (ddd, J = 10.3, 1.5, 1.5 Hz, 1 H), 5.28 (ddd, J = 17.2, 1.5, 1.5 Hz, 1 H), 5.47 (t, J = 7.1 Hz, 1 H), 5.86 (ddd, J = 5.8, 10.3, 17.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 22.6, 27.6, 27.7, 29.3, 29.4, 31.6, 32.2, 77.0, 114.6, 127.3, 139.9, 140.6; MS m/z (rel intensity) 224 (M^+, 4), 153 (64), 97 (31), 83 (100), 55 (87). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.29; H, 12.82.

(*E*)-3-Methyl-4-pentyl-1,4-decadien-3-ol: bp 92–94 °C (bath temp, 0.14 Torr); IR (neat) 3392, 2856, 2926, 1730, 1648, 1467, 1378, 1120, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.2–1.5 (m, 12 H), 1.38 (s, 3 H), 1.42 (s, 1 H), 1.9–2.1 (m, 4 H), 5.06 (dd, J = 10.6, 1.3 Hz, 1 H), 5.23 (dd, J = 17.3, 1.3 Hz, 1 H), 5.50 (t, J = 7.1 Hz, 1 H), 5.92 (dd, J = 10.6, 17.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.4, 22.5, 27.0, 27.9, 28.0, 29.5, 30.2, 31.6, 32.5, 76.1, 111.6, 125.4, 143.4, 144.6; MS m/z (rel intensity) 238 (M^+, 0.3), 220 (2), 167 (17), 71 (40), 43 (100). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.45; H, 12.76.

(*E*)-10-Henicosen-9-ol: bp 145–147 °C (bath temp, 0.12 Torr); IR (neat) 3314, 2922, 2850, 1669, 1467, 1378, 1147, 1086, 1055, 1035, 968, 720, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 6 H), 1.1–1.7 (m, 31 H), 2.02 (dt, J = 6.4, 6.6 Hz, 2 H), 4.0–4.1 (m, 1 H), 5.44 (dd, J = 7.0, 15.4 Hz, 1 H), 5.64 (dt, J = 15.4, 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.8, 23.4, 26.2, 29.9, 30.0, 30.1, 30.2, 30.3, 30.4, 32.6, 32.9, 38.1, 73.8, 132.7, 133.9; MS m/z (rel intensity) 292 ($M^+ - H_2O$, 13), 197 (75), 169 (29), 95 (77), 57 (100). Anal. Calcd for $C_{21}H_{42}O$: C, 81.22; H, 13.63. Found: C, 81.02; H, 13.85.

(*E*)-1-Dodecenylcyclohexanol: bp 117–119 °C (bath temp, 0.12 Torr); IR (neat) 3364, 2922, 2852, 1449, 1055, 1034, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H), 1.1–1.5 (m, 17 H), 1.3–1.7 (m, 10 H), 1.9–2.1 (m, 2 H), 5.62 (d, J = 15.6 Hz, 1 H), and 5.66 (dt, J = 15.6, 5.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.8, 22.9, 23.3, 26.3, 29.8, 30.0, 30.1, 30.3, 32.6, 33.0, 38.8, 71.9, 128.8, 138.3; MS m/z (rel intensity) 266 (M^+, 24), 233 (45), 125 (100), 83 (35), 57 (13). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.26; H, 12.84.

(*E*)-1-Cyclohexyl-2-hexyl-5-phenyl-1-penten-3-ol (A) and (*E*)-4-Cyclohexyl-1-phenyl-4-undecen-3-ol (B). The regioisomer ratio was determined by ^1H NMR analysis (A/B = 65/35): bp 147–149 °C (bath temp, 0.20 Torr); IR (neat, mixture of A/B = 65/35) 3340, 2922, 2850, 1601, 1496, 1449, 1048, 1031, 896, 745, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.1 (m, 3 H), 1.0–1.5 (m, 14 H), 1.5–1.9 (m, 7 H), 1.9–2.4 (m, 3 H), 2.5–2.9 (m, 2 H), 4.0–4.2 (m, 1 H), 5.23 (d, J = 9.4 Hz, 1 H (A)), 5.45 (t, J = 7.3 Hz, 1 H (B)), 7.1–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 25.9, 26.0, 26.1, 26.9, 27.6, 29.0, 29.8, 30.0, 30.5, 31.6, 31.7, 32.2, 32.6, 33.3, 33.4, 36.6, 37.3, 38.4, 39.0, 73.0 (B), 75.8 (A), 125.6, 126.1, 128.2, 128.4, 132.9, 139.8 (A), 142.2 (B), 142.3 (A), 146.6 (B); MS m/z (rel intensity) 328 (M^+, 5), 245 (44), 219 (38), 105 (21), 91 (100). Anal. Calcd for $C_{23}H_{36}O$: C, 84.09; H, 11.05. Found: C, 84.29; H, 11.06.

(*E*)-1-(2-Cyclohexyl-1-hexylethenyl)cyclohexanol (A) and (*E*)-1-(1-Cyclohexyl-1-octenyl)cyclohexanol (B). The regioisomer ratio was determined by ^1H NMR analysis (A/B = 76/24): bp 135–137 °C (bath temp, 0.22 Torr); IR (neat, mixture of A/B = 76/24) 3434, 2924, 2850, 1448, 1150, 968, 894 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H), 1.0–1.5 (m, 15 H), 1.4–1.9 (m, 14 H), 1.9–2.3 (m, 3 H), 5.29 (d, J = 10.0 Hz, 1 H (A)), 5.42 (t, J = 7.6 Hz, 1 H (B)); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.1, 22.1, 22.4, 22.6, 22.7, 23.5, 25.7, 26.1, 26.3, 27.5, 27.8, 28.8, 29.1, 29.2, 30.1, 30.5, 31.6, 31.7, 31.8, 32.0, 32.7, 33.5, 34.0, 35.7, 36.5, 37.1, 39.5, 74.1 (A), 75.0 (B), 124.0 (B), 129.9 (A), 144.1 (A), 149.0 (B); MS m/z (rel intensity) 292 (M^+, 15), 274 (28), 221 (71), 189 (100), 55 (41). Anal. Calcd for $C_{20}H_{36}O$: C, 82.12; H, 12.40. Found: C, 82.36; H, 12.62.

