Allylbarium Reagents: Unprecedented Regio- and Stereoselective Allylation Reactions of Carbonyl Compounds

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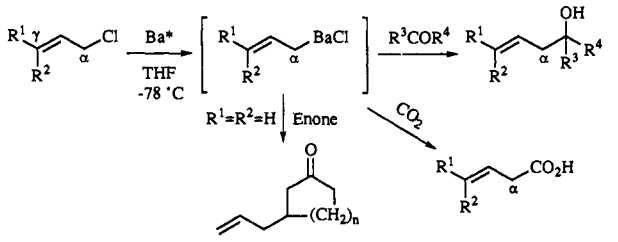
Abstract: The first direct preparation of allylbarium reagents by reaction of *in situ* generated reactive barium with various allylic chlorides and their new and unexpected selective allylation reactions with carbonyl compounds are disclosed. Highly reactive barium was readily prepared by the reduction of barium iodide with 2 equiv of lithium biphenylide in dry THF at room temperature. A variety of carbonyl compounds reacted with barium reagents generated from (*E*)- or (*Z*)-allylic chlorides in THF at −78 °C. All reactions resulted in high yields with remarkable α-selectivities not only with aldehydes but also with ketones. The double bond geometry of the starting allylic chloride was completely retained in each case. Stereochemically homogeneous (*E*)- and (*Z*)-β,γ-unsaturated carboxylic acids were easily prepared in good yields by highly α-selective carboxylation of allylic barium reagents with carbon dioxide. A selective Michael addition reaction with α,β-unsaturated cycloalkanone was also achieved using an allylbarium reagent. Treatment of 2-cyclopentenone (1 equiv) with allylbarium chloride (2 equiv) in THF at −78 °C for 20 min afforded 3-allylcyclopentanone in 94% yield with a 1,4/1,2 ratio of >99/1. Furthermore, the *in situ* generated barium enolate was efficiently trapped with various kinds of electrophiles ($Me_2C{=}CHCH_2Br$, $^nC_5H_{11}CHO$, and CH_3COCl).

Introduction

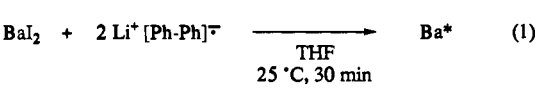
An allylmetal is one of the most useful reagents for the formation of carbon–carbon bonds.[1] Although a large number of allylic organometallics have been developed for selective allylation reactions, the allylic organometallic compounds of heavier alkaline earth metals have found little application in organic synthesis. Indeed, they do not offer any particular advantages over simple Grignard reagents.[2] We have been interested in using barium and strontium reagents with the anticipation that such species should exhibit stereochemical stabilities different from that of the ordinary magnesium reagent.[3] Reported herein are the first direct preparation of allylbarium reagents by reaction of *in situ* generated reactive barium with a variety of allylic chlorides[4] and their new and unexpected selective allylation reactions with carbonyl compounds (Scheme 1).[6]

Scheme 1



Results and Discussion

Preparation of Allylic Barium Reagents. Highly reactive barium was readily prepared by the reduction of barium iodide with 2 equiv of lithium biphenylide[7] in dry THF at room temperature for 30 min (eq 1). The dark brown suspension thus obtained was exposed to an allylic chloride at −78 °C. A slightly exothermic reaction took place immediately to give a dark red solution[8] of allylic barium that could be used directly (eq 2).



Stereochemical Stability of Allylic Barium Reagents. In the realm of stereoselectivity one great challenge that had not previously been met was the preparation of stereochemically homogeneous alkali and alkaline-earth allylmetals directly from

* Abstract published in *Advance ACS Abstracts,* June 1, 1994.

(1) Reviews: (a) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1. (b) Biellmann, J. F.; Ducep, J. B. *Org. React.* **1982**, *27*, 1. (c) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Heathcock, C. H., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 2, p 1. (d) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. Reviews of allylic Grignard reagents: (e) Benkeser, R. A. *Synthesis* **1971**, 347. (f) Nützel, K. In *Houben-Weyl: Methoden der Organischen Chemie*; Müller, E., Eds.; Thieme Verlag: Stuttgart, Germany, 1973; Vol.13/2a, p 88. See also: (g) Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988. (h) Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627.

(2) Reviews: (a) Ioffe, S. T.; Nesmeyanov, A. N. *The Organic Compounds of Magnesium. Beryllium. Calcium. Strontium and Barium*; North-Holland: Amsterdam, 1967. (b) Nützel, K. In *Houben-Weyl: Methoden der Organischen Chemie*; Müller, E., Eds.; Thieme Verlag: Stuttgart, Germany, 1973; Vol.13/2a, p 529. (c) Gowenlock, B. G.; Lindsell, W. E. In *Journal of Organometallic Chemistry Library 3, Organometallic Chemistry Reviews*; Seyferth, D., Davies, A. G., Fischer, E. O., Normant, J. F., Reutov, O. A., Eds.; Elsevier: Amsterdam, 1977; p 1. (d) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: Oxford, U.K., 1982; Vol. 1, Chapter 4, p 223. (e) Wakefield, B. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: Oxford, U.K., 1982; Vol. 7, Chapter 44.

(3) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 5893.

(4) Allylbarium has, as yet, been prepared only by transmetalation with diallylmercury[5a] or tetraallyltin[5b] in THF.

(5) (a) West, P.; Woodville, M. C. Ger. Offen. 2,132,955, 1972. (b) West, P.; Woodville, M. C. U.S. Pat. 3,766,281, 1973.

(6) A preliminary communication of this work has been published: Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 8955.

(7) Highly reactive calcium was prepared by the lithium biphenylide reduction of $CaBr_2$ or CaI_2, see: Wu, T.-C.; Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1990**, *55*, 5045.

(8) Sometimes a dark red suspension is obtained which can be used without difficulty.

0002-7863/94/1516-6130$04.50/0

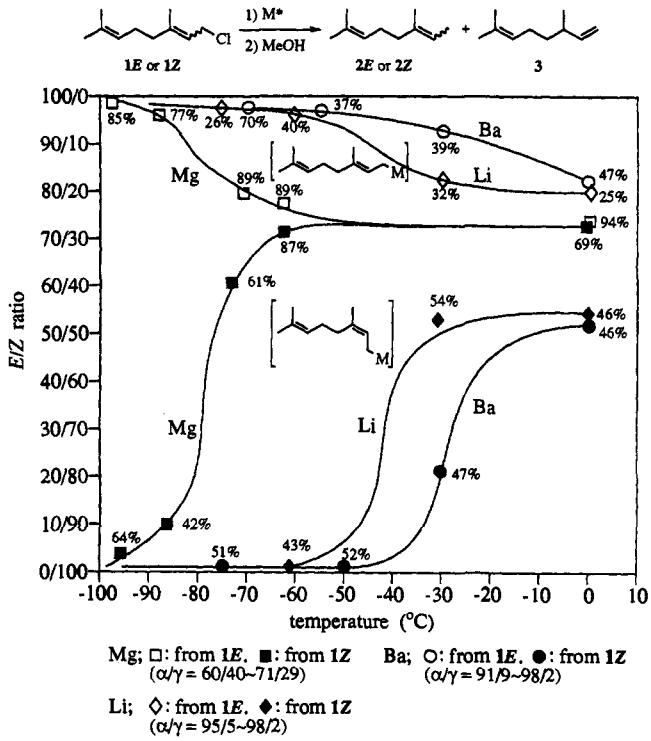


Figure 1. Temperature dependence of the E/Z ratio of the allylic metals (Li, Mg, and Ba) derived from geranyl chloride (**1E**; $E/Z > 99/1$) and neryl chloride (**1Z**; $E/Z < 1/99$). Numbers refer to combined yields of the products **2** and **3**.

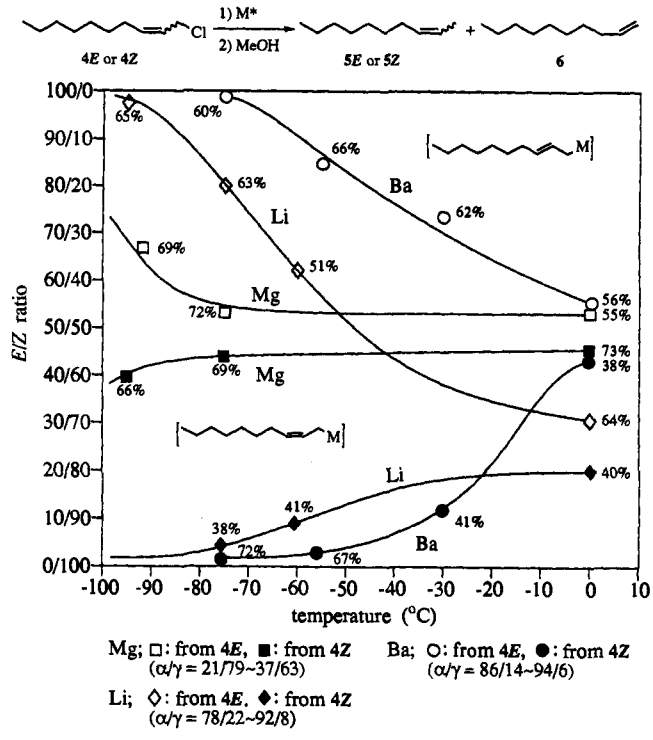
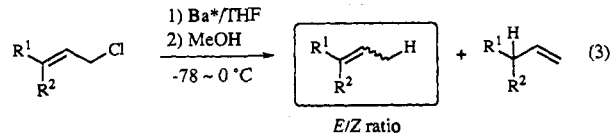


Figure 2. Temperature dependence of the E/Z ratio of the allylic metals (Li, Mg, and Ba) derived from (*E*)-2-decenyl chloride (**4E**; $E/Z > 99/1$) and (*Z*)-2-decenyl chloride (**4Z**; $E/Z = 2/98$). Numbers refer to combined yields of the products **5** and **6**.

allylic halides.[9] This is not a simple problem, since γ-substituted allylmetals, crotylmagnesium bromide, for example, are known to isomerize rapidly between the *Z* and *E* isomers even at low temperature.[10] Our interest in the structural aspects of these species has led us to undertake a careful investigation of these well-known organometallics.

Our initial assumption was that stereoisomerization of the allylmetal was due to the rapid isomerization through metallotropic rearrangements that were temperature dependent. Thus, a γ-substituted allylic chloride was transformed to the corresponding barium reagent at −78 ~ 0 °C in 25 °C intervals. The mixture was stirred for 30 min at each temperature[11] and quenched with methanol. The rate of isomerization was measured by analyzing a mixture of *E* and *Z* hydrocarbons (eq 3).



(3)

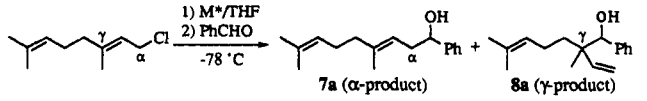
The results with geranyl- and nerylbarium compounds are shown in Figure 1. Similarly, magnesium[12] and lithium derivatives[14] were prepared and quenched as above. The implications of Figure 1 are apparent. There are two experimental variables (the temperature of the system and the choice of metal) and three consequences (the E/Z ratio of the olefins produced, the yield (%), and the α/γ ratio of the protonation products). Although there was no remarkable E/Z selectivity obtained by protonation of magnesium derivatives above −60 °C, extremely high stereoretention was observed below −95 °C.[3] In contrast, the double bond geometry of the allylic barium compounds was retained even at −50 °C, a temperature higher than that for the corresponding lithium compounds. The superiority of barium reagent is thus apparent for stereoselectivity. It should be further noted that the yields of the derived olefins were sufficiently high for practical purposes.

The temperature dependence of the E/Z ratio of 2-decenylmetals was also investigated, and the results are summarized in Figure 2. In contrast to the disubstituted allylmetals, a significant isomerization rate enhancement was observed for these monosubstituted allylmetals and rapid stereoisomerization of magnesium derivatives was observed even at −100 °C.[3] Although the cause of this enhancement was not immediately apparent, it does indicate that barium at below −70 °C rather than magnesium or lithium should be chosen for the effective generation of configurationally homogeneous monosubstituted allylmetals.

Metal Effects on the α/γ Selectivity in the Reactions of Various Geranylmetals with Benzaldehyde. The versatility of stereochemically homogeneous mono- and disubstituted allylmetals in synthesis is noteworthy, as is their complementary relationship to other key functional groups. Thus, we examined the metal effects on the α/γ selectivity in the reactions of various geranylmetals with benzaldehyde (Table 1). It is well established that the allylic magnesium or calcium reagent gives the γ-substituted product predominantly (entries 3 and 4) and the allylation with the lithium reagent is less selective (entry 1). In marked contrast, however, the barium reagent reacted with remarkable α-selectivity ($\alpha/\gamma = 92/8$) and retention of configuration of the starting halide ($E/Z = 98/2$, entry 6). Geranylcerium reagent

(9) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: Oxford, U.K., 1982; Vol. 1, Chapter 2.
(10) Hutchinson, D. A.; Beck, K. R.; Benkeser, R. A.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 7075.
(11) A digital thermometer (Model HH81, OMEGA Engineering, Inc.) was used to measure the internal reaction temperatures.
(12) The corresponding allylic Grignard reagents were generated using Rieke-Mg.[13]
(13) Burns, T. P.; Rieke, R. D. *J. Org. Chem.* **1987**, *52*, 3674.
(14) Prepared using lithium biphenylide[15] or lithium 4,4′-di-*tert*-butylbiphenylide (LDBB).[16]
(15) (a) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243. (b) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152.
(16) (a) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924. (b) Cohen, T.; Jeong, I.; Mudryk, B.; Bhupathy, M.; Awad, M. M. A. *J. Org. Chem.* **1990**, *55*, 1528.

Table 1. Reactions of Various Geranylmetals with Benzaldehyde[a]



7a (α-product) 8a (γ-product)

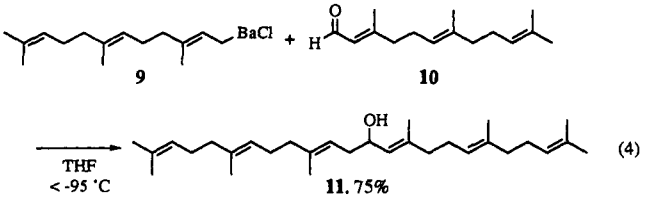
entry	M*	combined yield, %[b]	α/γ[c]	α-product, E/Z[c]
1[d]	Li⁺[Ph–Ph]•⁻	36	47/53	>99/1
2[e]	K⁺[Ph–Ph]•⁻	35	67/33	98/2
3	Mg	99	<1/99	
4	Ca	70	12/88	98/2
5	Sr	89	54/46	97/3
6	Ba	90	92/8	98/2
7	Cu[f]	39	45/55	97/3
8	Ce	52	72/28	>99/1

[a] Unless otherwise specified, the reaction was carried out by using geranyl chloride, reactive metal, and benzaldehyde (2, 2, and 1 equiv, respectively) at −78 °C for 30 min. [b] Isolated yield. [c] Determined by GLC analysis. [d] Geranyl chloride, lithium biphenylide, and benzaldehyde (2.5, 5.6, and 1 equiv, respectively) were used. [e] Geranyl chloride, potassium biphenylide, and benzaldehyde (1.2, 2.9, and 1 equiv, respectively) were used. [f] Prepared by reduction of CuI·PBu$_3$ with lithium naphthalenide.[42]

also showed a moderate α-selectivity (α/γ = 72/28, entry 8).[17] The extraordinary α-selectivity and stereospecificity of the carbonyl addition of barium reagent provide an unprecedented route to homoallylic alcohols.

