Facile and Highly Stereoselective Synthesis of Homoallylic Alcohols Using Organosilicon Intermediates

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Allyltrichlorosilanes regioselectively reacted with aldehydes in *N,N*-dimethylformamide (DMF) without a catalyst to afford the corresponding homoallylic alcohols in high yields. The reactions proceeded under neutral conditions, and *syn*- and *anti*-homoallylic alcohols were stereoselectively obtained from (*Z*)- and (*E*)-allyltrichlorosilanes, respectively. In these reactions, DMF coordinated to the silicon atom of the allyltrichlorosilanes to form hypervalent silicates, which in turn reacted with aldehydes smoothly. Solvent effects in these reactions were also examined. The reactions were applied to the one-pot synthesis of homoallylic alcohols from allylic chlorides via organosilicon intermediates. While *syn*-homoallylic alcohols were prepared from (*Z*)-allyl chlorides, *anti*-homoallylic alcohols were obtained from (*E*)-allyl chlorides. Unique regioselectivities in the reactions of 1-chloro-2,4-pentadiene were also found. Finally, the one-pot synthesis of homoallylic alcohols from 1,3-dienes is reported.

Introduction

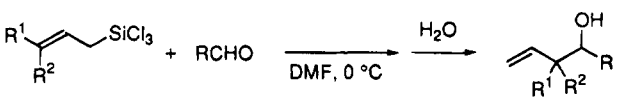
Synthesis of homoallylic alcohols by the reaction of allyl organometallics with carbonyl compounds is one of the most important processes in organic synthesis.[1] Acyclic stereocontrol during the carbon–carbon bond formation has also increased the importance of this process.[2] In order to obtain both *syn*- and *anti*-homoallylic alcohols in high stereoselectivities, preparation of geometrically pure (*E*)- and (*Z*)-allyl organometallics and the reactions via the six-membered cyclic transition states are inevitable.[1d,e,2] Moreover, it is synthetically desirable to use easily available allyl halides as starting materials. However, although many allyl organometallic reagents have been developed, examples which satisfy the above criteria, direct and highly regio- and stereoselective preparation of homoallylic alcohols from allyl halides, are few, and development of new methodologies is strongly desired.

In this paper, we report a solution to this problem: the highly regio- and diastereoselective synthesis of homoallylic alcohols via organosilicon intermediates.[3]

The Reactions of Allyltrichlorosilanes with Aldehydes. Lewis acid-promoted reactions of allyltrimethylsilanes with aldehydes (Sakurai–Hosomi reaction) have been versatile and broadly applicable.[4] Although the reactions proceed with high regioselectivities, the yields and stereoselectivities are sometimes moderate. On the other hand, allylation reactions of pentacoordinated allylsilicates with aldehydes were developed.[5] Sakurai et al. also reported that allyltrifluorosilanes reacted with aldehydes to afford the homoallylic alcohols in high diastereoselectivities, but even in these reactions more than a stoichiometric amount of cesium fluoride was required as a promoter.[6]

Recently, we reported that trimethylsilyl cyanide (TMS-CN) reacted with aldehydes smoothly in the presence of a catalytic amount of a Lewis base such as amine, phosphine, arsine, or antimony compound to afford the corresponding cyanohydrin trimethylsilyl ethers in excellent yields.[7] In this reaction, the Lewis bases would coordinate to TMS-CN to form a reactive intermediate, a pentacoordinated silicate, which has the potential for reacting with aldehydes to give the corresponding cyanohydrin trimethylsilyl ethers.

Assuming a similar intermediate, we tested the reaction of allyltrichlorosilane with aldehydes. After screening several solvents, we found that the allylation reactions proceeded *without a catalyst* by simply mixing the allyltrichlorosilanes and aldehydes in *N,N*-dimethylformamide (DMF) at 0 °C.



Several examples of the present allylation reaction are shown in Table 1. In every case including the reactions of sterically hindered prenyltrichlorosilane, the corresponding homoallylic alcohols were obtained in high yields. One feature of these reactions is the excellent regio- and diastereoselectivities. New carbon–carbon bond formation takes place only at the γ-positions of the

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(1) For example: (a) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 8955. (b) Jubert, C.; Nowotny, S.; Kornemann, D.; Antes, I.; Tucker, C. E.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 6384. (c) Wipf, P.; Lim, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1654, and references cited therein. Review: (d) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (e) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, p 1.

(2) Review: (a) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3. (b) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357. (c) Hoffman, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (d) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243.

(3) For a preliminary communication: Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453.

(4) (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (b) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (c) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

(5) (a) Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1988**, *110*, 4599. (b) Hosomi, A.; Kohra, S.; Ogata, K.; Yanagi, T.; Tominaga, Y. *J. Org. Chem.* **1990**, *55*, 2415. (c) Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *J. Organomet. Chem.* **1987**, *328*, C17.

(6) (a) Kira, M.; Kobayashi, M.; Sakurai, H. *Tetrahedron Lett.* **1987**, *28*, 4081. (b) Kira, M.; Hino, T.; Sakurai, H. *Ibid.* **1989**, *30*, 1099. Allyltrifluorosilanes were prepared from allyltrichlorosilanes.

(7) Kobayashi, S.; Tsuchiya, Y.; Mukaiyama, T. *Chem. Lett.* **1991**, 537.

0022-3263/94/1959-6620$04.50/0

Table 1. Reactions of Allyltrichlorosilanes with Aldehydes

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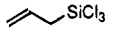
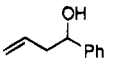
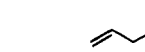
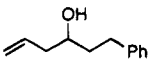
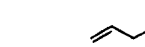
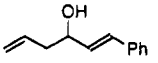
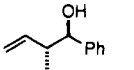
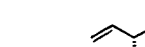
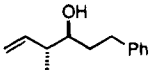
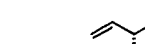
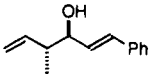
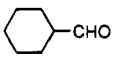
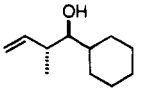
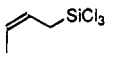
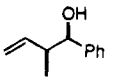
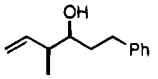
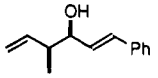
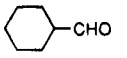
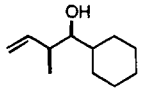
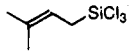
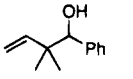
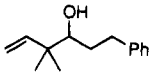
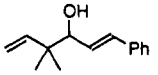
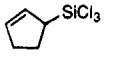
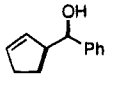
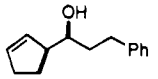
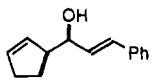
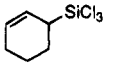
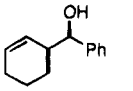
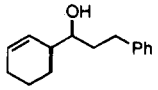
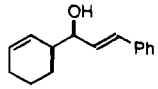
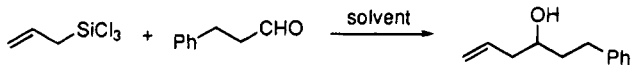
1		PhCHO		1	91	—
2				2	90	—
3				3	88	—
4	 (E/Z=97/ 3)	PhCHO		4A	89	3/97
5				5A	87	3/97
6				6A	88	7/93
7				7A	83	4/96
8	 (E/Z=<1/>99)	PhCHO		4S	82	>99/1
9				5S	90	>99/1
10				6S	96	96/4
11				7S	85	97/3
12		PhCHO		8	89	—
13				9	81	—
14				10	90	—
15		PhCHO		11 [a]	88	>99/1
16				12 [a]	81	>99/1
17				13 [a]	90	>99/1
18		PhCHO		14 [a]	94	>99/1
19				15 [a]	87	>99/1
20				16 [a]	94	>99/1

[a] *Syn* assignment is tentative.