(*E*)-6,6-Dimethyl-4-heptyl-1-phenyl-4-hepten-3-ol: bp 133–135 °C (bath temp, 0.18 Torr); IR (neat) 3358, 2952, 2924, 2856, 1604, 1467, 1362, 1096, 745, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H), 1.02 (s, 1 H), 1.12 (s, 9 H), 1.2–1.6 (m, 10 H), 1.84 (ddd, J = 6.8, 8.0, 8.0 Hz, 2 H), 1.9–2.1 (m, 1 H), 2.1–2.3 (m,

1 H), 2.60 (dt, J = 14.0, 8.0 Hz, 1 H), 2.74 (dt, J = 14.0, 8.0 Hz, 1 H), 3.9–4.1 (m, 1 H), 5.42 (s, 1 H), 6.8–7.1 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.3, 29.1, 30.4, 30.6, 31.3, 31.8, 32.4, 32.5, 37.9, 76.8, 125.6, 128.2, 128.4, 136.2, 140.9, 142.2; MS m/z (rel intensity) 316 (M^+, 3), 259 (89), 211 (48), 91 (100), 55 (28). Anal. Calcd for $C_{22}H_{36}O$: C, 83.48; H, 11.46. Found: C, 83.19, H, 11.53.

(*E*)-1,4-Diphenyl-4-undecen-3-ol (A) and (*E*)-1,5-Diphenyl-2-hexyl-1-penten-3-ol (B). The regioisomer ratio was determined by ^{1}H NMR analysis (A/B = 83/17): bp 159–161 °C (bath temp, 0.18 Torr); IR (neat, mixture of A/B = 83/17) 3340, 2950, 2924, 2852, 1602, 1495, 1454, 1071, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H), 1.1–1.5 (m, 8 H), 1.5–1.6 (m, 1 H), 1.7–2.1 (m, 4 H), 2.1–2.5 (m, 2 H (B)), 2.6–2.8 (m, 2 H (A)), 4.2–4.4 (m, 1 H (B)), 4.3–4.4 (m, 1 H (A)), 5.70 (t, J = 7.4 Hz, 1 H (A)), 6.54 (s, 1 H (B)), 7.1–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.5, 28.4, 28.8, 29.0, 29.6, 29.7, 31.4, 31.6, 31.9, 32.2, 37.1, 37.5, 75.4 (B), 75.9 (A), 125.4 (B), 125.6 (A), 125.7 (B), 126.3 (B), 126.8 (A), 128.0 (A), 128.1 (B), 128.2 (A), 128.3 (A), 128.5 (B), 129.0 (B), 129.1 (A), 137.6 (B), 138.2 (A), 141.9 (A), 145.3 (B); MS m/z (rel intensity) 322 (M^+, 10), 237 (16), 217 (25), 133 (38), 105 (32), 91 (100). Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.65; H, 9.67.

(*E*)-1-(1-Phenyl-1-octenyl)cyclohexanol (A) and (*E*)-1-(1-Hexyl-2-phenylethenyl)cyclohexanol (B). The regioisomer ratio was determined by ^{1}H NMR analysis (A/B = 79/21): bp 147–149 °C (bath temp, 0.18 Torr); IR (neat, mixture of A/B = 79/21) 3424, 2924, 2852, 1598, 1449, 1263, 738, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7–0.9 (m, 3 H), 1.0–1.3 (m, 8 H + 2 H (A)), 1.3–1.8 (m, 11 H), 2.1–2.3 (m, 2 H (B)), 5.75 (t, J = 7.3 Hz, 1 H (A)), 6.59 (s, 1 H (B)), 7.0–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.8, 22.8, 23.3, 26.3, 26.4, 29.0, 29.6, 29.7, 30.5, 30.6, 31.0, 32.2, 32.4, 37.4, 74.2 (A), 75.7 (B), 124.6 (B), 126.8 (B), 127.1 (A), 127.2 (A), 128.4 (A), 128.9 (B), 129.3 (B), 130.7 (A), 139.4 (B), 140.1 (A), 149.0 (A), 150.8 (B); MS m/z (rel intensity) 286 (M^+, 62), 268 (39), 201 (79), 117 (87), 91 (100). Anal. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.89; H, 10.77.

(*E*)-4-Hexyl-5-phenyl-1,4-pentadien-3-ol (A) and (*E*)-4-Phenyl-1,4-undecadien-3-ol (B). The regioisomer ratio was determined by ^{1}H NMR analysis (A/B = 71/29): bp 116–118 °C (bath temp, 0.18 Torr); IR (neat, mixture of A/B = 71/29) 3340, 2952, 2922, 2854, 1728, 1459, 1072, 989, 920, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.0 (m, 3 H), 1.1–1.6 (m, 8 H), 1.8–2.1 (m, 1 H + 2 H (A)), 2.1–2.4 (m, 2 H (B)), 4.7–4.8 (m, 1 H (B)), 4.8–4.9 (m, 1 H (A)), 5.09 (dd, J = 1.2, 10.3 Hz, 1 H (A)), 5.18 (dd, J = 1.1, 17.1 Hz, 1 H (A)), 5.20 (d, J = 10.3 Hz, 1 H (B)), 5.35 (d, J = 17.1 Hz, 1 H (B)), 5.76 (t, J = 7.4 Hz, 1 H (A)), 5.87 (ddd, J = 5.8, 10.3, 17.1 Hz, 1 H (A)), 5.91 (ddd, J = 5.8, 10.3, 17.1 Hz, 1 H (B)), 6.59 (s, 1 H (B)), 7.1–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 28.8, 29.1, 29.9, 31.7, 31.8, 77.5 (A), 77.9 (B), 115.3 (A), 115.7 (B), 126.0 (B), 126.7 (B), 127.1 (A), 128.1 (A), 128.3 (B), 128.8 (B), 129.0 (A), 129.7 (A), 137.8 (B), 138.4 (A), 139.5 (A), 139.7 (B), 142.2 (A), 144.0 (B); MS m/z (rel intensity) 244 (M^+, 7), 159 (74), 117 (80), 91 (100), 55 (50). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.61; H, 10.08.