α-Selective and Stereospecific Allylation of Carbonyl Compounds with Allylic Barium Reagents Prepared from Various Allylic Chlorides. We investigated the generality of the α-selective allylation using allylic barium reagents. Table 2 summarizes the results obtained for the reactions of a variety of carbonyl compounds with barium reagents generated from primary (*E*)- and (*Z*)-allylic chlorides in THF at −78 °C. Some characteristic features of the reaction are as follows: (1) All reactions resulted in high yields with remarkable α-selectivities not only with aldehydes but also with ketones. (2) The double bond geometry of the starting allylic chloride was completely retained in each case. (3) In the reaction with an α,β-unsaturated aldehyde, 1,2-addition proceeded preferentially (entry 3). (4) (*Z*)-γ-Monosubstituted allylbarium showed relatively low α-selectivities in reactions with carbonyl compounds (entries 6–9 and 13). However, condensations with bulky carbonyl compounds 2,2,4,4-tetramethyl-3-pentanone and *n*-hexanoyltrimethylsilane produced the α-product exclusively (entries 10 and 11).[18] (5) The alkyl substituent at the β-position of allylic barium had no effect on the regioselectivity (entries 23 and 25). (6) Existence of a triple bond or benzyl ether group in the allylic barium reagent had no effect on its preparation or the course of the reaction (entries 24 and 25).

12-Hydroxysqualene (**11**), an important intermediate of squalene biosynthesis,[19] was readily prepared by this new allylation reaction. Treatment of (*E*,*E*)-farnesal (**10**) with the allylic barium reagent **9** derived from (*E*,*E*)-farnesyl chloride in THF at −95 °C afforded **11** almost exclusively in 75% yield (eq 4).[20]



9 10 11, 75% (4)

(17) Highly stereocontrolled α-selective allylation using allylceriums has been reported by Cohen, see: Guo, B.-S.; Doubleday, W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710.

(18) (a) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 5198. (b) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 1969.

(19) Private communication from Professor T. Nishino, Kyoto University.

(20) The γ-isomer of **11** was obtained as a minor product (7% yield).

Next, we turned our attention to secondary allylic barium compounds. It is more difficult to control regio- and stereochemistries of secondary alkali and alkaline-earth allylmetals than those of the corresponding primary allylmetals because of their rapid stereoisomerization. Results of allylation of carbonyl compounds with allylic barium reagents prepared from various secondary allylic chlorides are shown in Table 3. Reaction of benzaldehyde with allylic barium reagents generated from 3-chloro-1-butene at −78 °C gave a 40:60 mixture of the α-product and γ-product in 98% yield (entry 2). At lower temperature (−95 °C), a slight increase of α-selectivity was observed (α/γ = 50/50, entry 3). Existence of two methyl groups at the γ-position of the secondary allylic chloride proved effective for obtaining a higher regioselectivity (α/γ = 56/44, entry 4). The highest α-selectivity (α/γ = 91/9) was gained using 2-chloro-4,8-dimethylnona-3,7-diene, which possesses a long alkyl chain at the γ-position (entry 5). A similar regioselectivity (α/γ = 92/8) was observed in the condensation of the same barium reagent with acetone, and the double bond geometry of the starting allylic chloride was completely retained throughout the reaction (*E*/*Z* > 99/1, entry 6).

Figure 3 provides a graphical interpretation of the reaction pathway of primary allylic barium reagents with carbonyl compounds. Selective formation of the *E* isomer of α-product F from (*E*)-allylic chloride A is readily accounted for by the oxidative addition of barium metal to halide A to generate a primary allylic barium compound (A → C), followed by its condensation at the α-carbon with a carbonyl compound (C → F). Since stereoisomerization of the barium reagent (C → D → E) does not occur at −78 °C, no *Z* isomer of the α-product H is formed from (*E*)-allylic chloride A at this temperature. Similarly, the formation of the *Z* isomer of α-product H from (*Z*)-allylic chloride B proceeds by the pathway B → E → H. Minor γ-product G may arise from C or E via a six-membered cyclic transition structure. On the other hand, the secondary allylic barium reagent seems to isomerize rapidly between the α- and γ-isomers even at low temperature. Existence of a long alkyl substituent at the γ-position is requisite to stop such metallotropic rearrangement.

At present the reason is not clear why an allylic barium compound reacts selectively at the α-carbon with a carbonyl compound; however, the unusually long barium–carbon bond (2.76~2.88 Å)[21] might prevent the formation of a six-membered cyclic transition structure leading to the γ-product. A four-membered cyclic structure including Ba—C and C=O bonds is one of the possible transition-state models for the α-selective allylation.

Regioselective and Stereospecific Synthesis of β,γ-Unsaturated Carboxylic Acids Using Allylbariums. β,γ-Unsaturated carboxylic acids and their derivatives are valuable synthetic intermediates of various natural products. Two typical multistep processes for the synthesis of β,γ-unsaturated acids, (1) Knoevenagel reaction/isomerization with base[22] and (2) allylic cyanide/hydrolysis,[23] are those most commonly used. Other new methods have been developed;[24–27] however, most of these suffer from the problem of *E*/*Z* stereoselectivity. One straightforward way to obtain β,γ-unsaturated acids is by the carboxylation of

(21) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 491.

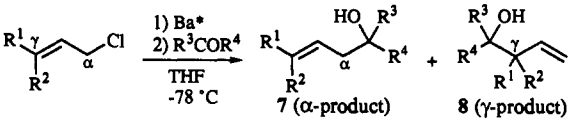
(22) (a) Caspi, E.; Varma, K. R. *J. Org. Chem.* **1968**, *33*, 2181. (b) Maercker, A.; Streit, W. *Chem. Ber.* **1976**, *109*, 2064. (c) Mikolajczak, K. L.; Smith, C. R., Jr. *J. Org. Chem.* **1978**, *43*, 4762. (d) Grob, C. A.; Waldner, A. *Helv. Chim. Acta* **1979**, *62*, 1854. (e) Ragoussis, N. *Tetrahedron Lett.* **1987**, *28*, 93.

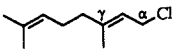
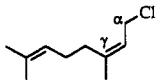
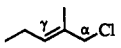
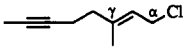
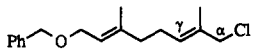
(23) (a) Katagiri, T.; Agata, A.; Takabe, K.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3715. (b) Hirai, H.; Matsui, M. *Agric. Biol. Chem.* **1976**, *40*, 169. (c) Garbers, C. F.; Beukes, M. S.; Ehlers, C.; McKenzie, M. J. *Tetrahedron Lett.* **1978**, 77. (d) Hoye, T. R.; Kurth, M. J. *J. Org. Chem.* **1978**, *43*, 3693. (e) Gosselin, P.; Rouessac, F. *C. R. Seances Acad. Sci., Ser. 2* **1982**, *295*, 469. (f) Mori, K.; Funaki, Y. *Tetrahedron* **1985**, *41*, 2369.

(24) Ene reaction of diethyl oxomalonate: (a) Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2473. (b) Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 3797.

(25) β-Vinyl-β-propiolactone/organocopper reagent: Kawashima, M.; Sato, T.; Fujisawa, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3255.

Table 2. Regio- and Stereoselective Allylation of Carbonyl Compounds with Allylic Barium Reagents Prepared from Primary Allylic Chlorides[a]



entry	allylic chloride[b]	carbonyl compound	products	combined yield, %[c]	α/γ[d]	α-product, E/Z[d]
1	(*E*)-^{n}C$_7$H$_{15}$CH=CHCH$_2$Cl	PhCHO	**7b + 8b**	80	97/3	>99/1
2		^{n}C$_5$H$_{11}$CHO	**7c + 8c**	82	98/2	97/3
3		(*E*)-PhCH=CHCHO	**7d + 8d**	73[e]	94/6	98/2
4		cyclohexanone	**7e + 8e**	95	99/1	99/1
5		PhCOCH$_3$	**7f + 8f**	94	96/4	99/1
6	(*Z*)-^{n}C$_7$H$_{15}$CH=CHCH$_2$Cl	PhCHO	**7g + 8g**	98	73/27	2/98
7		^{n}C$_5$H$_{11}$CHO	**7h + 8h**	75	86/14	2/98
8		cyclohexanone	**7i + 8i**	89	75/25	2/98
9		^{i}PrCO^{i}Pr	**7j + 8j**	99	82/18	2/98
10		^{t}BuCO^{t}Bu	**7k + 8k**	99	>99/1	<1/99
11		^{n}C$_5$H$_{11}$COSiMe$_3$	**7h + 8h**[f]	89	99/1	<1/99
12	(*E*)-CH$_3$CH=CHCH$_2$Cl	^{n}C$_5$H$_{11}$CHO	**7l + 8l**	65	83/17	97/3
13	(*Z*)-CH$_3$CH=CHCH$_2$Cl	^{n}C$_5$H$_{11}$CHO	**7m + 8m**	56	77/23	1/99
14		PhCHO	**7a + 8a**	90	92/8	98/2
15		^{n}C$_5$H$_{11}$CHO	**7n + 8n**	90	94/6	>99/1
16		cyclohexanone	**7o + 8o**	98	89/11	>99/1
17		PhCOCH$_3$	**7p + 8p**	96	93/7	99/1
18		PhCHO	**7q + 8q**	89	94/6	2/98
19		^{n}C$_5$H$_{11}$CHO	**7r + 8r**	73	96/4	<1/99
20		cyclohexanone	**7s + 8s**	98	91/9	<1/99
21		PhCOCH$_3$	**7t + 8t**	84	94/6	<1/99
22		^{n}C$_5$H$_{11}$CHO	**7u + 8u**	64	94/6	>99/1
23		cyclohexanone	**7v + 8v**	92	96/4	99/1
24		PhCHO	**7w + 8w**	98	91/9	>99/1
25		C_2H_5CHO	**7x + 8x**	74	97/3	>99/1

[a] Allylation was carried out by using an allylic chloride, reactive barium, and carbonyl compound (2, 2, and 1 equiv, respectively) at −78 °C for 30 min. [b] Stereochemically pure (>99%) allylic chlorides were used. [c] Isolated yield. [d] Determined by GLC analysis. [e] The 1,4-adduct was also obtained in 14% yield. [f] The intermediate α-hydroxysilanes were desilylated with ^{n}BuNF in DMF.[18]

an allylmetal. In the substituted allylic series, the reaction usually occurs at the more sterically hindered terminus.[1a] A stereospecific route for the synthesis of homogeranic acid and homoneric acid by carboxylation of the lithiated allylic sulfone has also been reported.[28] We anticipated that carboxylation of allylic barium would show α-selectivity without loss of the double bond geometry. Actually, treatment of excess carbon dioxide with allylic barium reagent resulted in α-carboxylation, whereas γ-carboxylation occurred with allylic magnesium reagent[1a] (Scheme 2).

Some results of carboxylation of allylic bariums are summarized in Table 4,[29] and the characteristic features of the reaction are as follows: (1) Allylic barium reagents generated from a variety of γ-mono- and γ-disubstituted allyl chlorides showed high α-selectivities without exception. (2) The double-bond geometry of the allylbarium was completely retained in each case. (3) The alkyl substituent at the β-position of allylic barium had no effect on the regioselectivity. In conclusion, this is one of the most straightforward and practical methods to date for regioselective

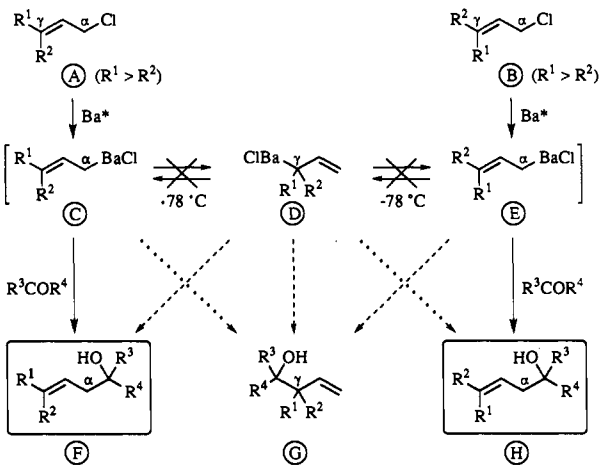


Figure 3. Reaction pathway of primary allylic barium reagents with carbonyl compounds.

and stereospecific synthesis of β,γ-unsaturated carboxylic acids using allylmetals.

Selective Michael Addition Reactions of Allylbarium with α,β-Unsaturated Cycloalkanones. The conjugate addition of an allylic anion to an α,β-enone is an extremely useful process for the introduction of a β-functionalized substituent.[30] However, allylic copper reagents are unstable and do not always give satisfactory

(26) Transition-metal-catalyzed carbonylation: (a) Alper, H.; Amer, I. *J. Mol. Catal.* **1989**, *54*, L33. (b) Garlaschelli, L.; Marchionna, M.; Iapalucci, M. C.; Longoni, G. *J. Organomet. Chem.* **1989**, *378*, 457. (c) Satyanarayana, N.; Alper, H.; Amer, I. *Organometallics* **1990**, *9*, 284. (d) Imada, Y.; Shibata, O.; Murahashi, S.-I. *J. Organomet. Chem.* **1993**, *451*, 183. For synthesis of the β,γ-unsaturated ester: (e) (Review) Murahashi, S.-I.; Imada, Y. *J. Synth. Org. Chem., Jpn.* **1991**, *49*, 919 and references cited therein. (f) Murahashi, S.-I.; Imada, Y.; Taniguchi, Y.; Higashiura, S. *J. Org. Chem.* **1993**, *58*, 1538. (g) Okano, T.; Okabe, N.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2589.

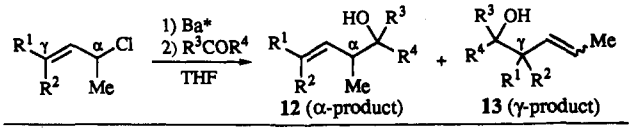
(27) Review: (a) Colvin, E. W. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, U.K., 1979; Vol. 2, p 620. The Büchi–Wüest rearrangement is a useful method for synthesis of β,γ-unsaturated amides: (b) Büchi, G.; Cushman, M.; Wüest, H. *J. Am. Chem. Soc.* **1974**, *96*, 5563.

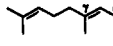
(28) Gosselin, P.; Maignan, C.; Rouessac, F. *Synthesis* **1984**, 876.

(29) Yanagisawa, A.; Yasue, K.; Yamamoto, H. *Synlett* **1992**, 593.

(30) Reviews: (a) Posner, G. H. *Org. React.* **1972**, *19*, 1. (b) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.: Pergamon Press: Oxford, U.K., 1991; Vol. 4, p 1–268. (c) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon Press: Oxford, U.K., 1992. (d) Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135.