Table 2. Effect of Solvents



solvent	T (°C)	time (h)	yield[a] (%)
CH_2Cl_2	r.t.	24	trace
CH_3CN	r.t.	24	trace
benzene	r.t.	24	trace
Et_2O	r.t.	24	trace
THF	r.t.	24	trace
DMF	0	2	90
HMPA	0	3	28
CH_2Cl_2–DMF (1:1)	0	4	97
CH_3CN–DMF (1:1)	0	4	90
toluene–DMF (1:1)	0	4	89
Et_2O–DMF (1:1)	0	4	89
CH_3CN–DMF (5:1)	0	4	91
CH_3CN–DMF (10:1)	0	4	87
CH_3CN–DMF (20:1)	0	4	70
CH_3CN–DMF (30:1)	0	4	63
CH_3CN–DMF (40:1)	0	4	65
CH_2Cl_2–HMPA (2:1)	0	18	83
CH_3CN–HMPA (2:1)	0	14	70
toluene–HMPA (2:1)	0	14	23

[a] Isolated yield.

Table 3. ^{29}Si NMR Chemical Shifts of (Z)-Crotyltrichlorosilane in Several Solvents

solvent	chemical shift (ppm)
$CDCl_3$	+8.0
CD_3CN	+8.6
C_6D_6	+7.9
THF-d_8	+8.5
DMF-d_7	−170
HMPA	−22

allyltrichlorosilanes. In addition, *syn*-isomers are obtained from (*Z*)-allyltrichlorosilanes while *anti*-isomers are produced from (*E*)-allyltrichlorosilanes in almost complete selectivities.

In the present reactions, use of DMF is crucial. The effects of different solvents on the reaction are shown in Table 2. While only a trace amount of the product was detected on TLC in dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), benzene, ether, or tetrahydrofuran (THF), the reaction proceeded smoothly in DMF. A moderate product yield was obtained in hexamethylphosphoric triamide (HMPA). We also examined cosolvent systems (Table 2). When the solvents in which the reaction did not proceed were combined with DMF or HMPA, moderate to high yields of the product were obtained.

We assumed that the intermediate and key species of this reaction is a hypervalent silicate. The ^{29}Si NMR spectra of (*Z*)-crotyltrichlorosilane support this hypothesis. While signals were observed at around 6 ppm in solvents other than DMF-d_7 and HMPA, absorption in DMF was found at −170 ppm (Table 3), which indicated that DMF coordinated to the silicon atom of (*Z*)-crotyltrichlorosilane to form the corresponding five- or six-coordinated organosilicate.[8] This hypervalent silicate has enough Lewis acidity based on the electron-withdrawing chlorine groups as well as nucleophilicity due to electron donation from the hypervalent silicon atom to the allyl π systems (s–p conjugation),[5a] which enable the reaction to proceed smoothly. The high stereoselectivities can be explained by the six-membered cyclic transition state[9] shown in Scheme 1.

Scheme 1. Assumed Transition States

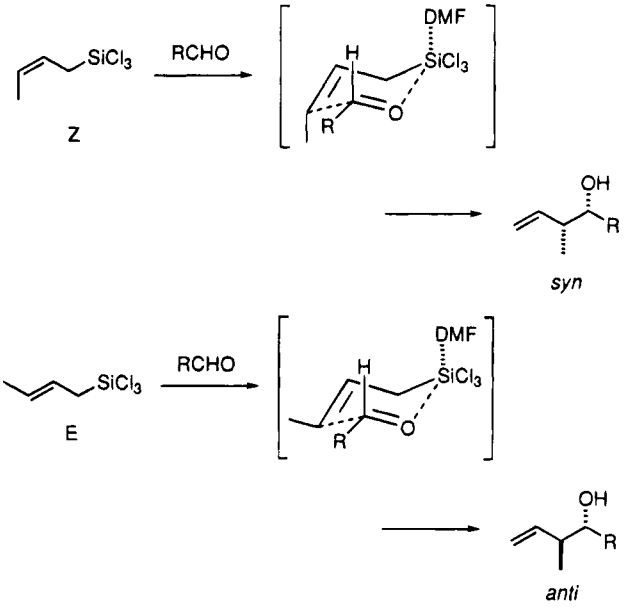
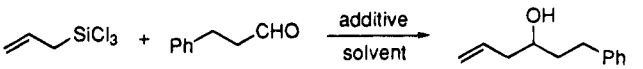


Table 4. Effect of Additives



additive	eq.	solvent	temp. (°C)	time (h)	yield (%)
Et_3N	20	CH_2Cl_2	r.t.	24	0
Ph_3P	5	CH_2Cl_2	r.t.	24	0
Ph_3P=O	5	CH_2Cl_2	r.t.	24	0
DMSO	5	CH_2Cl_2	r.t.	24	0
DMA	30	CH_2Cl_2	r.t.	24	0
Me_2NCHS	5	CH_2Cl_2	r.t.	24	0
	5	CH_2Cl_2	0	60	16
	5	CH_3CN	0	60	63
	5	CH_3CN	0	4	85
	2.5	CH_3CN	0	15	85
	1	CH_3CN	0	12	79
DMF	5	CH_3CN	0	15	86
	1	CH_3CN	0	12	68

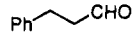
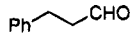
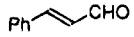
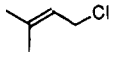
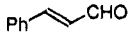
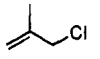
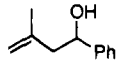
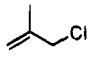
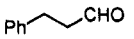
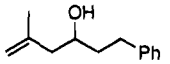
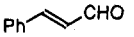
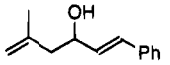
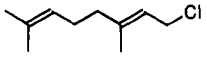
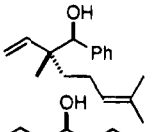
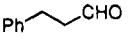
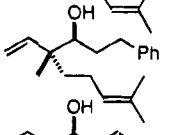
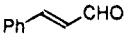
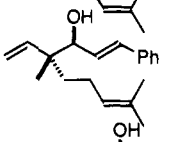
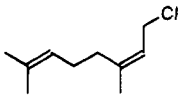
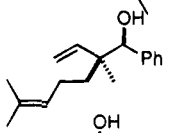
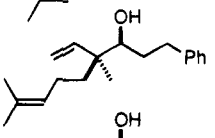
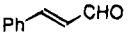
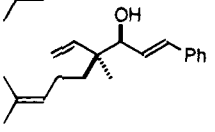
On the basis of this hypothesis, we examined "DMF analogues" and the amount of DMF and "DMF analogues" in the allylation reaction. These results are summarized in Table 4. Triethylamine or triphenylphosphine was found to be ineffective in this reaction, and no adduct was obtained when dimethylacetamide (DMA) was used as well. On the other hand, cyclic formamides worked well. In particular, 1-formylpyrrolidine gave excellent results, and it is noteworthy that the product was obtained in a 79% yield in the presence of 1 equiv of the formamide, which strongly supported the above hypothesis.