(*E*)-2-Decyl-5-phenyl-1-(trimethylsilyl)-1-penten-3-ol (A) and (*Z*)-1-Phenyl-4-(trimethylsilyl)-4-pentadecen-3-ol (B). The regioisomer ratio was determined by ^{1}H NMR analysis (A/B = 89/11): bp 150–152 °C (bath temp, 0.18 Torr); IR (neat, mixture of A/B = 89/11) 3336, 2922, 2852, 1612, 1456, 1248, 855, 837, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H (A)), 0.14 (s, 9 H (B)), 0.7–1.0 (m, 3 H), 1.1–1.5 (m, 17 H), 1.7–2.4 (m, 4 H), 2.6–2.9 (m, 2 H), 4.0–4.2 (m, 1 H (A)), 4.2–4.3 (m, 1 H (B)), 5.52 (s, 1 H (A)), 6.23 (t, J = 7.6 Hz, 1 H (B)), 7.1–7.4 (m, 5 H); ^{13}C NMR (A, $CDCl_3$) δ 0.3, 14.2, 22.7, 29.3, 29.5, 29.6, 30.2, 30.5, 31.9, 32.2, 33.5, 38.0, 75.0, 122.2, 125.8, 128.3, 128.4, 142.1, 161.5; MS m/z (rel intensity) 374 (M^+, 1), 359 (4), 270 (13), 233 (16), 143 (57), 73 (100). Anal. Calcd for $C_{24}H_{42}OSi$: C, 76.94; H, 11.30. Found: C, 77.09; H, 11.47.

(*E*)-1-(1-Decyl-2-(trimethylsilyl)ethenyl)cyclohexanol: bp 134–136 °C (bath temp, 0.20 Torr); IR (neat) 3410, 2924, 2852, 1600, 1459, 1247, 858 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 0.88 (t, J = 6.5 Hz, 3 H), 1.1–1.5 (m, 17 H), 1.4–1.8 (m, 10 H), 2.1–2.2 (m, 2 H), 5.55 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.4, 14.1, 22.1, 22.7, 25.6, 29.3, 29.6, 29.7, 30.6, 31.9, 32.7, 32.8, 36.9, 75.5, 120.9, 166.0; MS m/z (rel intensity) 338 (M^+, 0.4), 323 (5), 320 (3), 122 (48), 73 (100). Anal. Calcd for $C_{21}H_{42}OSi$: C, 74.48; H, 12.50. Found: C, 74.32; H, 12.68.

(*E*)-4-Decyl-5-(trimethylsilyl)-1,4-pentadien-3-ol (A) and (*E*)-4-(Trimethylsilyl)-1,4-pentadecadien-3-ol (B). The regioisomer ratio was determined by ^{1}H NMR analysis (A/B = 97/3): bp 117–119 °C (bath temp, 0.20 Torr); IR (neat, mixture of A/B = 97/3) 3338, 2922, 2852, 1728, 1617, 1466, 1247, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 0.88 (t, J = 6.0 Hz, 3 H), 1.1–1.5 (m, 16 H), 1.60 (d, J = 4.3 Hz, 1 H), 1.9–2.3 (m, 2 H), 4.5–4.6 (m, 1 H), 5.15 (ddd, J = 10.2, 1.4, 1.4 Hz, 1 H), 5.27 (ddd, J = 17.1, 1.4, 1.4 Hz, 1 H), 5.57 (s, 1 H (A)), 5.80 (ddd, J = 6.4, 10.2, 17.1 Hz, 1 H), 6.24 (t, J = 7.6 Hz, 1 H (B)); ^{13}C NMR (A, $CDCl_3$) δ 0.2, 14.1, 22.6, 29.3, 29.5, 29.6, 29.8, 30.1, 31.9, 33.3, 76.7, 115.3, 122.8, 139.7, 159.3; MS m/z (rel intensity) 296 (M^+, 0.8), 281 (17), 165 (19), 80 (82), 73 (100). Anal. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24. Found: C, 73.14; H, 12.47.

(*E*)-4-Decyl-3-methyl-5-(trimethylsilyl)-1,4-pentadien-3-ol: bp 114–116 °C (bath temp, 0.14 Torr); IR (neat) 3374, 2952, 2922, 2852, 1728, 1602, 1466, 1247, 857 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 0.87 (t, J = 6.4 Hz, 3 H), 1.2–1.5 (m, 16 H), 1.40 (s, 3 H), 1.53 (s, 1 H), 2.1–2.2 (m, 2 H), 5.06 (dd, J = 1.2, 10.7 Hz, 1 H), 5.22 (dd, J = 1.2, 17.3 Hz, 1 H), 5.58 (s, 1 H), 5.94 (dd, J = 10.7, 17.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.3, 14.1, 22.7, 27.6, 29.3, 29.5, 29.6, 30.4, 31.9, 32.2, 32.8, 77.3, 111.9, 122.6, 144.6, 162.6; MS m/z (rel intensity) 310 (M^+, 0.2), 295 (4), 165 (6), 73 (100), 43 (10). Anal. Calcd for $C_{19}H_{38}OSi$: C, 73.47; H, 12.33. Found: C, 73.27; H, 12.53.

(*E*)-1-(1-Cyclohexenyl)-2-decyl-3-(trimethylsilyl)-2-propen-1-ol (9): bp 140–142 °C (bath temp, 0.18 Torr); IR (neat) 3346, 2924, 2852, 1730, 1617, 1459, 1247, 857, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 0.87 (t, J = 6.5 Hz, 3 H), 1.1–1.6 (m, 16 H), 1.4–1.7 (m, 5 H), 1.7–2.2 (m, 6 H), 4.4–4.5 (m, 1 H), 5.57 (s, 1 H), 5.7–5.8 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.4, 14.1, 22.5, 22.6, 23.2, 25.2, 29.4, 29.5, 29.6, 30.1, 31.9, 33.4, 79.7, 122.0, 125.1, 138.1, 158.5; MS m/z (rel intensity) 350 (M^+, 1), 277 (3), 134 (8), 75 (22), 73 (100). Anal. Calcd for $C_{22}H_{42}OSi$: C, 75.35; H, 12.07. Found: C, 75.61; H, 12.20.

(*E*)-1-(*tert*-Butyldimethylsilyl)-2-decyl-5-phenyl-1-penten-3-ol: bp 157–159 °C (bath temp, 0.18 Torr); IR (neat) 3564, 2950, 2922, 2852, 1611, 1464, 1249, 836, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.8–1.0 (m, 3 H), 0.88 (s, 9 H), 1.1–1.5 (m, 16 H), 1.45 (d, J = 3.9 Hz, 1 H), 1.7–2.1 (m, 2 H), 2.1–2.3 (m, 2 H), 2.5–2.9 (m, 2 H), 4.1–4.2 (m, 1 H), 5.55 (s, 1 H), 7.1–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −4.1, −4.0, 14.1, 17.0, 22.7, 26.5, 29.3, 29.5, 29.6, 30.2, 30.5, 31.6, 31.9, 32.1, 33.8, 38.2, 75.2, 119.1, 125.8, 128.4, 128.5, 142.2, 162.3; MS m/z (rel intensity) 359 (M^+ − t-Bu, 49), 135 (10), 91 (36), 75 (100), 57 (8). Anal. Calcd for $C_{27}H_{48}OSi$: C, 77.81; H, 11.61. Found: C, 77.70; H, 11.61.