Table 3. Allylation of Carbonyl Compounds with Allylic Barium Reagents Prepared from Secondary Allylic Chlorides[a]



entry	allylic chloride	carbonyl compound	T, °C	products	combined yield, %[b]	α/γ[c]
1		PhCHO	0	12a + 13a	98	34/64
2		PhCHO	-78	12a + 13a	98	40/60
3		PhCHO	-95	12a + 13a	95	50/50
4		PhCHO	-78	12b + 13b	81	56/44
5[d]		PhCHO	-78	12c + 13c	71	91/9
6[d]		CH_3COCH_3	-78	12d + 13d	70	92/8[e]

[a] Unless otherwise specified, allylation was carried out by using an allylic chloride, reactive barium, and carbonyl compound (2, 2, and 1 equiv, respectively) at −78 °C for 30 min. [b] Isolated yield. [c] Determined by GLC analysis. [d] Stereochemically pure (E/Z > 99/1) allylic chloride was used. [e] The E/Z ratio of the α-product was >99/1.

Scheme 2

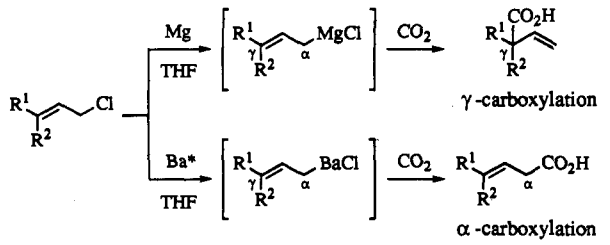
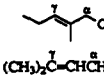
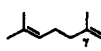
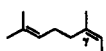


Table 4. Regio- and Stereoselective Carboxylation of Allylic Bariums[a]

entry	allylic chloride[b]	α-product	combined yield, %[c]	α/γ[d]	α-product, E/Z[d]
1	(E)-$^nC_7H_{15}$CH=CHCH$_2$Cl	(E)-$^nC_7H_{15}$CH=CHCH$_2$CO$_2$H (14)	82	98/2	99/1
2	(Z)-$^nC_7H_{15}$CH=CHCH$_2$Cl	(Z)-$^nC_7H_{15}$CH=CHCH$_2$CO$_2$H (15)	65	82/18	1/99
3		 (16)	58	95/5	99/1
4	$(CH_3)_2$C=CHCH$_2$Cl	$(CH_3)_2$C=CHCH$_2$CO$_2$H (17)	59	>99/1	
5		 (18)	87	>99/1	98/2
6		 (19)	51	>99/1	<1/99
7		 (20)	79	98/2	

[a] Allylation was carried out using an allylic chloride (1 equiv), reactive barium (1 equiv), and carbon dioxide (excess) at −78 °C for 30 min. [b] Stereochemically pure (>99%) allylic chloride was used. [c] Isolated yield. [d] Determined by GLC analysis after conversion to the methyl ester.

results.[31] In 1977, Hosomi and Sakurai reported the smooth reaction of allylsilane with an α,β-enone preferentially in a conjugate mode in the presence of titanium chloride as an activator of the enone, leading to a δ,ε-enone by simple protonolysis.[32]

Scheme 3

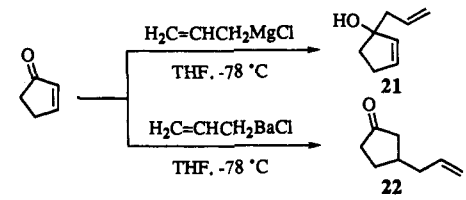
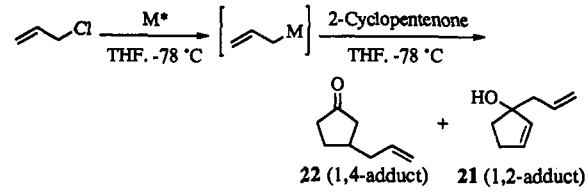


Table 5. Reaction of Various Allylmetals with 2-Cyclopentenone[a]



entry	M*	combined yield, %[b]	1,4/1,2[c]
1[d]	Li^+[Ph–Ph]$^{\bullet-}$	79	<1/99
2[d]	K^+[Ph–Ph]$^{\bullet-}$	38	62/38
3	Mg	81	5/95
4	Ca	65	28/72
5	Sr	63	67/33
6	Ba	94	>99/1

[a] Unless otherwise specified, the reaction was carried out using allyl chloride (2 equiv), reactive metal (2 equiv), and 2-cyclopentenone (1 equiv) at −78 °C for 20 min. [b] Isolated yield. [c] Determined by GLC analysis. [d] Allyl chloride, metal biphenylide, and 2-cyclopentenone (1.2, 2.7, and 1 equiv, respectively) were used.

Although the process is exceedingly useful, sequential regio- and stereoselective alkylation is not possible under Lewis acidic conditions. We then report that, by changing the metal from magnesium (or other ordinary metals)[1a,1c,30,33] to barium, the dominant course of the reaction can be transformed from a 1,2- to a 1,4-addition reaction (Scheme 3).

We first examined the 1,4/1,2 regioselectivity in the reactions of various allylmetals with cyclopentenone (Table 5). Treatment of the allylmetal, generated from a reactive alkali or alkaline-earth metal (2 equiv) and allyl chloride (2 equiv), with 2-cyclopentenone (1 equiv) at −78 °C in THF afforded a mixture of 1,4-adduct **22** and 1,2-adduct **21**. Among these allylmetals, allylbarium reagent was found to be unique for a Michael addition reaction (1,4/1,2 > 99/1, 94% yield, entry 6). In contrast, allyllithium and allylmagnesium reagents showed nearly exclusive 1,2-selectivities (entries 1 and 3). Reaction of allylpotassium and allylstrontium reagents resulted in moderate 1,4-selectivities (entries 2 and 5).

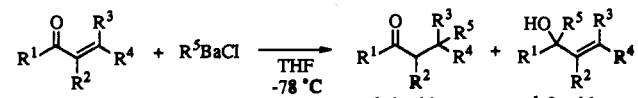
Some results of this new reaction between allylic barium reagents and α,β-unsaturated ketones are listed in Table 6 and have the following characteristic features: (1) Substituted allylbarium and benzylbarium reagents can be used for the reaction with 2-cyclopentenone with equal efficiency (1,4/1,2 > 99/1, entries 1–5). (2) The existence of a substituent at the C-2, C-3, or C-4 position of 2-cyclopentenone has no effect on the course of the reaction (entries 6–8). (3) In the reaction of 2-cyclohexenone with allylbarium reagent, lower temperature (<−95 °C) is requisite for obtaining a higher regioselectivity

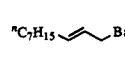
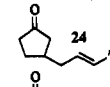
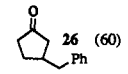
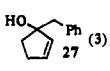
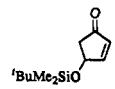
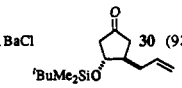
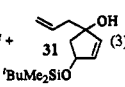
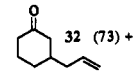
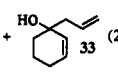
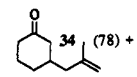
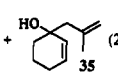
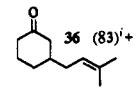
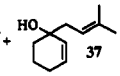
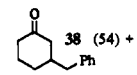
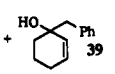
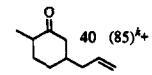
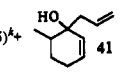
(31) (a) House, H. O.; Fischer, W. F., Jr. *J. Org. Chem.* **1969**, *34*, 3615. (b) Daviaud, G.; Miginiac, P. *Tetrahedron Lett.* **1973**, 3345. (c) House, H. O.; Sayer, T. S. B.; Yau, C.-C. *J. Org. Chem.* **1978**, *43*, 2153. (d) House, H. O.; Wilkins, J. M. *J. Org. Chem.* **1978**, *43*, 2443. (e) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969. (f) Luche, J. L.; Pétrier, C.; Gemal, A. L.; Zikra, N. *J. Org. Chem.* **1982**, *47*, 3805. (g) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6019. Recent excellent solutions to this problem: (h) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Smith, R. A. J. *J. Am. Chem. Soc.* **1990**, *112*, 4404. (i) Lipshutz, B. H.; Ung, C.; Elworthy, T. R.; Reuter, D. C. *Tetrahedron Lett.* **1990**, *31*, 4539. (j) Stack, D. E.; Dawson, B. T.; Rieke, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 4672. (k) Stack, D. E.; Dawson, B. T.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 5110. (l) Stack, D. E.; Klein, W. R.; Rieke, R. D. *Tetrahedron Lett.* **1993**, *34*, 3063.

(32) (a) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673. (b) Hosomi, A.; Kobayashi, H.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 955. (c) Sakurai, H.; Hosomi, A.; Hayashi, J. *Org. Synth. Collect. Vol. VII*, **1990**, 443. See also: (d) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043. (e) Hosomi, A.; Iguchi, H.; Endo, M.; Sakurai, H. *Chem. Lett.* **1979**, 977. (f) Ricci, A.; Fiorenza, M.; Grifagni, M. A.; Bartolini, G. *Tetrahedron Lett.* **1982**, *23*, 5079. (g) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *Tetrahedron Lett.* **1983**, *24*, 1909. (h) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *J. Org. Chem.* **1986**, *51*, 1745. (i) Hayashi, M.; Mukaiyama, T. *Chem. Lett.* **1987**, 289. (j) Takuwa, A.; Nishigaichi, Y.; Iwamoto, H. *Chem. Lett.* **1991**, 1013.

(33) (a) Macrosson, W. D. K.; Martin, J.; Parker, W.; Penrose, A. B. *J. Chem. Soc. C* **1968**, 2323. (b) Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1979**, 2845. (c) Bertz, S. H.; Dabbagh, G. *Tetrahedron* **1989**, *45*, 425.

Table 6. Conjugate Addition Reactions of Allylic Barium Reagents with Enones[a]



Entry	Enone	Barium reagent	Product(s) and yield(s) (%[b])	1,4/1,2[c]
1			 22 (94)	>99/1
2			 (96) 23	>99/1
3			 24 (69)[d]	>99/1
4			 25 (92)[e]	>99/1
5		$PhCH_2BaCl$	 26 (60) +  27 (3)	96/4
6			 28 (75)[f]	>99/1
7			 29 (86)	>99/1
8			 30 (93)[g] +  31 (3)	97/3
9			 32 (73) +  33 (20)	79/21
10[h]			32 (89) + 33 (11)	89/11
11[h]			 34 (78) +  35 (22)	78/22
12[h]			 36 (83)[i] +  37 (8)[j]	91/9
13[h]		$PhCH_2BaCl$	 38 (54) +  39 (3)	95/5
14[h]			 40 (85)[k] +  41 (7)	92/8
15[h]			42 (96) + 43 (1)	99/1
16[h]			44 (42) + 45 (58)	42/58
17[h]			(40) + (60) 46 47	40/60
18[h]			(53) + (40) 48 49	57/43
19[h]			(44) + (51) 50 51	46/54
20[h]			52 (57) + (35) 53	62/38
21[h]			(74) + (24) 54 55	76/24

[a] Unless otherwise specified, the reaction was carried out using an allylic barium reagent (2 equiv) and an enone (1 equiv) at −78 °C for 20 min. [b] Isolated yield. [c] Determined by GLC analysis. [d] The α/γ and E/Z ratios were 73/27 and >99/1, respectively. [e] The α/γ ratio was 36/64. [f] The trans/cis ratio was 62/38. [g] The trans/cis ratio was >99/1. [h] Run at −95 °C. [i] The α/γ ratio was 44/56. [j] The α/γ ratio was 68/32. [k] The ratio of the two diastereomers was 65/35.

Table 7. One-Pot Double Alkylation of α,β-Unsaturated Ketones[a]

entry	enone	electrophile	conditions T, °C	conditions T, h	product	yield, %[b]
1		$(CH_3)_2C{=}CHCH_2Br$	-30	1.5	56	81[c]
2		$^nC_5H_{11}C{\equiv}CCH_2Br$	-25	4	57	50[c]
3		$^nC_5H_{11}CHO$[d]	-78	0.3	58	85[c,e]
4		CH_3COCl	-78	0.3	59	87[f]
5		$(CH_3)_2C{=}CHCH_2Br$	-30	1	60	46[c]
6[g]		$(CH_3)_2C{=}CHCH_2Br$	-30	1.5	61	74[h]

[a] Unless otherwise specified, the reaction was carried out using an allylic barium reagent (2 equiv), enone (1 equiv), and electrophile (3 equiv). [b] Isolated yield. [c] The trans/cis ratio was >99/1. [d] 2 equiv of hexanal was used. [e] The threo/erythro ratio was 83/17. [f] A mixture of keto and enol compounds. [g] The conjugate addition reaction was performed at −95 °C. [h] The trans/cis ratio was 98/2.

(1,4/1,2 = 89/11, entries 9 and 10). The existence of methyl groups at the C-6 position of 2-cyclohexenone raised the 1,4-selectivities (entries 10, 14, and 15). (4) Not all competitive 1,2-addition reactions can be effectively controlled with barium reagent. Thus, use of 2-cycloheptenone and acyclic enones as electrophiles resulted in relatively lower 1,4-selectivities (entries 16–21).

The *in situ* generated barium enolate has sufficient nucleophilicity. Selected results of our double alkylation process are summarized in Table 7:[34] Direct alkylation of the enolate was achieved by treating it with an excess of prenyl bromide or 2-octynyl bromide (entries 1, 2, 5, and 6).[35] The aldol condensation and acylation reaction also proceeded smoothly with the same facility (entries 3 and 4).

The possible intermediacy of barium alkoxide **62** followed by an anionic oxy-Cope rearrangement was excluded by the following experiment (eq 5).[31c] Upon heating to 0 °C, no rearrangement

product **22** was obtained from barium alkoxide **62**, which was generated from the corresponding tertiary alcohol **21**. Thus, allylbarium reagent reacts directly at the β-carbons of enones, which reveals an additional unique feature of barium reagent.

Summary and Conclusion

Described herein are the first practical methods for α-selective allylation reactions of carbonyl compounds and new Michael addition reactions using allylic barium reagents. Main features of the present scheme are as follows: (1) Allylic barium reagents are readily prepared by treatment of the corresponding allylic chlorides with reactive barium. (2) No stereoisomerization of the primary allylic barium compound is observed below −70 °C.

(34) For a review of double alkylation of α,β-unsaturated carbonyl substrates, see: Chapdelaine, M. J.; Hulce, M. *Org. React.* **1990**, *38*, 225.
(35) Greene, A. E.; Crabbé, P. *Tetrahedron Lett.* **1976**, 4867.

(3) The barium reagent reacts selectively at the α-position with a variety of carbonyl compounds including carbon dioxide with complete retention of the stereochemistry of the starting halide. (4) A selective 1,4-addition reaction occurs with α,β-unsaturated ketones. The extraordinary α-selectivity and stereospecificity of the carbonyl addition of barium reagent provide an unprecedented route to homoallylic alcohols and are broadly applicable in organic synthesis.[17,18,36] Further work on the reactions of barium reagents and the precise reaction mechanisms is under current investigation.