One-Pot Synthesis of Homoallylic Alcohols from Allyl Halides. In addition to the synthetic utilities of this very simple procedure under neutral conditions and

(8) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Ed.; John Wiley and Sons, Inc.: New York, 1989; Part 1, p 511.

(9) (a) Hosomi, A.; Kohra, S.; Tominaga, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1517. (b) Hayashi, T.; Matsumoto, Y.; Kiyoi, Y.; Ito, Y.; Kohra, S.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 5667. See also: (c) Hoffmann, R. W.; Jeiss, H. J. *J. Org. Chem.* **1981**, *46*, 1309.

Table 5. One-Pot Synthesis of Homoallylic Alcohols from Allyl Halides

entry	allylic chloride	aldehyde	product		yield/%	*syn/anti*
1		PhCHO	1		89	—
2			2		89	—
3			3		88	—
4		PhCHO	4A		88	3/97
5			5A		86	3/97
6			6A		93	5/95
7		PhCHO	8		82	—
8			9		83	—
9			10		88	—
10		PhCHO		17	92	—
11				18	92	—
12				19	94	—
13		PhCHO		20A	82	<1/>99
14				21A	91	<1/>99
15				22A	97	<1/>99
16		PhCHO		20S	92	>99/1
17				21S	87	>99/1
18				22S	93	>99/1

the high regio- and stereoselectivities, the above allylation reaction is valuable because the starting materials, allyltrichlorosilanes, are commercially and readily available or can be easily prepared not only from the corresponding halides[6b,10] but also from the dienes[11] via stereoselective hydrosilylation reactions. On the other hand, from a synthetic point of view, the direct preparation of homoallylic alcohols from allyl halides or dienes is desirable.[12]

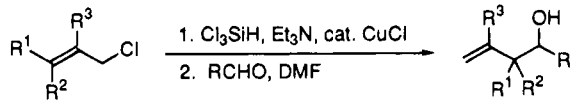
First, we examined the one-pot synthesis of homoallylic alcohols from allyl halides. A general scheme for the one-pot synthesis is shown in Scheme 2. An allyl chloride reacts with Cl_3SiH in the presence of triethylamine (1.1 equiv) and CuCl (0.03 equiv) to give an intermediate allyltrichlorosilane. To the same pot, an aldehyde in *N,N*-dimethylformamide (DMF) is added.

Selected examples of the synthesis of homoallylic alcohols from allyl halides are shown in Table 5. In every case, the desired homoallylic alcohols were obtained in

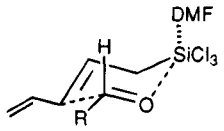
(10) Furuya, N.; Sukawa, T. *J. Organomet. Chem.* **1975**, *96*, C1.
(11) Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143. Cf. Takahashi, S.; Shibano, T.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1969**, 161.

(12) Habaue, S.; Yasue, K.; Yanagisawa, A.; Yamamoto, H. *Synlett* **1993**, 788.

Scheme 2. One-Pot Synthesis of Homoallylic Alcohols from Allyl Halides

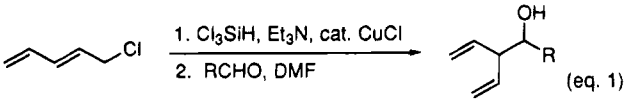


Scheme 3



high yields. Addition of the organosilicon intermediates to the aldehydes proceeded smoothly even in the presence of ether, CuCl, and triethylamine–hydrochloric acid salt (Et_3N·HCl). The additions occurred exclusively at the γ position of the allyl chlorides. Excellent diastereoselectivities were also observed; *syn*-homoallylic alcohols were formed from (*Z*)-allyl chlorides, whereas *anti*-homoallylic alcohols were produced from (*E*)-allyl chlorides. These selectivities can be ascribed to the stereospecific formation of (*Z*)- and (*E*)-allyltrichlorosilanes from the corresponding allyl chlorides.[13]

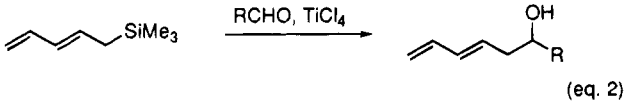
1-Chloro-2,4-pentadiene[14] also worked well under the same reaction conditions, and the reactions occurred at the γ position of the diene system exclusively (eq 1). It is noted that the selectivity is quite a contrast to that in the reactions of 2,4-pentadienyltrimethylsilane under the influence of a Lewis acid, which reacted with aldehydes at the terminal position of the diene system (eq 2).[15] This can be rationalized by assuming the six-membered cyclic transition state shown in Scheme 3.



(eq. 1)

23 - 25

23 : R = Ph	83%
24 : R = $Ph(CH_2)_2$	86%
25 : R = (E)-PhCH=CH	87%

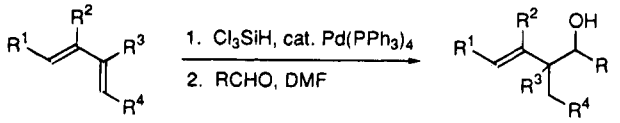


(eq. 2)

One-Pot Synthesis of Homoallylic Alcohols from 1,3-Dienes. We next examined the one-pot synthesis of homoallylic alcohols from 1,3-dienes. Although many methods for the preparations of homoallylic alcohols have been reported, one-pot preparations from 1,3-dienes are rare.

The process is shown in Scheme 4; an initial hydrosilylation of 1,3-diene using a palladium catalyst (1,4-addition)[6,11] and successive aldehyde coupling with the intermediate organosilicon compound in dimethylformamide (DMF). Consequently, two vicinal σ-bonds form

Scheme 4. One-Pot Synthesis of Homoallylic Alcohols from 1,3-Dienes



in one of two double bonds of the dienes by hydride addition–aldehyde coupling sequences.

Selected examples of the synthesis of homoallylic alcohols from 1,3-dienes are shown in Table 6. In every case (including both cyclic and acyclic 1,3-dienes), one-pot reactions of hydride addition–aldehyde coupling sequences proceeded smoothly to afford homoallylic alcohols in high yields. It should be noted that high regio- and diastereoselectivities were attained in this process. In the reaction with isoprene, the addition occurred exclusively at the less-substituted olefin. No adduct produced by addition to the more-substituted olefin part of the 1,3-diene was obtained. Moreover, *syn* homoallylic alcohols were produced in high selectivities, which can be ascribed to the geometry of the intermediary organosilicon compounds.

This process is an example of tandem vicinal difunctionalization of 1,3-dienes.[16] Tandem vicinal difunctionalization of α,β-unsaturated carbonyl compounds is well-known and provides a convenient method for introducing two functional groups to the olefins (Scheme 5, **A**).[17] One feature of this process is the rapid and convergent access to complex structures in a highly stereocontrolled manner, and considerable utility of this process as a synthetic tool has already been demonstrated in the total synthesis of natural products.[18] However, examples of tandem vicinal difunctionalization of 1,3-dienes (Scheme 5, **B**) are rather limited.[16,19] We believe that the process reported here not only provides a convenient method for the direct preparation of homoallylic alcohols from 1,3-dienes but also demonstrates the potential utility of this type of tandem vicinal difunctionalization of 1,3-dienes as a versatile synthetic tool.[20]

Further studies to apply this methodology to the synthesis of more complicated molecules (including natural products) as well as to develop other examples of tandem vicinal difunctionalization are in progress.

(13) Kobayashi, S.; Nishio, K. *Chem. Lett.*, in press.