(*E*)-1-(2-(*tert*-Butyldimethylsilyl)-1-decylethenyl)cyclohexanol: bp 157–159 °C (bath temp, 0.22 Torr); IR (neat) 3462, 2924, 2852, 1601, 1465, 1252, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 6 H), 0.7–1.0 (m, 12 H), 1.1–1.4 (m, 17 H), 1.3–1.7 (m, 10 H), 2.0–2.1 (m, 2 H), 5.57 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.1, 14.1, 17.1, 22.2, 22.7, 25.6, 26.6, 29.3, 29.6, 29.7, 30.5, 31.9, 32.8, 33.0, 37.2, 75.8, 117.9, 166.8; MS m/z (rel intensity) 323 (M^+ − t-Bu, 45), 305 (47), 139 (17), 75 (100), 57 (14). Anal. Calcd for $C_{24}H_{48}OSi$: C, 75.71; H, 12.71. Found: C, 75.42; H, 12.71.

(*E*)-2-Decyl-1-(*tert*-butyldimethylsilyl)-1,4-pentadien-3-ol: bp 135–137 °C (bath temp, 0.18 Torr); IR (neat) 3338, 2950, 2924, 2852, 1729, 1617, 1465, 1248, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.8–0.9 (m, 3 H), 0.87 (s, 9 H), 1.2–1.5 (m, 16 H), 1.59 (d, J = 4.3 Hz, 1 H), 2.0–2.3 (m, 2 H), 4.5–4.6 (m, 1 H), 5.14 (ddd, J = 1.4, 1.4, 10.2, Hz, 1 H), 5.27 (ddd, J = 1.4, 1.4, 17.1 Hz, 1 H), 5.59 (s, 1 H), 5.80 (ddd, J = 6.4, 10.2, 17.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −4.1, 14.1, 17.0, 22.7, 26.6, 29.3, 29.5, 29.6, 30.1, 30.2, 31.9, 33.6, 77.0, 115.4, 119.8, 139.9, 160.3; MS m/z (rel intensity) 338 (M^+, 0.1), 281 (92), 115 (9), 75 (100), 73 (75). Anal. Calcd for $C_{21}H_{42}OSi$: C, 74.48; H, 12.50. Found: C, 74.33; H, 12.80.

(*Z*)-5-Iodo-4-pentyl-1-phenyl-4-decen-3-ol (5). To a stirred solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc (0.20 g, 3.0 mmol), and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME–benzene (1:1, 2 mL) and the whole mixture was stirred at 25 °C for 30 min. THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 25 °C

for 15 min, 3-phenylpropanal (0.16 g, 1.2 mmol) was added to the mixture, and the resulting mixture was stirred at 25 °C for an additional 15 min. To the mixture was added at −25 °C a solution of I_2 (1.3 g, 5.0 mmol) in THF (6 mL), and the whole mixture was stirred at −25 °C for 10 min. Aqueous NaOH solution (15%, 2 mL) was added at −25 °C, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was filtered off with Hyflo-Super Cel and washed well with ethyl acetate (3 × 5 mL). The organic extracts were washed with saturated $NaHSO_3$ (10 mL) and brine. Organic layer was dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel with ethyl acetate–hexane (1:20) gave 0.33 g (76%) of (*Z*)-5-iodo-4-pentyl-1-phenyl-4-decen-3-ol: bp 155–157 °C (0.18 Torr); IR (neat) 3342, 2952, 2926, 2856, 1654, 1618, 1466, 1050, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.2–1.7 (m, 13 H), 1.7–1.9 (m, 2 H), 2.0–2.4 (m, 2 H), 2.4–2.6 (m, 2 H), 2.7–2.8 (m, 1 H), 2.8–2.9 (m, 1 H), 4.5–4.6 (m, 1 H), 7.1–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.4, 22.6, 28.4, 29.5, 30.6, 30.8, 32.3, 32.4, 36.9, 41.2, 81.1, 106.5, 125.8, 128.3, 128.5, 141.8, 144.9; MS *m/z* (rel intensity) 410 ($M^+ - H_2O$, 0.6), 301 (35), 196 (20), 105 (38), 91 (100). Anal. Calcd for $C_{21}H_{33}OI$: C, 58.88; H, 7.76. Found: C, 59.13; H, 7.94.

(*E*)-1-(1-Cyclohexyl)-2-decyl-3-(trimethylsilyl)-2-propen-1-one (10).[15] To a stirred suspension of NiO_2 (12 g, *f* = 0.15, 1.8 mmol) in benzene (10 mL) was added at 0 °C a solution of the allylic alcohol **9** (0.35 g, 1.0 mmol) in benzene (5 mL). The resulting mixture was stirred at 50 °C for 2 h. NiO_2 was removed by filtration and washed with benzene (3 × 5 mL). Organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography on silica gel with ethyl acetate–hexane (1:40) as eluent gave 0.30 g (85%) of (*E*)-1-(1-cyclohexyl)-2-decyl-3-(trimethylsilyl)-2-propen-1-one (**10**) as a colorless liquid: bp 129–131 °C (bath temp, 0.18 Torr); IR (neat) 2924, 2852, 1644, 1451, 1249, 1220, 856, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 0.85 (t, *J* = 6.5 Hz, 3 H), 1.1–1.4 (m, 16 H), 1.5–1.7 (m, 4 H), 2.1–2.3 (m, 4 H), 2.3–2.5 (m, 2 H), 5.76 (s, 1 H), 6.62 (bs, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.0, 14.1, 21.7, 22.0, 22.7, 23.6, 26.1, 29.1, 29.3, 29.4, 29.5, 29.8, 31.9, 33.1, 134.7, 138.6, 142.3, 156.8; MS *m/z* (rel intensity) 348 (M^+, 4), 333 (14), 275 (4), 221 (25), 73 (100). Anal. Calcd for $C_{22}H_{40}OSi$: C, 75.79; H, 11.56. Found: C, 75.53; H, 11.78.