Experimental Section

General Methods. Analytical TLC was done on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. Column chromatography was conducted by using silica gel 60 (E. Merck 9385, 230–400 mesh). Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^1H and ^{13}C NMR spectra were measured on a Varian Gemini-200 (200 MHz) or VXR-500S (500 MHz) spectrometer. Chemical shifts of ^1H NMR spectra were reported relative to tetramethylsilane (δ 0) or chloroform (δ 7.26). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.00). Splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra were recorded with a JEOR JMS-AX505HA mass spectrometer. Analytical gas–liquid phase chromatography (GLC) was performed on a Shimadzu GC-8A instrument equipped with a flame ionization detector and a capillary column of PEG-HT (0.25 × 25 000 mm) using nitrogen as the carrier gas. Microanalyses were accomplished at the Faculty of Agriculture, Nagoya University.

All experiments were carried out in a Schlenk tube under an atmosphere of standard grade argon gas (oxygen content < 10 ppm). The internal reaction temperature was measured by a digital thermometer (Model HH81, OMEGA Engineering, Inc.). For large-scale reactions the argon gas was further purified by passing it through a GAS CLEAN column (GC-RX, Nikka Seiko Co.) to remove traces of oxygen. Dry THF was used as purchased from Aldrich (anhydrous, 99.9%). Anhydrous BaI_2 was prepared by drying $BaI_2 \cdot 2H_2O$ (extra pure reagent, Nacalai Tesque) at 150 °C for 2 h under reduced pressure (<10 Torr). Products of Aldrich, Fluka, Kishida Chemical, and Wako Pure Chemical can be used with equal efficiency. Lithium (wire, 99.9%) was purchased from Aldrich. The wire was cut into 20–30-mg pieces which were rinsed with dry hexane before use. Biphenyl (guaranteed reagent) was used as purchased from Nacalai Tesque. Stereochemically pure (>99%) allylic chlorides were prepared by treatment of the corresponding allylic alcohols with a mixture of *N*-chlorosuccinimide and dimethyl sulfide in CH_2Cl_2.[37] Other chemicals were purchased and used as such.

Procedure for Generation of Reactive Barium (Ba*). An oven-dried, 20-mL Schlenk tube, equipped with a Teflon-coated magnetic stirring bar, was flushed with argon. Freshly cut lithium (15 mg, 2.2 mmol) and biphenyl (350 mg, 2.3 mmol) were placed into the apparatus and covered with dry THF (5 mL), and the mixture was stirred for 2 h at 20–25 °C (lithium was completely consumed).[15] Into a separate oven-dried, 50-mL Schlenk tube, equipped with a Teflon-coated magnetic stirring bar was placed anhydrous BaI_2 (430 mg, 1.1 mmol) under an argon atmosphere; this was covered with dry THF (5 mL) and stirred for 5 min at room temperature. To the resulting yellowish solution of BaI_2 in THF was added at room temperature a solution of the lithium biphenylide through a stainless steel cannula under an argon stream. The reaction mixture was stirred for 30 min at room temperature, and the resulting dark brown suspension of reactive barium thus prepared was ready to use.

General Procedure for Protonation of Allylic Barium Reagents (Figures 1 and 2). To the suspension of reactive barium (1.1 mmol) in THF (10 mL) was slowly added a solution of allylic chloride (1.0 mmol) in THF (1.5 mL) at the specified temperature. A digital thermometer was used to measure the internal reaction temperature by immersing the thermocouple sensor into the reaction mixture. The reaction mixture was stirred for 30 min at this temperature and quenched by slow addition of MeOH (0.5 mL). After being stirred for 5 min, 1 N HCl (10 mL) was added, and the aqueous layer was extracted with pentane (10 mL). The combined organic extracts were washed with 1 N sodium thiosulfate solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. The residual oil was purified by flash-column chromatography on silica gel (hexane as eluant) to afford a mixture of olefins: the α/γ and *E*/*Z* ratios were determined by GLC analysis. Results of the protonation of RBaCl (temperature, yield, α/γ ratio, *E*/*Z* ratio), for R = geranyl: 0 °C, 47%, 96/4, 82/18; –30 °C, 39%, 91/9, 93/7; –55 °C, 37%, 93/7, 97/3; –75 °C, 70%, 97/3, 98/2. For R = neryl: 0 °C, 46%, 98/2, 53/47; –30 °C, 47%, 96/4, 21/79; –50 °C, 52%, 95/5, 1/99; –75 °C, 51%, 96/4, <1/99. For R = (*E*)-2-decenyl: 0 °C, 56%, 86/14, 54/46; –30 °C, 62%, 89/11, 74/26; –55 °C, 66%, 91/9, 85/15; –75 °C, 60%, 94/6, >99/1. For R = (*Z*)-2-decenyl: 0 °C, 38%, 89/11, 42/58; –30 °C, 41%, 88/12, 12/88; –55 °C, 67%, 88/12, 4/96; –75 °C, 72%, 91/9, 2/98.

General Procedure for Protonation of Allylic Magnesium Reagents (Figures 1 and 2). A mixture of freshly cut lithium (10 mmol), anhydrous magnesium chloride (5 mmol), and naphthalene (1 mmol) in dry THF (15 mL) was stirred at room temperature for 12–15 h. To the resulting black suspension of reactive magnesium[13] in THF was slowly added a solution of allylic chloride (2.0 mmol) in THF (2 mL) at the specified temperature using the digital thermometer described above. The reaction mixture was stirred for 30 min at this temperature and quenched by slow addition of MeOH (1 mL). After being stirred for 5 min, 1 N HCl (20 mL) was added, and the aqueous layer was extracted with pentane (20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* after filtration. The residual oil was purified by flash-column chromatography on silica gel (hexane as eluant) to afford a mixture of olefins: the α/γ and *E*/*Z* ratios were determined by GLC analysis. Results of the protonation of RMgCl (temperature, yield, α/γ ratio, *E*/*Z* ratio), for R = geranyl: 0 °C, 94%, 66/34, 74/26; –63 °C, 89%, 71/29, 77/23; –71 °C, 89%, 67/33, 80/20; –87 °C, 77%, 66/34, 96/4; -98 °C, 85%, 65/35, 98/2. For R = neryl: 0 °C, 69%, 60/40, 73/27; –62 °C, 87%, 68/32, 71/29; –73 °C, 61%, 66/34, 61/39; –86 °C, 42%, 61/39, 11/89; –96 °C, 64%, 71/29, 4/96. For R = (*E*)-2-decenyl: 0 °C, 55%, 33/67, 53/47; –75 °C, 72%, 23/77, 53/47; –92 °C, 69%, 33/67, 67/33; –103 °C, 55%, 37/63, 71/29. For R = (*Z*)-2-decenyl: 0 °C, 73%, 23/77, 45/55; –75 °C, 69%, 21/79, 45/55; –95 °C, 66%, 23/77, 40/60.

General Procedure for Protonation of Allylic Lithium Reagents (Figures 1 and 2). A mixture of freshly cut lithium (15 mg, 2.2 mmol) and biphenyl (350 mg, 2.3 mmol) in dry THF (10 mL) was stirred at room temperature for 2 h. To the resulting dark blue solution of lithium biphenylide[15] in THF was slowly added a solution of allylic chloride (1 mmol) in THF (1.5 mL) at the specified temperature using the digital thermometer described above. The reaction mixture was stirred for 30 min at this temperature and quenched by slow addition of MeOH (0.5 mL). After being stirred for 5 min, 1 N HCl (10 mL) was added and the aqueous layer was extracted with pentane (10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* after filtration. The residual oil was purified by flash-column chromatography on silica gel (hexane as the eluant) to afford a mixture of olefins: the α/γ and *E*/*Z* ratios were determined by GLC analysis. Results of the protonation of RLi (temperature, yield, α/γ ratio, *E*/*Z* ratio), for R = geranyl: 0 °C, 25%, 95/5, 81/19; –30 °C, 32%, 96/4, 83/17; –60 °C, 40%, 97/3, 97/3; –75 °C, 26%, 97/3, 98/2. For R = neryl: 0 °C, 46%, 97/3, 54/46; –30 °C, 54%, 97/3, 54/46; –60 °C, 43%, 98/2, 2/98. For R = (*E*)-2-decenyl: 0 °C, 64%, 82/18, 32/68; –60 °C, 51%, 86/14, 63/37; –75 °C, 63%, 89/11, 81/19; –95 °C, 65%, 92/8, >99/1. For R = (*Z*)-2-decenyl: 0 °C, 40%, 80/20, 20/80; –60 °C, 41%, 80/20, 9/91; –75 °C, 38%, 78/22, 4/96.

(*E*)-2,6-Dimethyl-2,6-octadiene (2*E*):[38a] TLC R_f 0.59 (hexane); IR (neat) 2969, 2921, 1449, 1377 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.57 (d, 3 H, *J* = 6.6 Hz, CH_3), 1.59 (s, 6 H, 2 CH_3), 1.67 (s, 3 H, CH_3), 1.90–2.15 (m, 4 H, 2 CH_2), 5.09 (t, 1 H, *J* = 6.6 Hz, vinyl), 5.20 (q, 1 H, *J* = 6.6 Hz, vinyl); MS (EI, 70 eV) *m*/*z* (relative intensity) 138 (100, M^+), 123 (99.64), 109 (20.24), 95 (99.31), 81 (56.58), 70 (99.50).

(*Z*)-2,6-Dimethyl-2,6-octadiene (2*Z*):[38] TLC R_f 0.59 (hexane); IR (neat) 2961, 2920, 1458, 1377 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.56 (d, 3 H, *J* = 6.8 Hz, CH_3), 1.61 (s, 3 H, CH_3), 1.68 (s, 6 H, 2 CH_3), 1.95–2.10 (m, 4 H, 2 CH_2), 5.13 (m, 1 H, vinyl), 5.21 (q, 1 H, *J* = 6.8

(36) Recent approaches to α-selective allylation: (a) Yamamoto, Y.; Maruyama, K. *J. Org. Chem.* **1983**, *48*, 1564. (b) Yamamoto, Y.; Maeda, N.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1983**, 742. (c) Clarembeau, M.; Krief, A. *Tetrahedron Lett.* **1984**, *25*, 3629. (d) Araki, S.; Hatano, M.; Ito, H.; Butsugan, Y. *J. Organomet. Chem.* **1987**, *333*, 329. (e) Araki, S.; Butsugan, Y. *Chem. Lett.* **1988**, 457. (f) Iqbal, J.; Joseph, S. P. *Tetrahedron Lett.* **1989**, *30*, 2421. Indirect methods using acylsilanes as electrophiles: (g) Wilson, S. R.; Hague, M. S.; Misra, R. N. *J. Org. Chem.* **1982**, *47*, 747. (h) Suzuki, M.; Morita, Y.; Noyori, R. *J. Org. Chem.* **1990**, *55*, 441.

(37) Davisson, V. J.; Woodside, A. B.; Neal, T. R.; Stremler, K. E.; Muehlbacher, M.; Poulter, C. D. *J. Org. Chem.* **1986**, *51*, 4768.

(38) (a) Matsushita, H.; Negishi, E. *J. Org. Chem.* **1982**, *47*, 4161. (b) Normant, J. F.; Cahiez, G.; Chuit, C.; Villieras, J. *J. Organomet. Chem.* **1974**, *77*, 269.

Hz, vinyl); MS (EI, 70 eV) *m/z* (relative intensity) 138 (65.99, M^+), 123 (100), 109 (11.28), 95 (99.96), 81 (31.71), 70 (99.43).

(*E*)-2-Decene (5*E*):[39a-d] TLC R_f 0.66 (hexane); IR (neat) 2959, 2926, 2857, 1466, 1457, 1379, 965, 911, 723 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.6 Hz, CH_3), 1.20–1.45 (m, 10 H, 5 CH_2), 1.64 (d, 3 H, J = 4.6 Hz, CH_3), 1.97 (m, 2 H, CH_2), 5.42 (m, 2 H, 2 vinyls); MS (EI, 70 eV) *m/z* (relative intensity) 140 (100, M^+), 111 (32.34), 97 (57.15), 84 (62.80), 70 (99.11).

(*Z*)-2-Decene (5*Z*):[39] TLC R_f 0.66 (hexane); IR (neat) 2959, 2926, 2857, 1467, 1458, 1404, 1379, 911, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.6 Hz, CH_3), 1.20–1.45 (m, 10 H, 5 CH_2), 1.59 (d, 3 H, J = 5.2 Hz, CH_3), 2.02 (m, 2 H, CH_2), 5.40 (m, 2 H, 2 vinyls); MS (EI, 70 eV) *m/z* (relative intensity) 140 (100, M^+), 111 (32.22), 97 (68.47), 84 (69.52), 70 (99.65).

Procedure for Reaction of Geranyllithium with Benzaldehyde (Table 1, Entry 1). To the dark blue solution of lithium biphenylide, generated from lithium (15 mg, 2.2 mmol) and biphenyl (350 mg, 2.3 mmol) in dry THF (10 mL), was slowly added a solution of geranyl chloride (170 mg, 0.98 mmol) in THF (1.5 mL) at −78 °C. The reaction mixture was stirred for 20 min at this temperature and treated with a solution of benzaldehyde (40 μL, 0.39 mmol) in THF (1 mL). After being stirred for another 20 min at this temperature, 1 N HCl (10 mL) was added and the aqueous layer was extracted with ether (10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* after filtration. The crude product was purified by flash-column chromatography on silica gel (1:10 ether/hexane) to afford a mixture of homoallylic alcohols **7a** and **8a** (34 mg, 36% combined yield) as a colorless oil: the α/γ and E/Z ratios were determined to be 47/53 and >99/1, respectively, by GLC analysis.

(*E*)-4,8-Dimethyl-1-phenyl-3,7-nonadien-1-ol (7a):[40] TLC R_f 0.33 (1:5 ethyl acetate/hexane); IR (neat) 3630–3120, 2967, 2917, 2857, 1670, 1603, 1495, 1453, 1377, 1049, 911 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.61 (s, 6 H, 2 CH_3), 1.70 (s, 3 H, CH_3), 1.92 (br, 1 H, OH), 1.98–2.18 (m, 4 H, 2 CH_2), 2.34–2.60 (m, 2 H, CH_2), 4.69 (dd, 1 H, J = 5.6, 7.5 Hz, CH), 5.08 (m, 1 H, vinyl), 5.17 (t, 1 H, J = 7.8 Hz, vinyl), 7.22–7.43 (m, 5 H, aromatic). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.55; H, 10.10.

2,6-Dimethyl-1-phenyl-2-vinyl-5-hepten-1-ol (8a).[41] *Threo*-isomer: TLC R_f 0.42 (1:5 ethyl acetate/hexane); IR (neat) 3700–3300, 2971, 2926, 1636, 1455, 1375, 1049, 1013, 912, 733, 704 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.93 (s, 3 H, CH_3), 1.40 (m, 2 H, CH_2), 1.55 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 1.85 (m, 2 H, CH_2), 2.04 (d, 1 H, J = 2.2 Hz, OH), 4.43 (d, 1 H, J = 2.2 Hz, CH), 5.04 (m, 1 H, vinyl), 5.11 (dd, 1 H, J = 1.4, 17.6 Hz, vinyl), 5.29 (dd, 1 H, J = 1.4, 11.0 Hz, vinyl), 5.87 (dd, 1 H, J = 11.0, 17.6 Hz, vinyl), 7.20–7.40 (m, 5 H, aromatic). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.40; H, 10.11. *Erythro*-isomer: TLC R_f 0.42 (1:5 ethyl acetate/hexane); IR (neat) 3700–3300, 2967, 2928, 1453, 1375, 1046, 1009, 914, 729, 704 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.08 (s, 3 H, CH_3), 1.40 (m, 2 H, CH_2), 1.55 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 1.85 (m, 2 H, CH_2), 2.02 (d, 1 H, J = 4.4 Hz, OH), 4.45 (d, 1 H, J = 4.4 Hz, CH), 5.02 (d, 1 H, J = 17.6 Hz, vinyl), 5.04 (m, 1 H, vinyl), 5.20 (d, 1 H, J = 10.8 Hz, vinyl), 5.80 (dd, 1 H, J = 10.8, 17.6 Hz, vinyl), 7.20–7.40 (m, 5 H, aromatic).