(14) (a) Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020. (b) Shishido, K.; Hiroya, K.; Ueno, Y.; Fukumoto, K.; Kametani, T.; Honda, T. *J. Chem. Soc., Perkin Trans. 1* **1986**, 829.

(15) (a) Seyferth, D.; Pornet, J. *J. Org. Chem.* **1980**, *45*, 1722. (b) Hosomi, A.; Saito, M.; Sakurai, H. *Tetrahedron Lett.* **1980**, 3783. (c) Seyferth, D.; Pornet, J.; Weinstein, R. M. *Organometallics* **1982**, *1*, 1651.

(16) Hulce, M.; Chapdelaine, M. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 4, p 242.

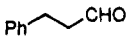
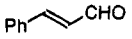
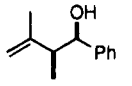
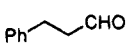
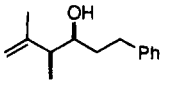
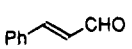
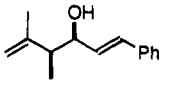
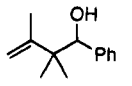
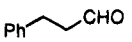
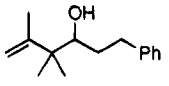
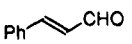
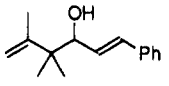
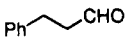
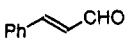
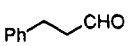
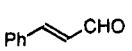
(17) (a) Hulce, M.; Chapdelaine, M. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 4, p 237. (b) Chapdelaine, M. J.; Hulce, M. *Org. React.* **1990**, *38*, 225. (c) Taylor, R. J. K. *Synthesis* **1985**, 364. (d) Normat, J. F.; Alexakis, A. *Ibid.* **1981**, 841. See also: (e) Houri, A. F.; Didink, M. T.; Xu, Z.; Horan, N. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6614. (f) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *Ibid.* **1989**, *111*, 366.

(18) For example: (a) Ihara, M.; Takahashi, T.; Shimizu, N.; Ishida, Y.; Sudow, I.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1467. (b) Franck, R. W.; Bhat, V.; Subramaniam, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 2455. (c) Asaoka, M.; Ishibashi, K.; Yanagida, T.; Takei, H. *Tetrahedron Lett.* **1983**, *24*, 5127. (d) Suzuki, M.; Kawagishi, T.; Suzuki, T.; Noyori, R. *Ibid.* **1982**, *23*, 4057. Review: (e) Ward, R. S. *Tetrahedron* **1990**, *46*, 5029. (f) Vandewalle, M.; DeClercq. P. *Ibid.* **1985**, *41*, 1767.

(19) Rieke and Xiong reported that the reaction of 1,3-dienes with bis-electrophiles using highly reactive magnesium realized "tandem vicinal difunctionalization of 1,3-dienes" by oxidative addition–alkyl halide substitution sequences. (a) Xiong, H.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 4415. (b) Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1992**, *57*, 6560; **1991**, *56*, 3109. (c) Xiong, H.; Rieke, R. D. *Ibid.* **1989**, *54*, 3247, and references cited therein.

(20) Kobayashi, S.; Nishio, K. *Synthesis* **1994**, 457.

Table 6. One-Pot Synthesis of Homoallylic Alcohols from 1,3-Dienes

entry	1,3 - diene	aldehyde	product		yield/%	*syn/anti*
1		PhCHO	**4S**		95	>99/1
2			**5S**		94	>99/1
3			**6S**		96	>99/1
4		PhCHO		**26**	91	94/6
5				**27**	81	92/8
6				**28**	92	92/8
7		PhCHO		**29**	92	—
8				**30**	83	—
9				**31**	88	—
10		PhCHO	**11** [a]		91	>99/1
11			**12** [a]		88	>99/1
12			**13** [a]		86	>99/1
13		PhCHO	**14** [a]		95	>99/1
14			**15** [a]		85	>99/1
15			**16** [a]		90	>99/1

[a] *Syn* assignment is tentative.

Scheme 5. Tandem Vicinal Difunctionalization of α,β-Unsaturated Carbonyl Compounds (A) and 1,3-Dienes (B)

Conclusion

We found that allyltrichlorosilanes reacted with aldehydes in DMF without a catalyst to afford the corresponding homoallylic alcohols in high yields. The reactions proceeded under neutral conditions, and high regio- and stereoselectivities were attained. In these reactions, hypervalent silicates were formed by the coordination of DMF to silicon atoms of allyltrichlorosilanes. One-pot synthesis of homoallylic alcohols from allyl chlorides was realized via organosilicon intermediates. *Syn* and *anti* homoallylic alcohols were stereoselectively obtained from (*Z*)- and (*E*)-allyl chlorides, respectively. One-pot preparations of homoallylic alcohols from 1,3-dienes were also attained.

The present homoallylic alcohol syntheses are superior over conventional methods in regard to high yields, high regio- and stereoselectivities, mild reaction conditions, and quite simple procedures. Facile preparations of the

reactive hypervalent silicates are also noteworthy, and this may be an elegant example of utilizing hypervalent silicates in organic synthesis. Since a small amount of DMF or "DMF analogues" promoted the reactions, a designed chiral DMF analogue may lead to preparations of optically active homoallylic alcohols.

Experimental Section

General. Melting points are uncorrected. IR spectra were recorded on a Horiba FT-300 infrared spectrometer. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL JNR-EX270L spectrometer, and tetramethylsilane (TMS) served as internal (^1H, ^{13}C) or external (^{29}Si) standard. Column chromatography was performed on silica gel 60 (Merck) or Wakogel B5F. All reactions were carried out under argon atmosphere in dried glassware.

Dimethylformamide (DMF) was distilled from P_2O_5 and dried over MS4A. Allyltrichlorosilanes were prepared according to the literature.[6,11,12] (*E*)-Crotyl chloride was prepared from crotonaldehyde[6b] via reduction with $LiAlH_4$,[21] followed by the reaction with PCl_3.[22] (*E*)-1-Chloro-3,7-dimethyl-2,6-octadiene (geranyl chloride) and (*Z*)-1-chloro-3,7-dimethyl-2,6-octadiene (neryl chloride) were prepared from geraniol and nerol, respectively.[23] 1-Chloro-2,4-pentadiene was synthesized from ethyl formate.[13]

The Reactions of Allyltrichlorosilanes with Aldehydes. A typical experimental procedure is described for the reaction of (*Z*)-crotyltrichlorosilane with 3-phenylpropionaldehyde. A mixture of (*Z*)-crotyltrichlorosilane (*Z*/*E* = >99/1, 0.40 mmol) and benzaldehyde (0.32 mmol) in DMF (2 mL) was stirred at 0 °C for 2 h. Saturated aqueous sodium hydrogen carbonate was added to quench the reaction, and the aqueous layer was extracted with ether. The ether layer was washed with water and brine successively and then dried (Na_2SO_4). The crude product was purified by TLC (silica gel) to afford *syn*-1-phenyl-2-methyl-3-buten-1-ol (**4S**) in an 82% yield. ^1H and ^{13}C NMR showed a single isomer which was assigned as the *syn* adduct after comparison with the ^1H NMR data of the literature.[24] The *anti* adduct was not observed in the NMR spectra. **4S:** IR (neat) 3450, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (d, 1H, J = 6.9 Hz), 2.20 (s, 1H), 2.50−2.58 (m, 1H), 4.55 (dd, 1H, J = 2.6, 5.6 Hz), 4.98−5.05 (m, 2H), 5.72 (ddd, 1H, J = 6.9, 9.9, 17.7 Hz), 7.20−7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.0, 44.5, 77.2, 115.4, 126.5, 127.2, 128.0, 140.2, 142.5.