8-Decylbicyclo[4.3.0]-8-nonen-7-one (11). To a stirred solution of the divinyl ketone **10** (0.34 g, 1.0 mmol) in CH_2Cl_2 (10 mL) at −25 °C under an argon atmosphere was added $FeCl_3$ (0.18 g, 1.1 mmol). After being stirred at −25 °C for 40 min, the reaction mixture was poured into water and extracted with ether. The organic extracts were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel with ethyl acetate–hexane (1:20) as eluent gave 0.23 g (82%) of 8-decylbicyclo[4.3.0]-8-nonen-7-one (**11**) as a colorless liquid: bp 132–134 °C (bath temp, 0.18 Torr); IR (neat) 2922, 2852, 1706, 1459 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3 H), 1.0–1.6 (m, 14 H), 1.5–1.7 (m, 6 H), 1.7–2.1 (m, 4 H), 2.17 (t, *J* = 7.5 Hz, 2 H), 2.42 (dt, *J* = 6.3, 6.4 Hz, 1 H), 2.8–3.0 (m, 1 H), 7.21 (bs, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 21.1, 21.2, 22.6, 22.8, 24.8, 27.7, 28.2, 29.3, 29.5, 31.9, 38.6, 45.8, 144.4, 160.2, 211.6; MS *m/z* (rel intensity) 276 (M^+, 50), 191 (28), 151 (100), 81 (27), 43 (35). Anal. Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. Found: C, 82.28; H, 11.80.

Reactions between a Tantalum–6-Dodecyne Complex and (*E*)-2-Hexenal. Tantalum–6-dodecyne complex **1** (1.0 mmol scale) was prepared as mentioned in the synthesis of iodo compound **5**. (*E*)-2-Hexenal (0.20 g, 2.0 mmol) was added at 0 °C to the mixture, and the resulting mixture was stirred at 0 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 0 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel and washed well with ethyl acetate (3 × 5 mL). Organic extracts were concentrated in vacuo, diluted with hexane, dried over $MgSO_4$, and concentrated again in vacuo. Purification of the crude product by column chromatography on silica gel (ethyl acetate–hexane (1:30–1:5)) gave 52 mg (15%) of 2,5-dihydrofuran **13** and 0.13 g (49%) of (4*E*,7*E*)-7-pentyl-4,7-tridecadien-6-ol (**12**).

(*E*,*E*)-2,5-Di(1-pentenyl)-3,4-dipentyl-3-oxolene (13). Two isomers were produced, and the ratio was determined by ^1H NMR analysis (major/minor = 92/8): R_f = 0.57 (ethyl acetate:hexane = 1:10); bp 137–139 °C (bath temp, 0.18 Torr); IR (neat, mixture of major/minor = 92/8) 2954, 2926, 2858, 1719, 1664, 1466, 966 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 12 H), 1.1–1.5 (m, 16 H), 1.8–2.3 (m, 8 H), 4.95 (d, *J* = 8.1 Hz, 2 H (minor)), 5.04 (d, *J* = 7.6 Hz, 2 H (major)) 5.2–5.4 (m, 2 H), 5.68 (dt, *J* = 7.6, 8.4 Hz, 2 H); ^{13}C NMR (major, $CDCl_3$) δ 13.6, 14.0, 22.3, 22.4, 25.0, 27.5, 31.7, 34.2, 88.3, 130.6, 133.9, 134.4; MS *m/z* (rel intensity) 346 (M^+, 18), 302 (36), 275 (100), 249 (77), 97 (55). Anal. Calcd for $C_{24}H_{42}O$: C, 83.17; H, 12.21. Found: C, 82.97; H, 12.42.

(4*E*,7*E*)-7-Pentyl-4,7-tridecadien-6-ol (12): R_f = 0.39 (ethyl acetate:hexane = 1:10); bp 120–122 °C (bath temp, 0.20 Torr); IR (neat) 3316, 2954, 2924, 2856, 1648, 1466, 1378, 966 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 9 H), 1.2–1.5 (m, 15 H), 1.9–2.2 (m, 6 H), 4.4–4.5 (m, 1 H), 5.44 (dd, *J* = 6.7, 15.2 Hz, 1 H), 5.47 (t, *J* = 6.7 Hz, 1 H), 5.68 (dt, *J* = 15.2, 6.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 14.0, 22.3, 22.5, 22.6, 27.6, 27.8, 29.3, 29.5, 31.6, 32.2, 34.3, 76.7, 126.3, 131.8, 140.1; MS *m/z* (rel intensity) 266 (M^+, 6), 223 (14), 195 (49), 99 (25), 71 (81), 43 (100). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; 12.86. Found: C, 81.16; H, 12.97.

General Procedure for the Synthesis of 1,3-Diene Derivatives. In a 50-mL reaction flask was placed $NbCl_5$ (1.1 g, 4.0 mmol) under an argon atmosphere. To the salt was added at 25 °C benzene (5 mL) and DME (5 mL) successively. Zinc (0.39 g, 6.0 mmol) was added to a stirring pale orange solution of $NbCl_5$, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned to dark brown with slightly exothermic process. To the mixture was added at 0 °C a solution of an alkyne (1.0 mmol) in DME–benzene (1:1, 2 mL), and the whole mixture was stirred at 0 °C. After the consumption of the alkyne was confirmed by TLC, THF (6 mL) was added at 25 °C to the mixture and the resulting mixture was stirred for an additional 15 min. A carbonyl compound (4.0 mmol) was added to the mixture at 25 °C, and the mixture was stirred at 25 °C for another 30 min. Aqueous NaOH solution (15%, 4 mL) was added, and the mixture was stirred at 25 °C for 1 h. The deposited brown solid was removed by filtration with Hyflo-Super Cel and washed with ethyl acetate (3 × 5 mL). The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel with hexane as an eluent gave 1,3-diene derivatives.

(1*E*,3*E*)-2-Decyl-1,4-diphenyl-1,3-butadiene: R_f = 0.53 (hexane); bp 180–182 °C (bath temp, 0.24 Torr); IR (neat) 2922, 2850, 1729, 1492, 1466, 1445, 958, 743, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.3 Hz, 3 H), 1.2–1.6 (m, 14 H), 1.5–1.8 (m, 2 H), 2.5–2.6 (m, 2 H), 6.62 (s, 1 H), 6.66 (d, *J* = 15.7 Hz, 1 H), 6.89 (d, *J* = 15.7 Hz, 1 H), 7.2–7.6 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 27.8, 29.2, 29.4, 29.6, 30.0, 31.9, 126.4, 126.5, 126.7, 127.3, 127.6, 128.3, 128.6, 128.8, 131.8, 133.3, 137.7, 140.9; MS *m/z* (rel intensity) 346 (M^+, 18), 205 (100), 129 (22), 91 (24), 43 (8). Anal. Calcd for $C_{26}H_{34}$: C, 90.11; H, 9.89. Found: C, 90.37; H, 10.11.