Procedure for Reaction of Geranylpotassium with Benzaldehyde (Table 1, Entry 2). A mixture of freshly cut potassium (90 mg, 2.3 mmol) and biphenyl (350 mg, 2.3 mmol) in dry THF (10 mL) was stirred at room temperature for 1.5 h under an argon atmosphere. To the resulting dark blue solution of potassium biphenylide was slowly added a mixture of geranyl chloride (170 mg, 0.98 mmol) and benzaldehyde (80 μL, 0.79 mmol) in THF (2 mL) at −78 °C. The reaction mixture was stirred for 30 min at this temperature. After the standard workup and purification described in the reaction of geranyllithium, a mixture of homoallylic alcohols 7a and 8a was obtained (68 mg, 35% combined yield): the α/γ and E/Z ratios were determined to be 67/33 and 98/2, respectively, by GLC analysis.

Procedure for Reaction of Other Geranylmetals with Benzaldehyde (Table 1, Entries 3–8). The reaction was carried out using geranyl chloride, reactive metal, and benzaldehyde (2, 2, and 1 equiv, respectively) at −78 °C for 30 min by a procedure similar to the reaction of geranyllithium. Reactive calcium[7] and copper[42] were prepared by Rieke's methods in which the corresponding anhydrous metal halide was reduced by lithium biphenylide or naphthalenide. Reactive strontium and cerium were prepared by the lithium biphenylide reduction of SrI_2 and $CeCl_3$. A representative procedure for the preparation of reactive cerium is as follows: to a suspension of $CeCl_3$ (450 mg, 1.8 mmol) in dry THF (8 mL) was added a solution of preformed lithium biphenylide (5.0 mmol) in dry THF (7 mL) at room temperature. The mixture was stirred for 2.5 h at this temperature to afford a brown suspension of reactive cerium.

General Procedure for Allylation of Carbonyl Compounds with Allylic Barium Reagents (Tables 2 and 3). To the suspension of reactive barium (1.1 mmol) in THF (10 mL) was slowly added a solution of allylic chloride (1.0 mmol) in THF (1.5 mL) at −78 °C. After being stirred for 20 min, the mixture was treated with a solution of carbonyl compound (0.5 mmol) in THF (1 mL) at −78 °C and stirred for another 20 min at this temperature. To the mixture was added 1 N HCl (10 mL), and the aqueous layer was extracted with ether (10 mL). The combined organic extracts were washed with 1 N sodium thiosulfate solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. The crude product was purified by flash-column chromatography on silica gel (ether/hexane or ethyl acetate/hexane as the eluant) to afford a mixture of homoallylic alcohols: the α/γ and E/Z ratios were determined by GLC analysis.

(*E*)-1-Phenyl-3-undecen-1-ol (7b, 96 mg, 78% Yield): TLC R_f 0.38 (1:5 ethyl acetate/hexane); IR (neat) 3650–3125, 2926, 2855, 1602, 1495, 1455, 968, 758, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.5 Hz, CH_3), 1.13–1.45 (m, 10 H, 5 CH_2), 1.94–2.10 (m, 3 H, CH_2 and OH), 2.42 (m, 2 H, CH_2), 4.68 (m, 1 H, CH), 5.30–5.67 (m, 2 H, 2 vinyls), 7.21–7.43 (m, 5 H, aromatic); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.5, 25.3, 29.0, 29.3, 31.7, 32.5, 42.7, 73.4, 125.5, 126.0 (2 C), 127.5, 128.5 (2 C), 135.5, 144.2. Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.81; H, 10.66.

(*E*)-8-Hexadecen-6-ol (7c, 94 mg, 78% Yield): TLC R_f 0.44 (1:5 ethyl acetate/hexane); IR (neat) 3700–3100, 2957, 2926, 2857, 1467, 1380, 1125, 1074, 1029, 968, 724 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.5 Hz, CH_3), 0.89 (t, 3 H, J = 6.6 Hz, CH_3), 1.18–1.54 (m, 18 H, 9 CH_2), 1.60 (br, 1 H, OH), 1.95–2.32 (m, 4 H, 2 CH_2), 3.58 (m, 1 H, CH), 5.48 (m, 2 H, 2 vinyls); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9 (2 C), 22.5, 25.2, 25.3, 29.0, 29.1, 29.3, 31.7, 31.8, 32.5, 36.6, 40.6, 70.9, 125.9, 135.0. Anal. Calcd for $C_{16}H_{32}O$: C, 79.93; H, 13.41. Found: C, 79.81; H, 13.76.

(1*E*, 5*E*)-1-Phenyl-1,5-tridecadien-3-ol (7d, 91 mg, 67% Yield): TLC R_f 0.32 (1:5 ethyl acetate/hexane); IR (neat) 3650–3120, 2957, 2926, 2855, 1600, 1578, 1495, 1450, 1029, 967, 749, 693 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.4 Hz, CH_3), 1.15–1.47 (m, 10 H, 5 CH_2), 1.80 (d, 1 H, J = 3.8 Hz, OH), 2.03 (m, 2 H, CH_2), 2.35 (m, 2 H, CH_2), 4.30 (m, 1 H, CH), 5.72 (m, 2 H, 2 vinyls), 6.23 (dd, 1 H, J = 6.2, 16.0 Hz, vinyl), 6.61 (d, 1 H, J = 16.0 Hz, vinyl), 7.19–7.47 (m, 5 H, aromatic). Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.69; H, 10.39.

1-[(*E*)-2-Decenyl]cyclohexan-1-ol (7e, 111 mg, 93% Yield): TLC R_f 0.45 (1:5 ethyl acetate/hexane); IR (neat) 3625–3130, 2926, 2855, 1449, 1379, 1263, 1152, 1037, 970, 702 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.5 Hz, CH_3), 1.17–1.70 (m, 21 H, 10 CH_2 and OH), 2.03 (m, 2 H, CH_2), 2.14 (d, 2 H, J = 6.0 Hz, CH_2), 5.49 (m, 2 H, 2 vinyls). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.52; H, 12.74.

(*E*)-2-Phenyl-4-dodecen-2-ol (7f, 116 mg, 89% Yield): TLC R_f 0.39 (1:5 ethyl acetate/hexane); IR (neat) 3640–3200, 2957, 2926, 2855, 1602, 1495, 1447, 1375, 1069, 1028, 972, 762, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.4 Hz, CH_3), 1.14–1.40 (m, 10 H, 5 CH_2), 1.52 (s, 3 H, CH_3), 1.96 (m, 2 H, CH_2), 2.09 (s, 1 H, OH), 2.42 (dd, 1 H, J = 8.0, 13.6 Hz, one proton of CH_2), 2.62 (dd, 1 H, J = 6.2, 13.6 Hz, one proton of CH_2), 5.20 (m, 1 H, vinyl), 5.55 (dt, 1 H, J = 6.6, 15.4 Hz, vinyl), 7.19–7.49 (m, 5 H, aromatic); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.5, 25.3, 29.0, 29.2, 29.7, 31.7, 32.5, 47.2, 73.6, 124.7, 124.9 (2 C), 126.6, 128.2 (2 C), 136.6, 144.1. Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.99; H, 10.82.

(*Z*)-1-Phenyl-3-undecen-1-ol (7g, 86 mg, 70% Yield): TLC R_f 0.38 (1:5 ethyl acetate/hexane); IR (neat) 3650–3125, 2955, 2926, 2855, 1603, 1493, 1455, 1046, 912, 758, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$)

(39) (a) Araki, S.; Butsugan, Y. *J. Chem. Soc., Perkin Trans 1* **1984**, 969. (b) Couperus, P. A.; Clague, A. D. H.; van Dongen, J. P. C. M. *Org. Magn. Reson.* **1976**, *8*, 426. (c) Satyanarayana, N.; Periasamy, M. *J. Organomet. Chem.* **1987**, *319*, 113. (d) Achyutha Rao, S.; Periasamy, M. *J. Organomet. Chem.* **1988**, *342*, 15. (e) Alexakis, A.; Cahiez, G.; Normant, J. F. *Synthesis* **1979**, 826.

(40) (a) Baldwin, J. E.; DeBernardis, J.; Patrick, J. E. *Tetrahedron Lett.* **1970**, 353. (b) Araki, S.; Butsugan, Y. *Chem. Lett.* **1988**, 457. (c) Masuyama, Y.; Hayakawa, A.; Kurusu, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 1102.

(41) (a) Koreeda, M.; Tanaka, Y. *Chem. Lett.* **1982**, 1299. (b) Masuyama, Y.; Kinugawa, N.; Kurusu, Y. *J. Org. Chem.* **1987**, *52*, 3702. (c) Jubert, C.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 5425. (d) Jubert, C.; Nowotny, S.; Kornemann, D.; Antes, I.; Tucker, C. E.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 6384.

(42) Rieke, R. D.; Stack, D. E.; Dawson, B. T.; Wu, T.-C. *J. Org. Chem.* **1993**, *58*, 2483 and references therein.

δ 0.88 (t, 3 H, J = 6.8 Hz, CH_3), 1.10–1.40 (m, 10 H, 5 CH_2), 1.95–2.10 (m, 3 H, CH_2 and OH), 2.52 (m, 2 H, CH_2), 4.71 (dd, 1 H, J = 5.6, 7.4 Hz, CH), 5.32–5.65 (m, 2 H, 2 vinyls), 7.20–7.42 (m, 5 H, aromatic); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.5, 27.3, 29.0, 29.1, 29.4, 31.7, 37.2, 73.9, 124.7, 126.0, 127.6, 128.5 (2 C), 134.1, 144.3, 150.8. Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.83; H, 10.59.

(*Z*)-8-Hexadecen-6-ol (7h, 76 mg, 63% Yield): TLC R_f 0.44 (1:5 ethyl acetate/hexane); IR (neat) 3650–3100, 2957, 2928, 2857, 1657, 1467, 1379, 1125, 1036, 725 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3 H, J = 6.4 Hz, CH_3), 0.88 (t, 3 H, J = 6.5 Hz, CH_3), 1.20–1.63 (m, 19 H, 9 CH_2 and OH), 2.05 (m, 2 H, CH_2), 2.22 (dd, 2 H, J = 6.2, 7.2 Hz, CH_2), 3.62 (m, 1 H, CH), 5.31–5.64 (m, 2 H, 2 vinyls); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 13.9, 22.5, 25.3 (2 C), 27.3, 29.1 (2 C), 29.5, 31.7, 31.8, 35.2, 36.7, 71.5, 125.2, 133.7. Anal. Calcd for $C_{16}H_{32}O$: C, 79.93; H, 13.41. Found: C, 79.80; H, 13.74.

1-[(*Z*)-2-Decenyl]cyclohexan-1-ol (7i, 78 mg, 65% Yield): TLC R_f 0.45 (1:5 ethyl acetate/hexane); IR (neat) 3700–3135, 2928, 2855, 1450, 1379, 1262, 1150, 1037, 965, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3 H, J = 6.8 Hz, CH_3), 1.55-1.75 (m, 21 H, 10 CH_2 and OH), 2.04 (m, 2 H, CH_2), 2.20 (d, 2 H, J = 7.0 Hz, CH_2), 5.25–5.70 (m, 2 H, 2 vinyls). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.59; H, 12.83.

(*Z*)-3-Isopropyl-2-methyl-5-tridecen-3-ol (7j, 102 mg, 80% Yield): TLC R_f 0.43 (1:5 ether/hexane); IR (neat) 3650–3300, 2961, 2926, 2857, 1468, 1385, 1148, 1096, 1003, 972, 950 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.8 Hz, CH_3), 0.93 (d, 6 H, J = 6.8 Hz, 2 CH_3), 0.97 (d, 6 H, J = 6.8 Hz, 2 CH_3), 1.20–1.45 (m, 11 H, 5 CH_2 and OH), 1.95 (septet, 2 H, J = 6.8 Hz, 2 H), 2.07 (m, 2 H, CH_2), 2.29 (d, 2 H, J = 5.4 Hz, CH_2), 5.46 (m, 2 H, 2 vinyls). Anal. Calcd for $C_{17}H_{34}O$: C, 80.25; H, 13.47. Found: C, 80.21; H, 13.73.

(*Z*)-3-*tert*-Butyl-2,2-dimethyl-5-tridecen-3-ol (7k, 140 mg, 99% yield): TLC R_f 0.65 (1:5 ether/hexane); IR (neat) 3650–3450, 2961, 2926, 2857, 1649, 1483, 1468, 1393, 1370, 1206, 1081, 1001 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.6 Hz, CH_3), 1.08 (s, 18 H, 6 CH_3), 1.17–1.45 (m, 10 H, 5 CH_2), 1.52 (s, 1 H, OH), 2.08 (m, 2 H, CH_2), 2.44 (d, 2 H, J = 6.0 Hz, CH_2), 5.40–5.66 (m, 2 H, 2 vinyls). Anal. Calcd for $C_{19}H_{38}O$: C, 80.78; H, 13.56. Found: C, 80.68; H, 13.69.

(*E*)-2-Decen-5-ol (7l, 41 mg, 52% Yield):[43] TLC R_f 0.37 (1:5 ethyl acetate/hexane); IR (neat) 3650–3120, 2957, 2930, 1457, 1377, 1126, 1070, 1028, 967, 760, 659 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3 H, J = 6.8 Hz, CH_3), 1.20–1.65 (m, 9 H, 4 CH_2 and OH), 1.70 (d, 3 H, J = 3.6 Hz, CH_3), 1.95–2.30 (m, 2 H, CH_2), 3.60 (m, 1 H, CH), 5.52 (m, 2 H, 2 vinyls). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.83; H, 13.25.

(*Z*)-2-Decen-5-ol (7m, 34 mg, 43% Yield):[43] TLC R_f 0.37 (1:5 ethyl acetate/hexane); IR (neat) 3700–3100, 2957, 2930, 2859, 1656, 1459, 1378, 1122, 1074, 1034, 845, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.6 Hz, CH_3), 1.25–1.60 (m, 9 H, 4 CH_2 and OH), 1.64 (d, 3 H, J = 6.6 Hz, CH_3), 2.21 (dd, 2 H, J = 6.2, 7.2 Hz, CH_2), 3.62 (m, 1 H, CH), 5.36–5.70 (m, 2 H, 2 vinyls). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.64; H, 13.30.