One-Pot Synthesis of Homoallylic Alcohols from Allyl Halides. A typical experimental procedure is described for the reaction of (*E*)-1-chloro-3,7-dimethyl-2,6-octadiene (geranyl chloride) with cinnamaldehyde: To a CuCl suspension in Et_2O (0.25 mL) was added diisopropylethylamine (0.66 mmol) in Et_2O (0.5 mL), geranyl chloride (0.6 mmol) in Et_2O (0.5 mmol), and trichlorosilane (0.6 mmol) successively at room temperature. The mixture was stirred for 10 h at this temperature, and then DMF (2 mL) was added. After the mixture was cooled, to 0 °C, cinnamaldehyde (0.5 mmol) in DMF (1 mL) was added and the mixture was further stirred for 12 h at 0 °C. Cold 1 N hydrochloric acid was added to quench the reaction, and the aqueous layer was extracted with Et_2O. After a usual workup, (*E*)-*anti*-3-hydroxy-4,8-dimethyl-1-phenyl-4-vinyl-1,7-nonadiene[12] (**22A**) was obtained in a 97% yield. **22A:** IR (neat) 3440, 1640, 1450, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (s, 3H), 1.41 (dd, 2H, J = 7.3, 9.9 Hz), 1.57 (s, 3H), 1.66 (s, 3H), 1.89 (m, 2H), 1.97 (br s, 1H), 3.96 (d, 1H, J = 7.4 Hz), 5.09 (d, 1H, J = 17.5 Hz), 5.06−5.17 (m, 1H), 5.24 (d, 1H, J = 10.8 Hz), 5.84 (dd, 1H, J = 10.8, 17.5 Hz), 6.20 (dd, 1H, J = 7.4, 15.9 Hz), 6.56 (dd, 1H, J = 7.4, 15.9 Hz), 7.18−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.8, 17.5, 22.6, 25.6, 37.4, 45.2, 78.5, 115.4, 124.6, 126.4, 127.5, 128.2, 128.4, 132.3, 132.4, 136.7, 143.6. Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.27; H, 9.75.

One-Pot Synthesis of Homoallylic Alcohols from 1,3-Dienes. A typical experimental procedure is described for the reaction of cyclopentadiene with trichlorosilane and benzaldehyde. Trichlorosilane (4 mmol), cyclopentadiene (4 mmol, freshly distilled before use), and $Pd(PPh_3)_4$ (8 mg) were combined in a sealed glass tube, and the mixture was heated at 90 °C for 5 h. The reaction pot was then cooled to 0 °C, and DMF (5 mL) was added. After the mixture was stirred for 10 min, benzaldehyde (3.2 mmol) in DMF (5 mL) was added and the mixture was further stirred for 3 h at 0 °C. Cold 1 N hydrochloric acid was then added in order to quench the reaction, and after a usual workup, 3-[(hydroxyphenyl)methyl]-cyclopentene (**11**) was isolated in a 91% yield (*syn*/*anti* = >99/1). **11:** bp 140 °C (bath temperature)/0.4 mmHg; IR (neat) 3400, 1450, 1020, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77−1.95 (m, 2H), 2.19 (brs, 1H), 2.26−2.36 (m, 2H), 3.03−3.08 (m, 1H), 4.49 (d, 1H, J = 6.6 Hz), 5.34−5.38 (m, 1H), 5.80−5.84 (m, 1H), 7.21−7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.1, 32.1, 53.8, 76.9, 126.2, 127.2, 128.1, 131.2, 133.4, 143.4. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.10; H, 8.11.

Other physical and spectral data of the homoallylic alcohols follow: **1-Phenyl-3-buten-1-ol (1):**[4a,25] IR (neat) 3350, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (s, 1H), 2.45−2.51 (m, 2H), 4.69 (t, 1H, J = 6.4 Hz), 5.11 (d, 1H, J = 10.0 Hz), 5.13 (d, 1H, J = 7.1 Hz), 5.78 (ddt, 1H, J = 7.1, 10.0, 17.0 Hz), 7.22−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 43.7, 73.2, 118.3, 125.8, 127.4, 128.3, 134.4, 143.8.

4-Hydroxy-6-phenyl-1-butene (2):[4a,26] bp 127 °C (bath temperature)/0.15 mmHg; IR (neat) 3370, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25−1.82 (m, 3H), 2.12−2.37 (m, 2H), 2.62−2.93 (m, 2H), 3.62−3.71 (m, 1H), 5.11 (d, 1H, J = 1.3 Hz), 5.16 (d, 1H, J = 1.7 Hz), 5.74−5.89 (m, 1H), 7.16−7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 32.0, 38.4, 42.0, 69.8, 118.3, 125.8, 128.3, 128.4, 128.8, 134.6, 142.0. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.98; H, 9.38.

***(E)*-3-Hydroxy-1-phenyl-1,5-hexadiene (3):**[25] bp 150 °C (bath temperature)/0.75 mmHg; IR (neat) 3380, 1640, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (br s, 1H), 2.32−2.49 (m, 2H), 4.35 (t, 1H, J = 6.4 Hz), 5.16 (d, 1H, J = 10.0 Hz), 5.17 (d, 1H, J = 17.3 Hz), 5.85 (ddt, 1H, J = 7.1, 10.0, 17.3 Hz), 6.23 (dd, 1H, J = 6.4, 15.9 Hz), 6.60 (d, 1H, J = 15.9 Hz), 7.20−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 42.0, 71.7, 118.5, 126.4, 127.6, 128.5, 130.3, 131.5, 134.0, 136.6. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.80; H, 8.11.

***anti*-2-Methyl-1-phenyl-3-buten-1-ol (4A):**[23] IR (neat) 3450, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (d, 3H, J = 6.6 Hz), 2.36−2.47 (m, 2H), 4.28 (d, 1H, J = 7.6 Hz), 5.11 (d, 1H, J = 10.7 Hz), 5.12 (d, 1H, J = 16.9 Hz), 5.76 (ddd, 1H, J = 8.0, 10.7, 16.9 Hz), 7.20−7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.2, 45.9, 77.6, 116.3, 126.6, 127.4, 128.0, 140.5, 142.4.

***syn*-4-Hydroxy-3-methyl-6-phenyl-1-hexene (5S):** bp 116 °C (bath temperature)/0.09 mmHg; IR (neat) 3380, 1450, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (d, 3H, J = 6.7 Hz), 1.60−1.87 (m, 3H), 2.28 (m, 1H), 2.57−2.69 (m, 1H), 2.80−2.90 (m, 1H), 3.49 (dd, 1H, J = 4.0, 8.6 Hz), 5.06 (d, 1H, J = 10.4 Hz), 5.07 (d, 1H, J = 16.7 Hz), 5.76 (ddd, 1H, J = 7.6, 10.4, 16.7 Hz), 7.14−7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.3, 32.3, 35.7, 43.6, 74.0, 115.3, 125.7, 128.3, 128.4, 140.7, 142.1. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.10; H, 9.60.

