Intramolecular Ene Reaction of Vinylphosphonates. Synthetic Application to Bicyclic Compounds and Cadalane and Valerenic Acid Terpenoids

Toru Minami,* Tomohisa Utsunomiya, Seigo Nakamura, Michiharu Okubo, Naotaka Kitamura, Yoshiharu Okada, and Junji Ichikawa

Department of Applied Chemistry, Kyushu Institute of Technology, Sensuicho, Tobata, Kitakyushu 804, Japan

Received February 2, 1994®

The Lewis-acid-catalyzed intramolecular ene reaction of vinylphosphonates **4**, **6**, and **7**, prepared by the Knoevenagel condensation of triethyl phosphonoacetate (**3**) with citronellal (**1**) or 2,6-dimethyl-5-heptenal (**2**), stereoselectively gave 2-(8′-*p*-menthen-3′-yl) or 2-(2′-isopropenyl-5′-methylcyclopent-1′-yl)phosphonoacetates **8**–**10** in high yields. The Wittig–Horner reaction of the phosphonates **8**–**10** with paraformaldehyde led to 1,5-diene compounds **12a,b** and **13b** in 87–90% yield. Subsequent Lewis-acid-catalyzed cyclization of the compounds **12**, **13** or **25**, **27** afforded 1,6-dimethyloctahydronaphthalene-4-carboxylates **17**, **22**, or carbaldehydes **28**, **29** and/or 8-methyl-2,5-dimethylenebicyclo[4.4.0]decan-4-ol (**30**). Palladium-catalyzed metallo-ene reaction of the acetate **32** afforded 2,5,8-trimethyl-1,2,3,4-tetrahydronaphthalene (**34**). The bicyclic compounds **17a** and **29** were applied to the synthesis of cadalane and valerenic acid sesquiterpenoids.

Developments of vinylphosphonates containing various functional groups and their synthetic applications have been widely studied in the last two decades.[1] In recent years α,β-unsaturated ketones and esters have been extensively utilized as enophiles in ene reactions in organic synthesis.[2] Although there have been a few simple precedents for the intermolecular ene reaction of vinylphosphonates[3] as α,β-unsaturated systems, their application to the intramolecular ene reaction[4] have, to our knowledge, not been made. As a continuation of the studies on vinylphosphonates, we became interested in development of a new demands singular throughout type of vinylphosphonate and its synthetic utilizations.

We now report the synthesis of vinylphosphonates bearing linear monoterpenoid functional groups and their application to the intramolecular ene reaction. We also describe the application of the resulting ene products to the synthesis of cadalane and valerenic acids sesquiterpenoids.

Results and Discussion

Synthesis of Vinylphosphonates. The Knoevenagel condensation of citronellal (**1**) with triethyl phosphonoacetate (**3**) in ethanol using piperidine as a catalyst resulted in a 71% yield of a 1:1 mixture of the vinylphosphonate, ethyl (*E*)-2-(diethoxyphosphinyl)-5,9-dimethyldeca-2,8-dienoate [(*E*)-**4**] and the allylphosphonate, ethyl 2-(diethoxyphosphinyl)-5,9-dimethyldeca-3,8-dienoate (**5**).[5] The stereochemistry of the vinylphosphonate (*E*)-**4** was determined to be the (*E*)-configuration on the basis of the phosphorus–*cis*-vinyl proton NMR coupling constant of $^3J_{P-H}$ = 23.0 Hz.[6] In order to prevent the formation of undesired **5**, we have attempted the titanium-mediated condensation. According to the reported procedure,[6] the titanation of a triethyl phosphonoacetate carbanion, generated from treatment of **3** with NaH in tetrahydrofuran (THF), with chlorotriethoxy- or chlorotriisopropoxytitanium [ClTi(OEt)$_3$ or ClTi(O*i*-Pr)$_3$],[7] followed by the condensation with **1** afforded stereoselectively ethyl or isopropyl (*Z*)-2-(diethoxyphosphinyl)-5,9-dimethyldeca-2,8-dienoate [(*Z*)-**4** or (*Z*)-**6**] in 52 or 86% yield, respectively, of which NMR spectra exhibited the phosphorus–*trans*-vinyl proton coupling constant $^3J_{P-H}$ = 46.1 and 46.3 Hz (see Experimental Section) (Scheme 1). No undesired allylic phosphonate was formed. A similar treatment of the homologous aldehyde, 2,6-dimethyl-5-heptenal (**2**), with **3** and ClTi(O*i*-Pr)$_3$ gave exclusively isopropyl (*Z*)-2-(diethoxyphosphinyl)-4,8-dimethylnona-2,7-dienoate [(*Z*)-**7**] in 54% yield as a single stereoisomer.