(*E*)-2,6-Dimethyl-2,6-tetradecadien-9-ol (7n, 101 mg, 85% Yield): TLC R_f 0.49 (1:5 ethyl acetate/hexane); IR (neat) 3700–3100, 2959, 2928, 2859, 1670, 1453, 1377, 1125, 1109, 1068, 1044 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, 3 H, J = 6.5 Hz, CH_3), 1.20–1.52 (m, 9 H, 4 CH_2 and OH), 1.60 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.95–2.21 (m, 6 H, 3 CH_2), 3.59 (m, 1 H, CH), 5.08 (m, 1 H, vinyl), 5.17 (t, 1 H, J = 7.5 Hz, vinyl); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 16.1, 17.5, 22.5, 25.3, 25.5, 26.4, 31.8, 36.0, 36.6, 39.7, 71.6, 120.3, 124.3, 131.8, 139.0. Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.53; H, 12.89.

1-[(*E*)-3,7-Dimethyl-2,6-octadienyl]cyclohexan-1-ol (7o, 103 mg, 87% Yield):[44] TLC R_f 0.35 (1:5 ethyl acetate/hexane); IR (neat) 3650–3150, 2930, 2855, 1670, 1449, 1377, 1150, 1061, 1036, 972, 735 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.36–1.72 (m, 11 H, 5 CH_2 and OH), 1.60 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.96–2.20 (m, 4 H, 2 CH_2), 2.15 (d, 2 H, J = 7.5 Hz, CH_2), 5.06 (m, 1 H, vinyl), 5.23 (t, 1 H, J = 7.9 Hz, vinyl). Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.38; H, 12.11.

(*E*)-5,9-Dimethyl-2-phenyl-4,8-decadien-2-ol (7p, 114 mg, 88% Yield):[44] TLC R_f 0.40 (1:5 ethyl acetate/hexane); IR (neat) 3625–3200, 2973, 2855, 1670, 1603, 1495, 1447, 1375, 1107, 1067, 1028, 949, 764, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.53 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.90–2.12 (m, 5 H, 2 CH_2 and OH), 2.54 (d, 2 H, J = 8.0 Hz, CH_2), 4.92–5.05 (m, 2 H, 2 vinyls), 7.19–7.50 (m, 5 H, aromatic); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.0, 17.5, 25.6, 26.2, 29.6, 39.8, 42.3, 74.3, 119.1, 124.2, 125.0 (2 C), 126.6, 128.2 (2 C), 132.1, 140.4, 148.3. Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.71; H, 10.04.

(*Z*)-4,8-Dimethyl-1-phenyl-3,7-nonadien-1-ol (7q, 100 mg, 82% Yield):[40] TLC R_f 0.33 (1:5 ethyl acetate/hexane); IR (neat) 3675–3135, 3031, 2965, 2857, 1669, 1602, 1493, 1453, 1377, 1049, 760, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.60 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 1.55–1.78 (hidden in this region, 1 H, CH), 1.90–2.15 (m, 4 H, 2 CH_2), 2.47 (m, 2 H, CH_2), 4.67 (dd, 1 H, J = 5.4, 7.8 Hz, CH), 5.10 (m, 1 H, vinyl), 5.19 (t, 1 H, J = 7.5 Hz, vinyl), 7.20–7.45 (m, 5 H, aromatic). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.53; H, 10.15.

(*Z*)-2,6-Dimethyl-2,6-tetradecadien-9-ol (7r, 84 mg, 70% Yield): TLC R_f 0.49 (1:5 ethyl acetate/hexane); IR (neat) 3700–3125, 2961, 2928, 2859, 1670, 1453, 1377, 1124, 1076, 1043, 831 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, 3 H, J = 6.4 Hz, CH_3), 1.20–1.55 (m, 9 H, 4 CH_2 and OH), 1.60 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 1.95–2.25 (m, 6 H, 3 CH_2), 3.58 (m, 1 H, CH), 5.11 (m, 1 H, vinyl), 5.18 (t, 1 H, J = 7.5 Hz, vinyl). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.59, H, 12.89.

1-[(*Z*)-3,7-Dimethyl-2,6-octadienyl]cyclohexan-1-ol (7s, 105 mg, 89% Yield): TLC R_f 0.35 (1:5 ethyl acetate/hexane); IR (neat) 3650–3150, 2930, 2857, 1670, 1449, 1377, 1150, 972, 834, 702 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20–1.80 (m, 11 H, 5 CH_2 and OH), 1.60 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 1.95–2.10 (m, 4 H, 2 CH_2), 2.16 (d, 2 H, J = 7.6 Hz), 5.11 (m, 1 H, vinyl), 5.25 (t, 1 H, J = 7.6 Hz, vinyl). Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.52; H, 12.26.

(*Z*)-5,9-Dimethyl-2-phenyl-4,8-decadien-2-ol (7t, 102 mg, 79% Yield): TLC R_f 0.40 (1:5 ethyl acetate/hexane); IR (neat) 3625–3150, 2969, 2857, 1667, 1603, 1495, 1447, 1375, 1069, 1028, 878, 764, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.53 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.99–2.11 (m, 5 H, 2 CH_2 and OH), 2.56 (d, 2 H, J = 7.8 Hz, CH_2), 5.01 (t, 1 H, J = 7.8 Hz, vinyl), 5.10 (m, 1 H, vinyl), 7.19–7.49 (m, 5 H, aromatic); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.5, 23.5, 25.5, 26.3, 29.8, 31.9, 42.0, 74.1, 119.5, 124.1, 125.0 (2 C), 126.6, 128.2 (2 C), 132.1, 140.4, 148.4. Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.64; H, 10.07.

(*E*)-4-Methyl-3-undecen-6-ol (7u, 55 mg, 60% Yield): TLC R_f 0.39 (1:5 ethyl acetate/hexane); IR (neat) 3700–3120, 2959, 2930, 1460, 1379, 1127, 1072, 1021, 758, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, 3 H, J = 5.8 Hz, CH_3), 0.96 (t, 3 H, J = 7.6 Hz, CH_3), 1.20–1.52 (m, 9 H, 4 CH_2 and OH), 1.63 (s, 3 H, CH_3), 1.90–2.25 (m, 4 H, 2 CH_2), 3.65 (m, 1 H, CH), 5.25 (t, 1 H, J = 7.0 Hz, vinyl). Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.21; H, 13.37.

1-[(*E*)-2-Methyl-2-pentenyl]cyclohexan-1-ol (7v, 79 mg, 87% Yield): TLC R_f 0.44 (1:5 ethyl acetate/hexane); IR (neat) 3700–3120, 2932, 2861, 1449, 1380, 1264, 1151, 972 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, 3 H, J = 7.5 Hz, CH_3), 1.17–1.76 (m, 11 H, 5 CH_2 and OH), 1.71 (s, 3 H, CH_3), 2.04 (dq, 2 H, J = 7.0, 7.6 Hz, CH_2), 2.13 (s, 2 H, CH_2), 5.22 (t, 1 H, J = 7.0 Hz, vinyl); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 18.7, 21.3, 22.2 (2 C), 25.7, 37.9 (2 C), 51.7, 71.0, 131.2, 132.0. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.25; H, 12.14.

(*E*)-1-Phenyl-3-nonen-7-yn-1-ol (7w, 102 mg, 89% Yield): TLC R_f 0.27 (1:5 ethyl acetate/hexane); IR (neat) 3700–3125, 3031, 2919, 2857, 1669, 1603, 1493, 1453, 1384, 1196, 1079, 1049, 760, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.61 (s, 3 H, CH_3), 1.77 (t, 3 H, J = 1.2 Hz, CH_3), 2.10–2.35 (m, 5 H, 2 CH_2 and OH), 2.40–2.60 (m, 2 H, CH_2), 4.69 (m, 1 H, CH), 5.25 (dt, 1 H, J = 1.4, 7.5 Hz, vinyl), 7.20–7.43 (m, 5 H, aromatic). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.14; H, 8.90.

(2*E*,6*E*)-1-(Benzyloxy)-3,7-dimethyl-2,6-undecadien-9-ol (7x, 109 mg, 72% Yield): TLC R_f 0.22 (1:5 ethyl acetate/hexane); IR (neat) 3700–3150, 3031, 2961, 2926, 1668, 1497, 1455, 1383, 1364, 1202, 1113, 1069, 1028, 972, 737, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.94 (t, 3 H, J = 7.5 Hz, CH_3), 1.46 (dq, 2 H, J = 6.1, 7.2 Hz, CH_2), 1.63 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 1.80 (br, 1 H, OH), 1.90–2.26 (m, 6 H, 3 CH_2), 3.56 (m, 1 H, CH), 4.02 (d, 2 H, J = 6.8 Hz, CH_2), 4.50 (s, 2 H, CH_2), 5.22 (t, 1 H, J = 6.4 Hz, vinyl), 5.40 (dt, 1 H, J = 1.2, 6.9 Hz, vinyl), 7.20–7.43 (m, 5 H, aromatic). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.41; H, 10.07.

2,4-Dimethyl-1-phenyl-3-penten-1-ol (12b, 43 mg, 45% Yield):[45] TLC R_f 0.36 (1:5 ethyl acetate/hexane); IR (neat) 3700–3130, 3031, 2967,

(43) Kanagawa, Y.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1992**, *57*, 6988.
(44) Araki, S.; Hatano, M.; Ito, H.; Butsugan, Y. *J. Organomet. Chem.* **1987**, *333*, 329.
(45) Hoffmann, R. W.; Zeiss, H.-J. *J. Org. Chem.* **1981**, *46*, 1309.

2928, 2872, 1672, 1603, 1495, 1453, 1377, 1192, 1021, 990, 760, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.76 (d, 1.5 H, J = 6.8 Hz, 0.5 CH_3), 0.97 (d, 1.5 H, J = 6.8 Hz, 0.5 CH_3), 1.47 (s, 1.5 H, 0.5 CH_3), 1.64 (s, 1.5 H, 0.5 CH_3), 1.69 (s, 1.5 H, 0.5 CH_3), 1.78 (s, 1.5 H, 0.5 CH_3), 2.01 (br, 1 H, OH), 2.70 (m, 1 H, CH), 4.23 (d, 0.5 H, J = 8.4 Hz, 0.5 CH), 4.51 (d, 0.5 H, J = 6.2 Hz, 0.5 CH), 4.94 (dt, 0.5 H, J = 1.4, 9.6 Hz, 0.5 vinyl), 5.06 (dt, 0.5 H, J = 1.4, 9.8 Hz, 0.5 vinyl), 7.23–7.45 (m, 5 H, aromatic). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.18; H, 9.70.

(*E*)-1-Phenyl-2,4,8-trimethyl-3,7-nonadien-1-ol (12c, 84 mg, 65% Yield): TLC R_f 0.41 and 0.39 (1:5 ethyl acetate/hexane); IR (neat) 3650–3150, 3031, 2967, 2926, 1669, 1603, 1495, 1453, 1377, 1192, 1022, 760, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.76 (d, 1.5 H, J = 6.6 Hz, 0.5 CH_3), 0.98 (d, 1.5 H, J = 6.6 Hz, 0.5 CH_3), 1.59 (s, 1.5 H, 0.5 CH_3), 1.63 (s, 1.5 H, 0.5 CH_3), 1.68 (s, 3 H, CH_3), 1.69 (s, 1.5 H, 0.5 CH_3), 1.70 (s, 1.5 H, 0.5 CH_3), 1.85–2.30 (m, 5 H, 2 CH_2 and OH), 2.55–2.85 (m, 1 H, CH), 4.20 (d, 0.5 H, J = 8.6 Hz, 0.5 CH), 4.51 (d, 0.5 H, J = 6.2 Hz, 0.5 CH), 4.91 (dd, 0.5 H, J = 1.2, 10.0 Hz, 0.5 vinyl), 4.96–5.14 (m, 1.5 H, 1.5 vinyl), 7.20–7.42 (m, 5 H, aromatic). Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.59; H, 10.20.

(*E*)-2,3,5,9-Tetramethyl-4,8-decadien-2-ol (12d, 67 mg, 64% Yield): TLC R_f 0.32 (1:5 ethyl acetate/hexane); IR (neat) 3700–3150, 2971, 2928, 1668, 1455, 1375, 1139, 945, 870 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.95 (d, 3 H, J = 6.9 Hz, CH_3), 1.12 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.55–1.70 (hidden in this region, 1 H, OH), 2.00–2.20 (m, 4 H, 2 CH_2), 2.45 (dq, 1 H, J = 6.8, 10.4 Hz, CH), 5.02 (d, 1 H, J = 10.4 Hz, vinyl), 5.05 (m, 1 H, vinyl). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.97; H, 12.64.

Procedure for Synthesis of 12-Hydroxysqualene (11).[19] To a suspension of reactive barium (1.2 mmol) in THF (10 mL) was slowly added a solution of farnesyl chloride (250 mg, 1.0 mmol) in THF (1.5 mL) below −95 °C. After being stirred for 30 min, a solution of farnesal (**10**, 100 mg, 0.45 mmol) in THF (1.0 mL) was slowly added and the mixture was stirred for another 20 min. To the mixture was added 1 N HCl (10 mL), and the aqueous layer was extracted with ether (10 mL). The combined organic extracts were washed with 1 N sodium thiosulfate solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. The crude product was purified by column chromatography on silica gel (1:20 ether/hexane) to afford 12-hydroxysqualene (**11**, 144 mg, 75% yield):[20] TLC R_f 0.41 (1:5 ethyl acetate/hexane); IR (neat) 3700–3150, 2967, 2923, 2855, 1670, 1447, 1382, 1107, 1034, 835 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.60 (s, 12 H, 4 CH_3), 1.65 (s, 3 H, CH_3), 1.68 (s, 9 H, 3 CH_3), 1.90–2.35 (m, 19 H, 9 CH_2 and OH), 4.37 (m, 1 H, CH), 5.02–5.27 (m, 6 H, 6 vinyls). Anal. Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.40; H, 11.98.

Typical Procedure for Carboxylation of Allylic Barium Reagent: Synthesis of (*E*)-4,8-Dimethyl-3,7-nonadienoic Acid (18).[23d-f,26d,28,46] To a solution of anhydrous BaI_2 (470 mg, 1.2 mmol) in dry THF (5 mL) was added at room temperature a solution of preformed lithium biphenylide, prepared from freshly cut lithium (16 mg, 2.3 mmol) and biphenyl (370 mg, 2.4 mmol) in THF (5 mL) under an argon atmosphere; the reaction mixture was stirred for 30 min at room temperature. To the resulting dark brown suspension of barium powder in THF was slowly added a solution of geranyl chloride (180 μL, 0.97 mmol) in THF (2 mL) at −78 °C. After being stirred for another 30 min, carbon dioxide was introduced into the solution through a stainless steel cannula under an argon stream for 30 min at −78 °C. To the mixture was added 1 N HCl (10 mL) at −78 °C, and the aqueous layer was extracted twice with ethyl acetate (2 × 20 mL). The combined organic extracts were washed with 1 N sodium thiosulfate solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude acid was purified by column chromatography on silica gel (ethyl acetate as the eluant) to afford the β,γ-unsaturated carboxylic acid **18** (154 mg, 87% yield). The α/γ and E/Z ratios were determined to be >99/1 and 98/2, respectively, by GLC analysis after conversion to the methyl ester with diazomethane in ether: TLC R_f 0.27 (1:1 ethyl acetate/hexane); bp 106 °C (0.4 Torr); IR (neat) 3650–2380, 2969, 2923, 2854, 1713, 1437, 1416, 1300, 1225, 1154, 1109, 939, 831 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.60 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 2.07 (m, 4 H, 2 CH_2), 3.10 (d, 2 H, J = 7.0 Hz, CH_2), 5.05–5.13 (m, 1 H, vinyl), 5.31 (t, 1 H, J = 7.0 Hz, vinyl), 10.2–11.4 (br, 1 H, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.9, 17.3, 25.3, 26.1, 33.2, 39.3, 115.1, 123.9, 131.5, 139.5, 178.8; MS (EI, 70 eV) m/z (relative intensity) 167 (3.36, M^+ − 15), 149 (7.45), 139 (17.87), 122 (9.11), 69 (62.75); MS (FAB) m/z 183 (M^+ + 1). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.51; H, 10.20.