***anti*-4-Hydroxy-3-methyl-6-phenyl-1-hexene (5A):** bp 116 °C (bath temperature)/0.09 mmHg; IR (neat) 3380, 1450, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, 3H, J = 6.9 Hz), 1.89−2.15 (m, 2H), 2.33 (br s, 1H), 2.43−2.56 (m, 1H), 2.88−2.99 (m, 1H), 3.06−3.17 (m, 1H), 3.65−3.72 (m, 1H), 5.36 (d, 1H, J = 17.9 Hz), 5.37 (d, 1H, J = 9.7 Hz), 6.02 (ddd, 1H, J = 8.3, 9.7, 17.9 Hz), 7.42−7.57 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.0, 32.0, 35.9, 44.0, 73.8, 44.0, 73.8, 116.0, 125.6, 128.2, 128.3, 140.0, 142.1. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.96; H, 9.50.

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(*E*)-*syn*-3-Hydroxy-4-methyl-1-phenyl-1,5-hexadiene (6S):[6b] bp 159 °C (bath temperature)/0.15 mmHg; IR (neat) 3390, 1450, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (d, 3H, J = 6.9 Hz), 2.23 (br s, 1H), 2.43 (ddq, 1H, J = 6.9, 7.8, 12.5 Hz), 4.15 (dd, 1H, J = 6.1, 12.5 Hz), 5.09 (d, 1H, J = 10.5 Hz), 5.10 (d, 1H, J = 17.2 Hz), 5.82 (ddd, 1H, J = 7.8, 10.5, 17.2 Hz), 6.19 (dd, 1H, J = 6.1, 16.1 Hz), 6.54 (d, 1H, J = 16.1 Hz), 7.17–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.8, 43.7, 75.7, 115.7, 126.3, 127.4, 128.4, 129.9, 131.0, 136.6, 139.8. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.70; H, 8.70.

(*E*)-*anti*-3-Hydroxy-4-methyl-1-phenyl-1,5-hexadiene (6A):[6b] IR (neat) 3390, 1450, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (d, 3H, J = 6.9 Hz), 2.29–2.43 (m, 2H), 4.01 (dd, 1H, J = 6.6, 6.9 Hz), 5.10 (d, 1H, J = 9.7 Hz), 5.11 (d, 1H, J = 17.7 Hz), 5.79 (ddd, 1H, J = 8.0, 9.7, 17.7 Hz), 6.19 (dd, 1H, J = 6.9, 15.8 Hz), 6.54 (d, 1H, J = 15.8 Hz), 7.16–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.7, 44.3, 75.9, 116.1, 126.3, 127.4, 128.3, 130.1, 131.3, 136.6, 140.1.

***syn*-1-Cyclohexyl-2-methyl-3-buten-1-ol (7S):** bp 100 °C (bath temperature)/0.65 mmHg; IR (neat) 3400, 1640, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (d, 3H, J = 6.9 Hz), 0.98–1.95 (m, 12H), 2.37–2.44 (m, 1H), 3.19 (t, 1H, J = 5.8 Hz), 5.07 (d, 1H, J = 10.0 Hz), 5.08 (d, 1H, J = 16.9 Hz), 5.81 (ddd, 1H, J = 6.9, 10.0, 16.9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.0, 25.9, 26.2, 26.4, 27.8, 29.6, 39.7, 40.2, 78.5, 114.5, 142.0. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 77.90; H, 11.90.

***anti*-1-Cyclohexyl-2-methyl-3-buten-1-ol (7A):** bp 100 °C (bath temperature)/0.65 mmHg; IR (neat) 3400, 1640, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (d, 3H, J = 6.9 Hz), 1.00–1.85 (m, 12H), 2.31–2.44 (m, 1H), 3.10 (t, 1H, J = 5.8 Hz), 5.09 (d, 1H, J = 16.2 Hz), 5.10 (d, 1H, J = 10.2 Hz), 5.78 (ddd, 1H, J = 8.1, 10.2, 16.2 Hz); ^{13}C NMR ($CDCl_3$) δ 16.9, 26.1, 26.36, 26.44, 27.0, 29.9, 40.3, 40.5, 78.7, 115.9, 140.3. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.36; H, 11.95.

2,2-Dimethyl-1-phenyl-3-buten-1-ol (8):[6a] IR (neat) 3410, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3H), 1.01 (s, 3H), 2.07 (s, 1H), 4.41 (s, 1H), 5.07 (dd, 1H, J = 1.5, 17.6 Hz), 5.13 (dd, 1H, J = 1.5, 10.8 Hz), 5.91 (dd, 1H, J = 10.8, 17.6 Hz), 7.24–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.0, 24.4, 42.2, 80.6, 113.8, 127.38, 127.44, 127.7, 140.7, 145.0.

4-Hydroxy-3,3-dimethyl-6-phenyl-1-hexene (9): bp 130 °C (bath temperature)/0.15 mmHg; IR (neat) 3430, 1640, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 6H), 1.49–1.64 (m, 2H), 1.77–1.90 (m, 1H), 2.55–2.67 (m, 1H), 2.87–2.98 (m, 1H), 3.28 (dd, 1H, J = 1.3, 10.6 Hz), 5.04 (dd, 1H, J = 1.5, 16.6 Hz), 5.09 (dd, 1H, J = 1.5, 9.9 Hz), 5.79 (dd, 1H, J = 9.9, 16.6 Hz), 7.18–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.9, 23.1, 33.2, 33.3, 41.6, 113.5, 125.7, 128.3, 128.5, 142.4, 145.2. Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.10; H, 10.10.

(*E*)-3-Hydroxy-4,4-dimethyl-1-phenyl-1,5-hexadiene (10):[6a] bp 155 °C (bath temperature)/0.08 mmHg; IR (neat) 3430, 1640, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 3H), 1.07 (s, 3H), 1.84 (s, 1H), 3.96 (d, 1H, J = 7.0 Hz), 5.10 (dd, 1H, J = 1.3, 17.5 Hz), 5.14 (dd, 1H, J = 1.3, 10.9 Hz), 5.91 (dd, 1H, J = 10.9, 17.5 Hz), 6.23 (dd, 1H, J = 7.0, 15.8 Hz), 6.58 (d, 1H, J = 15.8 Hz), 7.19–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.8, 23.8, 41.9, 79.2, 113.8, 126.4, 127.5, 128.5, 128.6, 132.0, 136.7, 144.8. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.90; H, 9.12.

3-(1-Hydroxy-3-phenylpropyl)cyclopentene (12): mp 42.5–44.0 °C. IR (KBr) 3300, 1600, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (brs, 1H), 1.69–1.97 (m, 4H), 2.22–2.40 (m, 2H), 2.60–2.71 (m, 1H), 2.76–2.90 (m, 2H), 3.56–3.63 (m, 1H), 5.55–5.60 (m, 1H), 5.84–5.89 (m, 1H), 7.13–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 23.6, 32.2, 32.3, 36.6, 52.1, 73.0, 125.7, 128.3, 128.4, 131.3, 133.6, 142.2. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.20; H, 9.21.

(*E*)-3-(1-Hydroxy-3-phenyl-2-propenyl)cyclopentene (13): bp 173 °C (bath temperature)/0.05 mmHg; IR (neat) 3400, 160, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66–2.05 (m, 3H), 2.24–2.42 (m, 2H), 2.92–3.01 (m, 1H), 4.14–4.22 (m, 1H), 5.63–5.67 (m, 1H), 5.87–5.93 (m, 1H), 6.22 (dd, 1H, J = 16.2, 6.9 Hz), 6.60 (d, 1H, J = 16.2 Hz), 7.19–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.6, 32.2, 52.2, 75.5, 126.4, 127.5, 128.5, 130.2, 130.7, 130.8, 133.7, 136.8. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.90; H, 8.10.