(1*Z*,3*E*)-2-Decyl-1,4-diphenyl-1,3-butadiene: R_f = 0.60 (hexane); bp 180–182 °C (bath temp, 0.24 Torr); IR (neat) 2922, 2852, 1730, 1492, 1465, 1448, 749, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3 H), 1.2–1.6 (m, 14 H), 1.5–1.8 (m, 2 H), 2.4–2.6 (m, 2 H), 6.54 (s, 1 H), 6.65 (d, *J* = 16.5 Hz, 1 H), 6.73 (d, *J* = 16.5 Hz, 1 H), 7.2–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 29.1, 29.4, 29.6, 29.7, 31.9, 34.5, 126.4, 126.5, 127.0, 127.3, 128.1, 128.6, 128.9, 129.5, 129.7, 137.8, 137.9, 139.1; MS *m/z* (rel intensity): 346 (M^+, 16), 205 (100), 129 (19), 91 (25), 43 (7). Anal. Calcd for $C_{26}H_{34}$: C, 90.11; N, 9.89. Found: C, 90.04; H, 10.09.

(3*E*,5*E*)-4-Decyl-1,8-diphenyl-3,5-octadiene ((3*E*)-20a): R_f = 0.35 (hexane); bp 215–217 °C (bath temp, 0.40 Torr); IR (neat) 2922, 2852, 1730, 1603, 1496, 1454, 964, 743, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.3 Hz, 3 H), 1.2–1.5 (m, 16 H), 2.1–2.3 (m, 2 H), 2.3–2.5 (m, 4 H), 2.6–2.8 (m, 4 H), 5.38 (t, *J* = 6.7 Hz, 1 H), 5.60 (dt, *J* = 15.6, 6.7 Hz, 1 H), 5.97 (d, *J* = 15.6 Hz, 1 H), 7.2–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 27.0, 29.1, 29.4, 29.6, 29.7, 30.0, 30.2, 31.9, 34.9, 36.1, 36.2, 125.7, 125.8, 126.6, 128.2, 128.3, 128.4, 129.5, 133.9, 138.9, 142.0; MS *m/z* (rel intensity) 402 (M^+, 6), 311 (24), 207 (36), 143 (13), 117 (11), 95 (11), 91 (100), 67 (26). Anal. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51. Found: C, 89.61; H, 10.56.

(3*Z*,5*E*)-4-Decyl-1,8-diphenyl-3,5-octadiene ((3*Z*)-20a): R_f = 0.40 (hexane); bp 215–217 °C (bath temp, 0.40 Torr); IR (neat) 2922, 2852, 1730, 1497, 1273, 964, 743, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3 H), 1.2–1.6 (m, 16 H), 2.1–2.3 (m, 2 H),

2.4–2.6 (m, 4 H), 2.6–2.8 (m, 4 H), 5.28 (t, J = 7.1 Hz, 1 H), 5.71 (dt, J = 15.7, 6.7 Hz, 1 H), 6.29 (d, J = 15.7 Hz, 1 H), 7.2–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 29.0, 29.3, 29.6, 30.0, 31.9, 34.2, 35.2, 39.7, 125.6, 125.8, 126.0, 126.7, 128.2, 128.3, 128.4, 128.5, 129.3, 136.6; MS m/z (rel intensity) 402 (M^+, 10), 311 (19), 207 (27), 129 (11), 117 (9), 91 (100), 67 (22). Anal. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51. Found: C, 89.60; H, 10.65.

(9*E*,11*E*)-10-Phenyl-9,11-icosadiene: R_f = 0.78 (hexane); bp 165–167 °C (bath temp, 0.26 Torr); IR (neat) 2922, 2852, 1730, 1459, 1272, 965, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.1–1.6 (m, 24 H), 2.12 (dt, J = 7.0, 7.0 Hz, 2 H), 2.28 (dt, J = 7.0, 7.0 Hz, 2 H), 5.41 (t, J = 7.2 Hz, 1 H), 5.52 (dt, J = 15.6, 7.0 Hz, 1 H), 6.49 (d, J = 15.6 Hz, 1 H), 7.2–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.9, 29.3, 29.4, 29.9, 31.9, 32.8, 126.5, 127.9, 129.5, 131.3, 131.7, 134.1, 139.0, 141.0; MS m/z (rel intensity) 354 (M^+, 52), 255 (49), 241 (95), 143 (100), 129 (59), 91 (77), 43 (48). Anal. Calcd for $C_{28}H_{42}$: C, 88.06; H, 11.94. Found: C, 88.12; H, 12.22.

(9*Z*,11*E*)-10-Phenyl-9,11-icosadiene: R_f = 0.73 (hexane); bp 165–167 °C (bath temp, 0.26 Torr); IR (neat) 2922, 2852, 1731, 1465, 1272, 967, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.1–1.5 (m, 24 H), 1.88 (dt, J = 7.6, 7.2 Hz, 2 H), 2.0–2.1 (m, 2 H), 5.11 (dt, J = 15.6, 7.0 Hz, 1 H), 5.58 (t, J = 7.6 Hz, 1 H), 6.23 (d, J = 15.6 Hz, 1 H), 7.1–7.2 (m, 2 H), 7.3–7.5 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.1, 29.3, 29.4, 29.5, 29.6, 29.8, 31.9, 33.3, 126.5, 126.6, 127.8, 128.8, 130.9, 134.7, 139.4, 142.8; MS m/z (rel intensity) 354 (M^+, 40), 255 (51), 241 (77), 143 (100), 129 (44), 91 (61), 43 (43). Anal. Calcd for $C_{28}H_{42}$: C, 88.06; H, 11.94. Found: C, 87.77; H, 11.91.