Procedure for Large-Scale Carboxylation of Geranylbarium Reagent. An oven-dried, three-necked round-bottomed 300-mL flask, equipped with a Teflon-coated magnetic stirring bar, was flushed with argon. Freshly cut lithium (210 mg, 30.3 mmol) and biphenyl (4.7 g, 30.5 mmol) were placed into the apparatus and covered with dry THF (80 mL), and the mixture was stirred for 2 h at room temperature. In a separate oven-dried, three-necked round-bottomed 500-mL flask, equipped with a Teflon-coated magnetic stirring bar and a 100-mL dropping funnel, was placed anhydrous BaI_2 (6.0 g, 15.3 mmol) under an argon atmosphere; this was covered with dry THF (80 mL) and stirred for 5 min at room temperature. To the resulting yellowish solution of BaI_2 in THF was added at room temperature a solution of the lithium biphenylide through a stainless steel cannula under an argon stream; the reaction mixture was stirred for 1 h at room temperature. To the resulting dark brown suspension of active barium in THF was added dropwise over 20 min a solution of geranyl chloride (1.19 g, 6.87 mmol) in THF (40 mL) from the 100-mL dropping funnel at −78 °C, and the mixture was stirred at this temperature for 30 min. An excess of dry ice (ca. 10 g) was added at −78 °C and stirring continued for 10 min. The reaction mixture was quenched with 1 N HCl (40 mL) at −78 °C, warmed to room temperature, and poured into a mixture of H_2O (200 mL) and EtOAc (200 mL). After vigorous shaking, the organic layer was separated and washed with 1 N sodium thiosulfate solution (200 mL). The two aqueous layers were combined, acidified (pH <3) with concentrated HCl, and extracted twice with EtOAc (2 × 100 mL). The combined organic extracts were washed with H_2O (200 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was then dissolved with MeOH (10 mL) by gentle heating and placed in a freezer (0 °C) for over 1 h to crystallize the biphenyl. The white solid was filtered off and washed with cold MeOH (0 °C, 40 mL), and the filtrate was concentrated under reduced pressure. The residual oil was purified by flash-column chromatography on silica gel (2–30% ethyl acetate in hexane as the eluent) to afford a crude β,γ-unsaturated carboxylic acid **18** (1.43 g). An additional vacuum distillation (160 °C, 0.7 Torr) provided a pure product (0.91–0.96 g, 73–77% yield) as a colorless oil: the α/γ and E/Z ratios were determined to be 99/1 by GLC analysis after conversion to the corresponding methyl ester with diazomethane in ether.

(*E*)-3-Undecenoic Acid (14, 143 mg, 80% Yield):[24b] TLC R_f 0.48 (1:1 ethyl acetate/hexane); IR (neat) 3500–2400, 2928, 2857, 1717, 1418, 1291, 1223, 968 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.5 Hz, CH_3), 1.17–1.47 (m, 10 H, 5 CH_2), 2.03 (q, 2 H, J = 6.6 Hz, CH_2), 3.07 (dd, 2 H, J = 0.8, 5.6 Hz, CH_2), 5.55 (m, 2 H, 2 vinyls), 9.0–11.0 (br, 1 H, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.5, 28.9 (3 C), 31.7, 32.3, 37.7, 120.7, 135.7, 179.2; MS (EI, 70 eV) m/z (relative intensity) 185 (10.30, M^+ + 1), 184 (18.30, M^+), 166 (59.01), 148 (48.82), 114 (100), 100 (59.55), 93 (53.65).

(*Z*)-3-Undecenoic Acid (15, 94 mg, 53% Yield):[24b] TLC R_f 0.49 (1:1 ethyl acetate/hexane); IR (neat) 3500–2400, 2928, 2857, 1715, 1460, 1411, 1289, 1219, 939 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.5 Hz, CH_3), 1.13–1.44 (m, 10 H, 5 CH_2), 2.04 (q, 2 H, J = 6.6 Hz, CH_2), 3.14 (d, 2 H, J = 5.8 Hz, CH_2), 5.58 (m, 2 H, 2 vinyls), 8.8–10.6 (br, 1 H, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.5, 27.2, 29.0 (2 C), 29.1, 31.7, 32.5, 120.0, 134.3, 178.7; MS (EI, 70 eV) m/z (relative intensity) 185 (13.00, M^+ + 1), 184 (28.59, M^+), 166 (65.35), 148 (44.43), 124 (100), 110 (57.67).

(*E*)-3-Methyl-3-hexenoic Acid (16, 68 mg, 55% Yield):[47] TLC R_f 0.52 (1:1 ethyl acetate/hexane); IR (neat) 3680–2370, 2963, 2926, 2857, 1713, 1456, 1412, 1298, 1231, 940, 910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, 3 H, J = 7.6 Hz, CH_3), 1.71 (s, 3 H, CH_3), 2.05 (dq, 2 H, J = 7.0, 7.6 Hz, CH_2), 3.03 (s, 2 H, CH_2), 5.33 (t, 1 H, J = 7.0 Hz, vinyl), 8.4–10.8 (br, 1 H, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.7, 21.2, 29.6, 44.3, 128.7, 132.1, 179.3; MS (EI, 70 eV) m/z (relative intensity) 129 (100, M^+ + 1), 128 (18.82, M^+), 117 (17.54), 102 (27.75).

4-Methyl-3-pentenoic Acid (17, 65 mg, 59% Yield):[22a,b,23b,48] TLC R_f 0.61 (1:1 ethyl acetate/hexane); IR (neat) 3750–2300, 2981, 2921, 1713, 1414, 1377, 1298, 1221, 1157, 939, 830 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.65 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 3.08 (d, 2 H, J = 7.0 Hz, CH_2), 5.30 (t, 1 H, J = 7.2 Hz, vinyl), 9.0–10.0 (br, 1 H, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.6, 25.4, 33.4, 115.2, 136.3, 179.1; MS (EI, 70 eV) m/z (relative intensity) 115 (13.05, M^+ + 1), 114 (100, M^+), 99 (13.51), 96 (27.47), 95 (12.15), 93 (10.44).

(46) Rouessac, A.; Rouessac, F.; Zamarlik, H. *Tetrahedron Lett.* **1981**, *22*, 2641.

(47) Schulte, K. E.; Rücker, G.; Feldkamp, J. *Chem. Ber.* **1972**, *105*, 24.

(48) Cane, D. E.; Yang, G.; Coates, R. M.; Pyun, H.-J.; Hohn, T. M. *J. Org. Chem.* **1992**, *57*, 3454.

(49) Pawson, B. A.; Saucy, G. Ger. Offen. 1,921,684, 1969.

(Z)-4,8-Dimethyl-3,7-nonadienoic Acid (19, 90 mg, 51% Yield):[23e,26d,28,46] TLC R_f 0.31 (1:1 ethyl acetate/hexane); IR (neat) 3800–2750, 2967, 2928, 2857, 1709, 1648, 1448, 1377, 823 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.61 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3), 2.05 (m, 4 H, 2 CH_2), 3.09 (d, 2 H, J = 7.2 Hz, CH_2), 5.10 (m, 1 H, vinyl), 5.32 (t, 1 H, J = 7.2 Hz, vinyl), 7.4–9.8 (br, 1 H, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.4, 23.2, 25.5, 26.1, 32.0, 33.1, 115.8, 123.8, 132.2, 139.9, 178.8; MS (EI, 70 eV) m/z (relative intensity) 183 (36.34, M^+ + 1), 182 (59.61, M^+), 181 (31.94, M^+ – 1), 167 (100), 155 (35.67), 135 (80.62), 124 (84.67), 104 (93.81), 92 (48.19).

(4-Isopropenyl-1-cyclohexenyl)acetic Acid (20, 135 mg, 77% Yield): TLC R_f 0.42 (1:1 ethyl acetate/hexane); IR (neat) 3700–2400, 3080, 2969, 2923, 2838, 1709, 1647, 1437, 1289, 1228, 887 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.39–1.67 (m, 1 H, one proton of CH_2), 1.73 (s, 3 H, CH_3), 1.77–1.92 (m, 1 H, one proton of CH_2), 1.92–2.30 (m, 5 H, 2 CH_2 and CH), 3.01 (s, 2 H, CH_2), 4.72 (s, 2 H, 2 vinyls), 5.64 (br s, 1 H, vinyl), 9.0–11.0 (br, 1 H, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.6, 27.5, 28.7, 30.6, 40.5, 42.8, 108.8, 126.1, 130.4, 149.9, 178.7; MS (EI, 70 eV) m/z (relative intensity) 181 (15.16, M^+ + 1), 180 (19.44, M^+), 179 (16.32, M^+ – 1), 167 (100), 155 (17.94), 150 (17.13), 135 (37.73), 119 (14.93), 113 (11.57), 106 (16.44).

Typical Procedure for Conjugate Addition Reactions of Allylic Barium Reagents to Enones: Synthesis of 3-(2-Propenyl)cyclopentanone (22).[32c,50,51] To a solution of anhydrous BaI_2 (450 mg, 1.2 mmol) in THF (5 mL) was added a preformed lithium biphenylide, prepared from freshly cut lithum (15 mg, 2.2 mmol) and biphenyl (350 mg, 2.3 mmol) in THF (5 mL), at room temperature, and the reaction mixture was stirred for 30 min at this temperature. To the resulting brown suspension of barium powder in THF was slowly added a solution of allyl chloride (75 mg, 0.98 mmol) in THF (1.5 mL) at –78 °C. After stirring for 30 min, the mixture was treated with a solution of 2-cyclopentenone (48 mg, 0.58 mmol) in THF (1 mL) at –78 °C and stirred for another 20 min at this temperature. To the mixture was added 1 N HCl (10 mL), and the organic material was extracted with ether (10 mL). The combined organic extracts were washed with 1 N sodium thiosulfate solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. The crude product was purified by flash-column chromatography on silica gel (1:10 to 1:5 ether/hexane as the eluant) to afford 3-(2-propenyl)cyclopentanone (**22**, 68 mg, 94% yield). The 1,4/1,2 ratio was determined to be >99/1 by GLC analysis: TLC R_f 0.35 (1:5 ethyl acetate/hexane); IR (neat) 2963, 1744, 1642, 1406, 1157, 997, 914 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.47–2.46 (m, 9 H, 4 CH_2 and CH), 5.01–5.12 (m, 2 H, 2 vinyls), 5.70–5.91 (m, 1 H, vinyl).

3-(2-Methyl-2-propenyl)cyclopentanone (23, 77 mg, 96% Yield):[32c] TLC R_f 0.34 (1:5 ethyl acetate/hexane); IR (neat) 2965, 1744, 1651, 1455, 1404, 1375, 1159, 889 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.40–1.93 (m, 2 H, CH_2), 1.74 (s, 3 H, CH_3), 2.05–2.50 (m, 7 H, 3 CH_2 and CH), 4.70 (d, 1 H, J = 1.2 Hz, vinyl), 4.77 (d, 1 H, J = 1.2 Hz, vinyl).

3-[(E)-2-Decenyl]cyclopentanone (24, 65 mg, 50% Yield): TLC R_f 0.41 (1:5 ethyl acetate/hexane); IR (neat, a mixture of α- and γ-products) 2957, 2926, 2855, 1744, 1458, 1406, 1157, 968 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) for the α-product δ 0.87 (t, 3 H, J = 6.5 Hz, CH_3), 1.15–1.45 (m, 10 H, 5 CH_2), 1.45–2.43 (m, 11 H, 5 CH_2 and CH), 5.41 (m, 2 H, 2 vinyls); ^1H NMR (200 MHz, $CDCl_3$) for the γ-product δ 0.87 (t, 3 H, J = 6.5 Hz, CH_3), 1.20–1.45 (m, 12 H, 6 CH_2), 1.50–2.42 (m, 8 H, 3 CH_2 and 2 CH), 4.92–5.11 (m, 2 H, 2 vinyls), 5.44–5.62 (m, 1 H, vinyl). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.78. Found: C, 81.03; H, 11.98.

3-(3-Methyl-2-butenyl)cyclopentanone (25, 29 mg, 33% Yield): TLC R_f 0.36 (1:5 ethyl acetate/hexane); IR (neat, a mixture of α- and γ-products) 2967, 1744, 1406, 1159, 914 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) for the α-product δ 1.61 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 1.77–2.43 (m, 9 H, 4 CH_2 and CH), 5.14 (t, 1 H, J = 7.0 Hz, vinyl); ^1H NMR (200 MHz, $CDCl_3$) for the γ-product δ 1.03 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.52–2.43 (m, 7 H, 3 CH_2 and CH), 4.99 (dd, 1 H, J = 1.4, 17.4 Hz, vinyl), 5.04 (dd, 1 H, J = 1.4, 11.0 Hz, vinyl), 5.82 (dd, 1 H, J = 11.0, 17.4 Hz, vinyl). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.96; H, 10.84.

3-Benzylcyclopentanone (26, 61 mg, 60% Yield): TLC R_f 0.30 (1:5 ethyl acetate/hexane); IR (neat) 3027, 2959, 1742, 1497, 1455, 1404, 1157, 754, 702 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.50–1.74 (m, 2 H, CH_2), 1.83–2.60 (m, 5 H, 2 CH_2 and CH), 2.75 (d, 2 H, J = 7.4 Hz, CH_2), 7.15–7.37 (m, 5 H, aromatic). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.74; H, 8.36.

2-Methyl-3-(2-propenyl)cyclopentanone (28, 56 mg, 75% Yield): TLC R_f 0.36 (1:5 ethyl acetate/hexane); IR (neat) 2965, 2931, 2874, 1742, 1642, 1456, 1159, 914 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.99 (d, 1.1 H, J = 7.0 Hz, 0.38 CH_3), 1.07 (d, 1.9 H, J = 6.6 Hz, 0.62 CH_3), 1.50–2.50 (m, 8 H, 3 CH_2 and 2 CH), 5.01–5.14 (m, 2 H, 2 vinyls), 5.68–5.93 (m, 1 H, vinyl). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.95; H, 10.37.

3-Methyl-3-(2-propenyl)cyclopentanone (29, 69 mg, 86% Yield): TLC R_f 0.40 (1:5 ethyl acetate/hexane); IR (neat) 2957, 1744, 1640, 1456, 1406, 1379, 1171, 995, 916 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.08 (s, 3 H, CH_3), 1.68–2.34 (m, 8 H, 4 CH_2), 5.02–5.15 (m, 2 H, 2 vinyls), 5.72–5.93 (m, 1 H, vinyl). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.15; H, 10.37.