***syn*-3-[(Hydroxyphenyl)methyl]cyclohexene (14):** IR (neat) 3400, 1450, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42–1.55 (m, 2H), 1.64–1.77 (m, 2H), 1.91–1.96 (m, 2H), 2.26 (s, 1H), 2.39–2.48 (m, 1H), 4.48 (d, 1H, J = 6.6 Hz), 5.33 (dd, 1H, J = 2.0, 12.2 Hz), 5.72–5.80 (m, 1H), 7.20–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.0, 23.9, 25.1, 42.8, 77.2, 126.4, 127.2, 127.9, 128.0, 130.0, 142.8. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.90; H, 8.61.

***syn*-3-(1-Hydroxy-3-phenylpropyl)cyclohexene (15):** IR (neat) 3320, 1500, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45–1.58 (m, 2H), 1.65–1.89 (m, 5H), 1.96–2.02 (m, 2H), 2.22–2.26 (m, 1H), 2.59–2.89 (m, 2H), 3.58 (dt, 1H, J = 5.7, 5.8 Hz), 5.54 (dd, 1H, J = 2.0, 9.8 Hz), 5.84 (ddd, 1H, J = 3.5, 6.2, 9.8 Hz), 7.13–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.3, 22.8, 25.1, 32.4, 35.5, 41.4, 73.8, 125.7, 128.27, 128.34, 128.4, 130.4, 142.2. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.28; H, 9.30.

(*E*)-*syn*-3-(1-Hydroxy-3-propenyl)cyclohexene (16): IR (neat) 3410, 1640, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37–1.67 (m, 2H), 1.71–1.86 (m, 2H), 1.95–1.97 (m, 2H), 2.27 (s, 1H), 2.33–2.39 (m, 1H), 4.11 (dd, 1H, J = 6.3, 6.9 Hz), 5.63 (dd, 1H, J = 2.0, 10.1 Hz), 5.81 (ddd, 1H, J = 3.5, 6.2, 10.1 Hz), 6.21 (dd, 1H, J = 6.9, 15.8 Hz), 6.54 (d, 1H, J = 15.8 Hz), 7.17–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.1, 24.2, 25.1, 41.6, 75.9, 126.3, 127.4, 127.5, 128.4, 129.8, 130.4, 131.3, 136.6. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.15; H, 8.49.

3-Methyl-1-phenyl-3-buten-1-ol (17): IR (neat) 3410, 1640, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77 (s, 3H), 2.31 (s, 1H), 2.40 (d, 2H, J = 6.8 Hz), 4.76 (t, 1H, J = 6.8 Hz), 4.82 (s, 1H), 4.89 (s, 1H), 7.21–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.2, 48.2, 71.3, 113.9, 125.7, 127.3, 128.3, 142.3, 144.0. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.67; H, 8.60.

4-Hydroxy-2-methyl-6-phenyl-1-hexene (18): IR (neat) 3390, 1640, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69–1.89 (m, 6H), 2.08–2.25 (m, 2H), 2.63–2.89 (m, 2H), 3.69–3.78 (m, 1H), 4.79 (s, 1H), 4.87 (s, 1H), 7.14–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.3, 32.0, 38.7, 46.1, 67.8, 113.5, 125.7, 128.28, 128.34, 142.1, 142.6. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.89; H, 9.45.

(*E*)-3-Hydroxy-5-methyl-1-phenyl-1,5-hexadiene (19): IR (neat) 3380, 1650, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (s, 3H), 2.20 (s, 1H), 2.31 (d, 2H, J = 6.5 Hz), 4.40 (dt, 1H, J = 6.2, 6.5 Hz), 4.83 (s, 1H), 4.89 (s, 1H), 6.21 (dd, 1H, J = 6.2, 15.9 Hz), 6.60 (d, 1H, J = 15.9 Hz), 7.18–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.4, 46.0, 69.8, 113.9, 126.3, 127.4, 128.4, 129.9, 131.7, 136.6, 141.8. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.73; H, 8.69.

***syn*-2,6-Dimethyl-1-phenyl-2-vinyl-5-hepten-1-ol (20S):**[12] IR (neat) 3450, 1630, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 3H), 1.34 (t, 2H, J = 7.6 Hz), 1.54 (s, 3H), 1.64 (s, 3H), 1.85 (dt, 2H, J = 6.9, 7.6 Hz), 2.19 (br s, 1H), 4.38 (s, 1H), 4.98 (dd, 1H, J = 1.6, 17.7 Hz), 5.02–5.06 (m, 1H), 5.16 (dd, 1H, J = 1.6, 10.9 Hz), 5.77 (dd, 1H, J = 10.9, 17.7 Hz), 7.19–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 17.5, 18.7, 22.7, 25.6, 36.3, 45.2, 80.6, 115.0, 124.8, 127.2, 127.3, 127.8, 131.0, 141.2, 142.6. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.86; H, 9.50.

***anti*-2,6-Dimethyl-1-phenyl-2-vinyl-5-hepten-1-ol (20A):**[12] IR (neat) 3450, 1630, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 3H), 1.19–1.46 (m, 2H), 1.54 (s, 3H), 1.64 (s, 3H), 1.84 (dt, 2H, J = 7.8, 7.9 Hz), 2.15 (br s, 1H), 4.38 (s, 1H), 5.01–5.10 (m, 2H), 5.24 (dd, 1H, J = 1.3, 10.9 Hz), 5.84 (dd, 1H, J = 10.9, 17.5 Hz), 7.22–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.1, 17.5, 22.7, 25.6, 37.4, 45.8, 79.9, 115.7, 124.7, 127.3, 127.4, 128.0, 131.1, 140.4, 143.8. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.54; H, 9.70.

***syn*-7-Hydroxy-2,6-dimethyl-9-phenyl-6-vinyl-2-nonene (21S):** IR (neat) 3440, 1650, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 3H), 1.38 (t, 2H, J = 8.8 Hz), 1.56 (s, 3H), 1.60–1.64 (m, 1H), 1.66 (s, 3H), 1.81–1.90 (m, 3H), 2.53–2.64 (m, 1H), 2.85–2.96 (m, 1H), 3.30 (d, 1H, J = 10.6 Hz), 5.01 (d, 1H, J = 17.5 Hz), 5.07–5.10 (m, 1H), 5.14 (dd, 1H, J = 1.3, 10.8 Hz), 5.68 (dd, 1H, J = 10.8, 17.5 Hz), 7.14–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 17.5, 17.6, 22.6, 25.6, 33.2, 33.6, 37.3, 44.7, 77.2,

114.6, 124.7, 125.7, 128.3, 128.4, 131.2, 142.3, 143.2. Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.94; H, 10.30.

***anti*-7-Hydroxy-2,6-dimethyl-9-phenyl-6-vinyl-2-nonene (21A):** IR (neat) 3440, 1650, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3H), 1.15–1.42 (m, 2H), 1.55 (s, 3H), 1.65 (s, 3H), 1.51–1.90 (m, 5H), 2.54–2.65 (m, 1H), 2.88–2.98 (m, 1H), 3.29 (d, 1H, J = 10.6 Hz), 5.01–5.08 (m, 2H), 5.19 (dd, 1H, J = 1.3, 10.9 Hz), 5.73 (dd, 1H, J = 10.9, 17.5 Hz), 7.13–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.5, 17.5, 22.7, 25.6, 32.8, 33.2, 37.3, 45.0, 76.2, 115.2, 124.7, 125.7, 128.3, 128.4, 131.2, 142.4, 144.0. Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.69; H, 10.20.