(3*E*,5*E*)-4,5-Dipentyl-1,8-diphenyl-3,5-octadiene ((5*E*)-20b): R_f = 0.30 (hexane); bp 170–172 °C (bath temp, 0.27 Torr); IR (neat) 2952, 2924, 2854, 1729, 1454, 1272, 744, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.7 Hz, 6 H), 1.1–1.4 (m, 12 H), 2.0–2.2 (m, 4 H), 2.38 (dt, J = 7.0, 7.6 Hz, 4 H), 2.68 (t, J = 7.8 Hz, 4 H), 5.37 (t, J = 7.0 Hz, 2 H), 7.2–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.0, 28.5, 30.3, 31.9, 36.3, 124.9, 125.7, 128.2, 128.5, 142.0, 142.2; MS m/z (rel intensity) 402 (M^+, 15), 311 (17), 207 (73), 117 (12), 91 (100), 67 (18), 43 (15). Anal. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51. Found: C, 89.64; H, 10.68.

(3*E*,5*Z*)-4,5-Dipentyl-1,8-diphenyl-3,5-octadiene ((5*Z*)-20b): R_f = 0.40 (hexane); bp 170–172 °C (bath temp, 0.27 Torr); IR (neat) 2952, 2924, 2852, 1730, 1453, 1271, 743, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 6.5 Hz, 3 H), 0.88 (t, J = 6.7 Hz, 3 H), 1.1–1.4 (m, 12 H), 1.9–2.1 (m, 4 H), 2.3–2.5 (m, 4 H), 2.6–2.8 (m, 4 H), 4.97 (t, J = 7.5 Hz, 1 H), 5.18 (t, J = 7.0 Hz, 1 H), 7.2–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 27.8, 27.9, 28.9, 29.7, 31.1, 31.4, 32.1, 36.3, 36.9, 125.2, 125.6, 125.7, 127.2, 128.2, 128.4, 128.5, 139.1, 142.2, 142.5, 143.9; MS m/z (rel intensity) 402 (M^+, 14), 311 (16), 207 (71), 117 (8), 91 (100), 67 (10), 43 (10). Anal. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51. Found: C, 89.55; H, 10.60.

(2*E*,4*E*)-4-Pentyl-1-phenyl-2,4-decadiene (17b) and 4-Pentyl-1-phenyl-3,5-decadiene (18b). The two compounds (**17b**/**18b** = 29/71) could not be separated: bp 123–125 °C (bath temp, 0.12 Torr); IR (neat, mixture of **17b**/**18b** = 29/71) 2954, 2924, 2856, 1605, 1496, 1466, 1455, 1378, 964, 744, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.8–1.0 (m, 6 H), 1.2–1.5 (m, 12 H (**17b**) + 10 H (**18b**)), 2.0–2.3 (m, 4 H), 2.43 (dt, J = 7.2, 7.9 Hz, 2 H (**18b**)), 2.68 (t, J = 7.9 Hz, 2 H (**18b**)), 3.43 (d, J = 6.7 Hz, 2 H (**17b**)), 5.36 (t, J = 7.2 Hz, 1 H), 5.57 (dt, J = 15.6, 6.8 Hz, 1 H (**18b**)), 5.69 (dt, J = 16.1, 6.7 Hz, 1 H (**17b**)), 5.92 (d, J = 15.6 Hz, 1 H (**18b**)), 6.01 (d, J = 16.1, 1 H (**17b**)), 7.2–7.4 (m, 5 H); MS m/z (rel intensity) 284 (M^+, 30), 193 (82), 137 (23), 91 (100), 67 (53). Anal. Calcd for $C_{21}H_{32}$: C, 88.66; H, 11.34. Found: C, 88.53; H, 11.58.

(*E*)-1-(1-Dodecenyl)cyclohexene (17c): R_f = 0.78 (hexane); bp 130–132 °C (bath temp, 0.30 Torr); IR (neat) 2952, 2924, 2854, 1733, 1466, 1273, 1136, 1073 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3 H), 1.2–1.6 (m, 14 H), 1.4–1.8 (m, 6 H), 2.0–2.2 (m, 6 H), 5.53 (dt, J = 15.6, 6.7 Hz, 1 H), 5.62 (bs, 1 H), 6.01 (d, J = 15.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 22.7, 24.6, 25.8, 26.9, 29.3, 29.4, 29.5, 29.6, 29.7, 30.1, 31.9, 32.9, 126.9, 127.0, 133.3, 135.7; MS m/z (rel intensity) 248 (M^+, 98), 135 (95), 93 (88), 79 (93), 41 (100). Anal. Calcd for $C_{18}H_{32}$: C, 87.02; H, 12.98. Found: C, 86.93; H, 13.11.

(*E*)-1-Phenyl-4-pentadecen-3-ol (16a). To a stirring solution of $NbCl_5$ (1.1 g, 4.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc (0.39 g, 6.0 mmol), and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 0 °C a solution of 1-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL), and the whole mixture was stirred at 0 °C for 1 h. THF (6 mL) was added to the mixture. The reaction mixture was stirred at 25 °C for 15 min. Immediately after addition of 3-phenylpropanal (0.16 g, 1.2 mmol) at 25 °C (10 s), aqueous NaOH solution (15%, 4 mL) was introduced at 25 °C to quench the reaction. The whole mixture was stirred at 25 °C for an additional 1 h. The deposited brown solid was removed by filtration with Hyfro-Super Cel and washed with ethyl acetate (3 × 5 mL). The organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel gave 0.11 g (38%) of (*E*)-1-phenyl-4-pentadecen-3-ol along with 96 mg (24%) of 1,3-diene derivatives **20a** and 7 mg (4%) of 1-dodecene. **16a**: R_f = 0.23 (ethyl acetate:hexane = 1:10; bp 140–142 °C (bath temp, 0.30 Torr); IR (neat) 3314, 2922, 2582, 1456, 1031, 968, 743, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3 H), 1.2–1.5 (m, 17 H), 1.7–2.0 (m, 2 H), 2.03 (dt, J = 6.6, 6.4 Hz, 2 H), 2.69 (dt, J = 2.2, 7.8 Hz, 2 H), 4.0–4.2 (m, 1 H), 5.48 (dd, J = 6.8, 15.4 Hz, 1 H), 5.66 (dt, J = 15.4, 6.6 Hz, 1 H), 7.2–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 29.1, 29.2, 29.4, 29.5, 31.6, 31.8, 32.1, 38.7, 72.0, 125.5, 128.1, 128.2, 131.9, 132.7, 141.9; MS m/z (rel intensity) 284 ($M^+ - H_2O$, 17), 143 (28), 91 (100), 81 (29), 67 (51). Anal. Calcd for $C_{21}H_{34}O$: C, 83.38; H, 11.33. Found: C, 83.18; H, 11.60. The content of deuterium in **16a**-*d* was determined by ^{1}H NMR analysis.