***trans*-3-(*tert*-Butyldimethylsiloxy)-4-(2-propenyl)cyclopentanone (30, 137 mg, 93% Yield):** TLC R_f 0.46 (1:5 ethyl acetate/hexane); IR (neat) 2997, 2990, 2859, 1752, 1645, 1254, 1115, 912, 837, 776 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.05 (s, 3 H, CH_3), 0.07 (s, 3 H, CH_3), 0.88 (s, 9 H, 3 CH_3), 1.80–2.60 (m, 7 H, 3 CH_2 and CH), 4.10 (dt, 1 H, J = 5.6, 5.8 Hz, CH), 5.02 (m, 1 H, vinyl), 5.08 (m, 1 H, vinyl), 5.67–5.89 (m, 1 H, vinyl). Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30. Found: C, 66.00; H, 10.44.

3-(2-Propenyl)cyclohexanone (32, 71 mg, 89% Yield):[31a,50] TLC R_f 0.35 (1:5 ethyl acetate/hexane); IR (neat) 2928, 2867, 1713, 1642, 1449, 1225, 995, 914 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.25–1.44 (m, 1 H, one proton of CH_2), 1.52–1.79 (m, 1 H, one proton of CH_2), 1.80–2.50 (m, 9 H, 4 CH_2 and CH), 4.98–5.06 (m, 2 H, 2 vinyls), 5.64–5.85 (m, 1 H, vinyl). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.11; H, 10.26.

3-(2-Methyl-2-propenyl)cyclohexanone (34, 69 mg, 78% Yield):[32c,52] TLC R_f 0.37 (1:5 ethyl acetate/hexane); IR (neat) 2934, 1715, 1649, 1449, 1225, 889 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.69 (s, 3 H, CH_3), 1.53–2.45 (m, 11 H, 5 CH_2 and CH), 4.68 (s, 1 H, vinyl), 4.77 (m, 1 H, vinyl).

3-(3-Methyl-2-butenyl)cyclohexanone (36, 36 mg, 37% Yield): TLC R_f 0.39 (1:5 ethyl acetate/hexane); IR (neat, a mixture of α- and γ-products) 2965, 2867, 1713, 1449, 1227, 912 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) for the α-product δ 1.60 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 1.46–2.48 (m, 11 H, 5 CH_2 and CH), 5.10 (t, 1 H, J = 7.4 Hz, vinyl); ^1H NMR (200 MHz, $CDCl_3$) for the γ-product δ 0.99 (s, 6 H, 2 CH_3), 1.40–2.50 (m, 9 H, 4 CH_2 and CH), 4.94 (dd, 1 H, J = 1.4, 17.4 Hz, vinyl), 5.01 (dd, 1 H, J = 1.4, 10.8 Hz, vinyl), 5.76 (dd, 1 H, J = 10.8, 17.4 Hz, vinyl). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.47; H, 11.13.

3-Benzylcyclohexanone (38, 59 mg, 54% Yield): TLC R_f 0.32 (1:5 ethyl acetate/hexane); IR (neat) 2932, 2865, 1713, 1495, 1455, 1225, 747, 702 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20–2.45 (m, 9 H, 4 CH_2 and CH), 2.63 (d, 2 H, J = 6.0 Hz, CH_2), 7.11–7.35 (m, 5 H, aromatic). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.89; H, 8.68.

2-Methyl-5-(2-propenyl)cyclohexanone (40, 75 mg, 85% Yield): TLC R_f 0.45 (1:5 ethyl acetate/hexane); IR (neat) 2967, 2930, 2863, 1713, 1642, 1377, 1217, 995 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.02 (d, 1 H, J = 6.4 Hz, 0.35 CH_3), 1.07 (d, 2 H, J = 7.0 Hz, 0.65 CH_3), 1.20–2.50 (m, 10 H, 4 CH_2 and 2 CH), 4.97–5.08 (m, 2 H, 2 vinyls), 5.61–5.91 (m, 1 H, vinyl). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.96; H, 10.49.

2,2-Dimethyl-5-(2-propenyl)cyclohexanone (42, 93 mg, 96% Yield): TLC R_f 0.48 (1:5 ethyl acetate/hexane); IR (neat) 2975, 2926, 2863, 1709, 1642, 1385, 1150, 995, 914 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.06 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.40–1.95 (m, 5 H, 2 CH_2 and CH), 2.05–2.40 (m, 4 H, 2 CH_2), 5.00–5.10 (m, 2 H, 2 vinyls), 5.65–5.86 (m, 1 H, vinyl). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.42; H, 11.12.

3-(2-Propenyl)cycloheptanone (44, 37 mg, 42% Yield): TLC R_f 0.36 (1:5 ethyl acetate/hexane); IR (neat) 2926, 2857, 1701, 1640, 1447, 995, 914 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20–2.23 (m, 7 H, 3 CH_2 and CH), 2.06 (t, 2 H, J = 7.0 Hz, CH_2), 2.30–2.55 (m, 4 H, 2 CH_2), 4.97–5.09 (m, 2 H, 2 vinyls), 5.65–5.86 (m, 1 H, vinyl). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.48; H, 11.05.

4-(2-Propenyl)decan-2-one (46, 46 mg, 40% Yield): TLC R_f 0.46 (1:5 ethyl acetate/hexane); IR (neat) 2957, 2926, 2857, 1717, 1640, 1356, 1163, 995, 912 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, 3 H, J = 6.4 Hz, CH_3), 1.10–1.40 (m, 10 H, 5 CH_2), 1.90–2.18 (m, 3 H, CH and CH_2), 2.12 (s, 3 H, CH_3), 2.34 (t, 2 H, J = 6.2 Hz, CH_2), 4.95–5.08 (m, 2 H, 2 vinyls), 5.68–5.85 (m, 1 H, vinyl). Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.58; H, 12.54.

(50) Ahlbrecht, H.; Weber, P. *Synthesis* **1992**, 1018.
(51) Posner, G. H.; Frye, L. L.; Hulce, M. *Tetrahedron* **1984**, *40*, 1401.
(52) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

4-Phenyl-6-hepten-2-one (48, 58 mg, 53% Yield):[31e,32c,h] TLC R_f 0.33 (1:5 ethyl acetate/hexane); IR (neat) 3031, 2924, 1717, 1640, 1495, 1455, 1358, 1161, 916, 758, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.02 (s, 3 H, CH_3), 2.36 (t, 2 H, J = 7.3 Hz, CH_2), 2.74 (d, 1 H, J = 8.1 Hz, one proton of CH_2), 2.74 (d, 1 H, J = 5.8 Hz, one proton of CH_2), 3.26 (m, 1 H, CH), 4.93–5.04 (m, 2 H, 2 vinyls), 5.55–5.75 (m, 1 H, vinyl), 7.15–7.35 (m, 5 H, aromatic).

1,3-Diphenyl-5-hexen-1-al (50, 64 mg, 44% Yield):[32a,c,53] TLC R_f 0.33 (1:5 ethyl acetate/hexane); IR (neat) 3029, 2926, 1686, 1640, 1597, 1582, 1495, 1449, 1204, 1001, 916, 749, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.46 (t, 2 H, J = 7.1 Hz, CH_2), 3.29 (d, 2 H, J = 7.4 Hz, CH_2), 3.48 (m, 1 H, CH), 4.93–5.05 (m, 2 H, 2 vinyls), 5.59–5.80 (m, 1 H, vinyl), 7.12–7.60 (m, 8 H, aromatic), 7.85–8.00 (m, 2 H, aromatic).

1-Cyclohexyl-5-hexen-1-al (52, 60 mg, 57% Yield): TLC R_f 0.55 (1:5 ethyl acetate/hexane); IR (neat) 2932, 2855, 1709, 1642, 1451, 1374, 1146, 997, 912 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10–1.40 (m, 4 H, 2 CH_2), 1.60–1.90 (m, 8 H, 4 CH_2), 2.05 (dt, 2 H, J = 6.6, 7.0 Hz, CH_2), 2.33 (m, 1 H, CH), 2.44 (t, 2 H, J = 7.3 Hz, CH_2), 4.93–5.07 (m, 2 H, 2 vinyls), 5.67–5.88 (m, 1 H, vinyl). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.89; H, 11.60.

2,2-Dimethyl-5-(2-propenyl)decan-3-one (54, 96 mg, 74% Yield): TLC R_f 0.22 (hexane); IR (neat) 2959, 2929, 2859, 1707, 1640, 1478, 1466, 1366, 1065, 997, 912 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.6 Hz, CH_3), 1.12 (s, 9 H, 3 CH_3), 1.16–1.47 (m, 8 H, 4 CH_2), 1.87–2.15 (m, 3 H, CH and CH_2), 2.40 (m, 2 H, CH_2), 4.90–5.06 (m, 2 H, 2 vinyls), 5.63–5.84 (m, 1 H, vinyl). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.26; H, 12.64.

Typical Procedure for One-Pot Double Alkylation of α,β-Unsaturated Ketones: Synthesis of *trans*-2-(3-Methyl-2-butenyl)-3-(2-propenyl)cyclopentanone (56). To a suspension of barium powder (1.2 mmol) in THF (10 mL) was slowly added a solution of allyl chloride (75 mg, 0.98 mmol) in THF (1.5 mL) at −78 °C. The reaction mixture was stirred for 20 min at this temperature. A solution of 2-cyclopentenone (48 mg, 0.58 mmol) in THF (1 mL) was introduced to the mixture at −78 °C. After being stirred for 20 min, the mixture was treated with prenyl bromide (250 mg, 1.7 mmol) at −78 °C and warmed to −30 °C over a period of 30 min. The stirring was continued for another 1 h at this temperature. To the mixture was added saturated aqueous NH_4Cl solution (10 mL), and the organic material was extracted with ether (10 mL). The combined organic extracts were washed with 1 N sodium thiosulfate solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* after filtration. The crude product was purified by flash-column chromatography on silica gel (1:50 to 1:10 ether/hexane as the eluant) to afford the α,β-diallylated cyclopentanone **56** (90 mg, 81% yield). The purity was checked by GLC analysis (>99/1): TLC R_f 0.45 (1:5 ethyl acetate/hexane); IR (neat) 2967, 1742, 1645, 1156, 912 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.62 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.77–2.50 (m, 10 H, 4 CH_2 and 2 CH), 5.01–5.13 (m, 3 H, 3 vinyls), 5.72–5.92 (m, 1 H, vinyl). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.22; H, 10.73. *Trans*-stereochemistry of the major double alkylation product **56** was assigned by the following equilibrium experiment: The ketone **56** (20 mg, 0.10 mmol) was dissolved in a 1 M solution of CH_3ONa in CH_3OH (1 mL), and the mixture was stirred for 1.5 h at room temperature. After the usual workup and purification by column chromatography on silica gel, the product **56** was obtained in quantitative yield. By GLC and ^{1}H NMR analysis, no stereoisomer of **56** was found to be produced under the thermodynamic reaction condition.

***trans*-2-(2-Octynyl)-3-(2-propenyl)cyclopentanone (57, 67 mg, 50% Yield):** TLC R_f 0.43 (1:5 ethyl acetate/hexane); IR (neat) 2959, 2932, 1746, 1642, 1460, 1339, 1157, 914 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, 3 H, J = 6.8 Hz, CH_3), 1.20–1.65 (m, 7 H, 3 CH_2 and one proton of CH_2), 1.80–1.93 (m, 1 H, CH), 2.00–2.66 (m, 10 H, 4 CH_2, one proton of CH_2, and CH), 5.02–5.18 (m, 2 H, 2 vinyls), 5.77–5.97 (m, 1 H, vinyl). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.62; H, 10.48.

***trans*-2-(1-Hydroxyhexyl)-3-(2-propenyl)cyclopentanone (58, 111 mg, 85% Yield):** TLC R_f 0.33 (1:3 ethyl acetate/hexane); IR (neat) 3700–3150, 2957, 2930, 2861, 1736, 1642, 1458, 1408, 1156, 914 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3 H, J = 6.5 Hz, CH_3), 1.20–2.62 (m, 17 H, 7 CH_2, 2 CH and OH), 3.72 (m, 0.83 H, 0.83 CH), 3.98 (m, 0.17 H, 0.17 CH), 5.03–5.18 (m, 2 H, 2 vinyls), 5.70–5.97 (m, 1 H, vinyl). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.91; H, 11.00.

***trans*-2-Acetyl-3-(2-propenyl)cyclopentanone (59, 84 mg, 87% Yield)** (for the mixture of keto and enol compounds): TLC R_f 0.30 (1:5 ethyl acetate/hexane); IR (neat) 3077, 2965, 2919, 1744, 1711, 1655, 1617, 1389, 1358, 1233, 916 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.40–3.10 (m, including singlets at 2.01 and 2.29 ppm, 11 H, CH_3, 3 CH_2, CH, 0.5 CH, and 0.5 OH), 4.98–5.11 (m, 2 H, 2 vinyls), 5.63–5.88 (m, 1 H, vinyl). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.97; H, 8.63.

***c*-4-(*tert*-Butyldimethylsiloxy)-*r*-2-(3-methyl-2-butenyl)-*t*-3-(2-propenyl)cyclopentanone (60, 86 mg, 46% Yield):** TLC R_f 0.48 (1:5 ethyl acetate/hexane); IR (neat) 2957, 2930, 2859, 1746, 1377, 1252, 1109, 837, 776 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.05 (s, 3 H, CH_3), 0.08 (s, 3 H, CH_3), 0.89 (s, 9 H, 3 CH_3), 1.61 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.89–2.65 (m, 8 H, 3 CH_2 and 2 CH), 4.05 (dt, 1 H, J = 6.7, 6.8 Hz, CH), 5.00–5.15 (m, 3 H, 3 vinyls), 5.69–5.90 (m, 1 H, vinyl). Anal. Calcd for $C_{19}H_{34}O_2Si$: C, 70.75; H, 10.62. Found: C, 70.74; H, 10.85.

***trans*-2-(3-Methyl-2-butenyl)-3-(2-propenyl)cyclohexanone (61, 87 mg, 73% Yield):** TLC R_f 0.48 (1:5 ethyl acetate/hexane); IR (neat) 2926, 2865, 1713, 1640, 1447, 1377, 995, 912 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.40–2.50 (m, 12 H, 5 CH_2 and 2 CH), 1.64 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 5.02–5.12 (m, 3 H, 3 vinyls), 5.67–5.87 (m, 1 H, vinyl). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.82; H, 11.02.

Procedure for Anionic Oxy-Cope Rearrangement of Barium Alkoxide 62. To the suspension of reactive barium (1.1 mmol) in THF (10 mL) was slowly added a solution of 1-bromopentane (0.12 mL, 0.97 mmol) in THF (1.5 mL) at −78 °C. After being stirred for 30 min, the mixture was treated with a solution of tertiary alcohol **21** (80 mg, 0.64 mmol, readily obtainable by the reaction of allylmagnesium chloride with 2-cyclopentenone in THF) in THF (1 mL) at −78 °C. The mixture was stirred for 30 min at this temperature, then for 30 min at −60 °C, and lastly for 30 min at 0 °C. At this moment no rearrangement product **22** was observed by TLC analysis. After usual workup and purification by column chromatography on silica gel, the starting material **21** (61 mg) was recovered in 76% yield.

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(53) Gautier, J.-A.; Miocque, M.; Duclos, J.-P. *Bull. Soc. Chim. Fr.* **1969**, 4348.