(*E*)-*syn*-3-Hydroxy-4,8-dimethyl-1-phenyl-4-vinyl-1,7-nonadiene (22S):[12] IR (neat) 3440, 1640, 1450, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (s, 3H), 1.37–1.51 (m, 2H), 1.57 (s, 3H), 1.66 (s, 3H), 1.87–1.93 (m, 3H), 4.00 (d, 1H, J = 6.3 Hz), 5.03–5.10 (m, 1H), 5.07 (d, 1H, J = 17.4 Hz), 5.20 (d, 1H, J = 10.9 Hz), 5.82 (dd, 1H, J = 10.9, 17.4 Hz), 6.25 (dd, 1H, J = 6.5, 15.8 Hz), 6.39 (d, 1H, J = 15.8 Hz), 7.18–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 17.5, 18.5, 22.6, 25.6, 36.9, 45.0, 78.7, 115.1, 124.7, 126.4, 127.4, 128.4, 129.0, 131.2, 131.5, 136.8, 142.8. Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.04; H, 9.38.

1-Phenyl-2-vinyl-3-buten-1-ol (23): IR (neat) 3410, 1640, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.34 (s, 1H), 3.07 (dt, 1H, J = 7.1, 8.1 Hz), 4.54 (d, 1H, J = 7.1 Hz), 4.98 (d, 1H, J = 17.2 Hz), 5.03 (d, 1H, J = 10.4 Hz), 5.15 (d, 1H, J = 17.2 Hz), 5.20 (d, 1H, J = 10.4 Hz), 5.66 (ddd, 1H, J = 8.1, 10.4, 17.2 Hz), 5.82 (ddd, 1H, J = 8.1, 10.4, 17.2 Hz), 7.21–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 56.0, 76.1, 116.9, 118.1, 126.8, 127.5, 128.0, 136.6, 136.7, 141.7. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.88; H, 8.12.

4-Hydroxy-6-phenyl-3-vinyl-1-butene (24): IR (neat) 3420, 1640, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–1.91 (m, 3H), 2.59–2.96 (m, 3H), 3.55 (dd, 1H, J = 3.1, 6.1 Hz), 5.07–5.20 (m, 4H), 5.71–5.87 (m, 2H), 7.14–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 32.0, 35.9, 55.0, 72.3, 116.9, 117.6, 125.7, 128.3, 128.4, 136.8, 137.3, 142.1; HRMS calcd for $C_{14}H_{18}O$ (M^+) 202.1346, found 202.1337. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.39; H, 8.90.

(*E*)-3-Hydroxy-1-phenyl-4-vinyl-1,5-hexadiene (25): IR (neat) 3420, 1640, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (s, 1H), 2.98 (dt, 1H, J = 6.9, 7.6 Hz), 4.23 (dd, 1H, J = 6.4, 6.9 Hz), 5.10–5.24 (m, 4H), 5.77–5.92 (m, 2H), 6.21 (dd, 1H, J = 6.4, 15.8 Hz), 6.59 (d, 1H, J = 6.4 Hz), 7.18–7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 54.8, 74.3, 117.4, 117.8, 126.4, 127.5, 128.4, 129.5, 131.3, 136.5, 136.6. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.74; H, 8.17.

2,3-Dimethyl-1-phenyl-3-buten-1-ol (26): mp 41.0–42.5 °C; IR (KBr) 3400, 1650, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (d, 3H, J = 6.9 Hz), 1.73 (s, 3H), 1.98 (brs, 1H), 2.42–2.52 (m, 1H), 4.71 (d, 1H, J = 5.3 Hz), 4.77 (brs, 1H), 4.84 (d, 1H, J = 1.5 Hz), 7.21–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.0, 21.8, 47.9, 74.8, 111.9, 126.0, 127.0, 128.0, 143.0, 147.4. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.81; H, 9.21.

4-Hydroxy-2,3-dimethyl-6-phenyl-1-hexene (27): bp 145 °C (bath temperature)/0.4 mmHg; IR (neat) 3400, 1650, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, 3H, J = 6.9 Hz), 1.67 (s, 3H), 1.69–1.81 (m, 3H), 2.14–2.23 (m, 1H), 2.59–2.70 (m, 1H), 2.79–2.90 (m, 1H), 3.53–3.60 (m, 1H), 4.76 (brs, 1H), 4.83 (d, 1H, J = 1.6 Hz), 7.14–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.5, 21.0, 32.5, 36.5, 46.4, 71.8, 111.5, 125.7, 128.3, 128.4, 142.1, 147.9. Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.32; H, 9.91.

(*E*)-4-Hydroxy-2,3-dimethyl-6-phenyl-1,5-hexadiene (28): bp 149 °C (bath temperature)/0.4 mmHg; IR (neat) 3400, 1650, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (d, 3H, J = 6.9 Hz), 1.77 (s, 4H), 2.31–2.42 (m, 1H), 4.29 (t, 1H, J = 6.1 Hz), 4.83 (d, 1H, J = 1.3 Hz), 4.89 (t, 1H, J = 1.3 Hz), 6.23 (dd, 1H, J = 16.0, 6.1 Hz), 6.61 (d, 1H, J = 16.0 Hz), 7.20–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.9, 21.3, 47.0, 73.8, 112.1, 126.4, 127.4, 128.5, 130.1, 131.9, 137.9, 147.0. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.52; H, 8.97.

2,2,3-Trimethyl-1-phenyl-3-buten-1-ol (29): bp 121 °C (bath temperature)/0.4 mmHg; IR (neat) 3410, 1640, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (s, 3H), 0.98 (s, 3H), 1.85 (s, 3H), 2.13 (brs, 1H), 4.61 (s, 1H), 4.95 (s, 1H), 5.02 (s, 1H), 7.24–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.8, 20.1, 24.2, 44.4, 77.4, 113.1, 127.2, 127.3, 127.9, 140.3, 150.6. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.00; H, 9.79.

4-Hydroxy-2,3,3-trimethyl-6-phenyl-1-hexene (30): bp 157 °C (bath temperature)/0.2 mmHg; IR (neat) 3440, 1640, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (s, 3H), 1.04 (s, 3H), 1.52–1.82 (m, 3H), 1.68 (s, 3H), 2.56–2.67 (m, 1H), 2.89–3.00 (m, 1H), 3.49 (dd, 1H, J = 10.3, 1.1 Hz), 4.83 (s, 1H), 4.90 (s, 1H), 7.15–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.6, 21.6, 22.4, 33.0, 33.5, 43.7, 74.8, 112.0, 125.7, 128.3, 128.5, 142.4, 150.8. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.40; H, 10.40.

(*E*)-4-Hydroxy-2,3,3-trimethyl-6-phenyl-1,5-hexadiene (31): bp 152 °C (bath temperature)/0.04 mmHg; IR (neat) 3430, 1640, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 3H), 1.11 (s, 3H), 1.81 (s, 3H), 4.18 (d, 1H, J = 6.6 Hz), 4.92 (s, 1H), 4.98 (s, 1H), 6.22 (dd, 1H, J = 16.3, 6.6 Hz), 7.19–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.8, 21.1, 23.5, 44.2, 76.4, 112.7, 126.4, 127.5, 128.3, 128.5, 131.9, 136.9, 150.3. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.10; H, 9.30.