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Registry No. **2**-d_2, 125642-23-1; **4**, 125642-22-0; **4**-*d*, 125642-20-8; **5**, 125642-21-9; **6**, 125641-95-4; **7**, 16967-02-5; **8**, 138924-62-6; **9**, 138924-69-3; **10**, 138924-81-9; **11**, 138924-82-0; **12**, 138924-83-1; (*E*,*E*)-**13**, 138924-84-2; (*E*,*Z*)-**13**, 138924-85-3; **16a**-*d*, 138924-86-4; **17b**, 138924-78-4; **17c**, 138924-80-8; **18b**, 138924-79-5; (3*E*,5*E*)-**20a**, 138924-73-9; (3*Z*,5*E*)-**20a**, 138924-74-0; (3*E*,5*E*)-**20b**, 138955-28-9; (3*E*,5*Z*)-**20b**, 138924-77-3; A (R^1 = R^2 = C_5H_{11}, R^3 = C_8H_{17}, R^4 = H), 125642-15-1; A (R^1 = R^2 = C_5H_{11}, R^3 = c-C_6H_{11}, R^4 = H), 125642-16-2; A (R^1 = R^2 = C_5H_{11}, R^3 = *t*-Bu, R^4 = H), 138924-60-4; A (R^1 = R^2 = C_5H_{11}, R^3,R^4 = -$(CH_2)_5$-), 125642-17-3; A (R^1 = R12 = C_5H_{11}, R^3 = c-C_6H_{11}, R^4 = C_6H_{13}), 138924-61-5; A (R^1 = R^2 = C_5H_{11}, R^3 = CH=CH_2, R^4 = Me), 138924-63-7; A (R^1 = $C_{10}H_{21}$, R^2 = R^4 = H, R^3 = C_8H_{17}), 125641-96-5; A (R^1 = $C_{10}H_{21}$, R^2 = H, R^3,R^4 = -$(CH_2)_5$-), 125641-97-6; A (R^1 = c-C_6H_{11}, R^2 = C_6H_{13}, R^3 = $(CH_2)_2$Ph, R^4 = H), 125642-00-4; A (R^1 = c-C_6H_{11}, R^2 = C_6H_{13}, R^3,R^4 = -$(CH_2)_5$-), 125642-02-6; A (R^1 = *t*-Bu, R^2 = C_7H_{15}, R^3 = $(CH_2)_2$Ph, R^4 = H), 125641-98-7; A (R^1 = C_6H_{13}, R^2 = Ph, R^3 = $(CH_2)_2$Ph, R^4 = H), 125642-04-8; A (R^1 = C_6H_{13}, R^2 = Ph, R^3,R^4 = -$(CH_2)_5$-), 125642-06-0; A (R^1 = C_6H_{13}, R^2 = Ph, R^3 = CH=CH_2, R^4 = H), 138924-64-8; A (R^1 = Me_3Si, R^2 = $C_{10}H_{21}$, R^3 = $(CH_2)_2$Ph, R^4 = H), 125642-08-2; A (R^1 = Me_3Si, R^2 = $C_{10}H_{21}$, R^3,R^4 = -$(CH_2)_5$-), 125642-10-6; A (R^1 = Me_3Si, R^2 = $C_{10}H_{21}$, R^3 = CH=CH_2, R^4 = H), 138924-67-1; A (R^1 = Me_3Si, R^2 = $C_{10}H_{21}$, R^1 = CH=CH_2, R^4 = Me), 138924-68-2; A (R^1 = *t*-$BuMe_2Si$, R^2 = $C_{10}H_{21}$, R^3 = $(CH_2)_2$Ph, R^4 = H), 125642-12-8; A (R^1 = *t*-$BuMe_2Si$, R^2 = $C_{10}H_{21}$, R^3,R^4 = -$(CH_2)_5$-), 125642-13-9; A (R^1 = *t*-$BuMe_2Si$, R^2 = $C_{10}H_{21}$, R^3 = CH=CH_2, R^4 = H), 138924-70-6; B (R^1 = c-C_6H_{11}, R^2 = C_6H_{13}, R^3 = $(CH_2)_2$Ph, R^4 = H), 125642-01-5; B (R^1 = c-C_6H_{11}, R^2 = C_6H_{13}, R^3,R^4 = -$(CH_2)_5$-), 125642-03-7; B (R^1 = C_6H_{13}, R^2 = Ph, R^3 = $(CH_2)_2$Ph, R^4 = H), 125642-05-9; B (R^1 = C_6H_{13}, R^2 = Ph, R^3,R^4 = -$(CH_2)_5$-), 125642-07-1; B (R^1 = C_6H_{13}, R^2 = Ph, R^3 = CH=CH_2, R^4 = H), 138924-65-9; B (R^1 = Me_3Si, R^2 = $C_{10}H_{21}$, R^3 = $(CH_2)_2$Ph, R^4 = H), 138924-66-0; $C_5H_{11}C{\equiv}C$-C_5H_{11}, 6975-99-1; $C_{10}H_{21}C{\equiv}CH$, 765-03-7; c-$C_6H_{11}C{\equiv}CC_6H_{13}$, 125641-94-3; $Me_3SiC{\equiv}CC_{10}H_{21}$, 121134-52-9; *t*-$BuMe_2SiC{\equiv}CC_{10}H_{21}$, 125641-99-8; $PhC{\equiv}CH$, 536-74-3; C_8H_{17}(H)C=O, 124-19-6; c-C_6H_{11}(H)C=O, 2043-61-0; *t*-Bu(H)C=O, 630-19-3; c-C_6H_{11}(C_6H_{13})C=O, 6064-43-3; (c-C_6H_{11})$_2$C=O, 119-60-8; H_2C=CH(H)C=O, 107-02-8; H_2C=CH(Me)C=O, 78-94-4; Ph$(CH_2)_2$-(H)C=O, 104-53-0; PhCHO, 100-52-7; (1*E*,3*E*)-2-decyl-1,4-diphenyl-1,3-butadiene, 138924-71-7; (1*Z*,3*E*)-2-decyl-1,4-diphenyl-1,3-butadiene, 138924-72-8; (9*E*,11*E*)-10-phenyl-9,11-icosadiene, 138924-75-1; (9*Z*,11*E*)-10-phenyl-9,11-isocadiene, 138924-76-2; 1,2,3,4-tetrahydrobenzaldehyde, 1192-88-7; *trans*-2-hexenal, 6728-26-3.