Lewis-Acid-Catalyzed Intramolecular Ene Reaction of the Vinylphosphonates 4, 6, and 7. Snider and co-worker have recently found that α-phosphonoacrylates undergo EtAlCl$_2$-catalyzed ene reactions with various alkenes under mild conditions.[3b] The vinylphosphonates **4**, **6**, and **7** prepared above can be similarly expected to undergo Lewis-acid-catalyzed intramolecular ene reactions, because the vinylphosphonates contain a phosphinyl- and carbonyl-doubly activated enophile and an ene component in the same molecule. Thus, the (*E*)-vinylphosphonate (*E*)-**4** was treated with 1.5 equiv of

® Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) For a review, see: Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333.

(2) For reviews, see: (a) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (b) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. (c) Fujita, Y.; Suzuki, S.; Kanehira, K. *J. Synth. Org. Chem. Jpn.* **1983**, *41*, 1152. (d) Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021. (e) Snider, B. B. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chap. 2.1 and Vol. 5, Chap. 1.1. (f) Snider, B. B. *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer Academic Publishers: Dordrecht; 1989; p 147.

(3) For the ene reaction of vinylphosphonates, see: (a) Albisetti, C. J.; Fisher, N. G.; Hogsed, M. J.; Joyce, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 2637. (b) Snider, B. B.; Philips, G. B. *J. Org. Chem.* **1983**, *48*, 3685.

(4) For reviews of intramolecular ene reactions, see: (a) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. (b) Conia, J. M.; Le Perchec, P. *Synthesis* **1975**, 1.

(5) Yamanaka et al. have similarly reported the formation of a mixture of α,β- and β,γ-unsaturated esters in the Knoevenagel condensation of hexenal with diethyl malonate. Yamanaka, H.; Yokoyama, M.; Sakamoto, T.; Shiraishi, T.; Sagi, M.; Mizugaki, M. *Heterocycles* **1983**, *20*, 1541.

(6) Reetz, M. T.; Peter, R.; von Itzstein, M. *Chem. Ber.* **1987**, *120*, 121.

(7) Reetz, M. T.; Westermann, J.; Steinbach, R.; Wenderoth, B.; Peter, R.; Ostarek, R.; Maus, S. *Chem. Ber.* **1985**, *118*, 1421.

0022-3263/94/1959-6717$04.50/0

Scheme 1

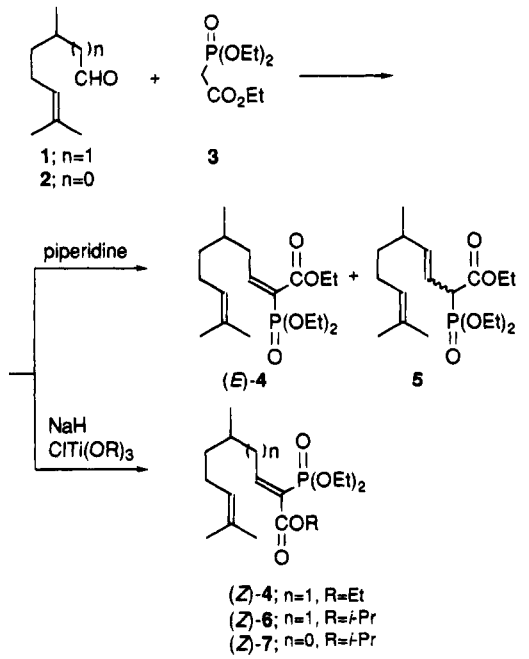


Table 1. Intramolecular Ene Reaction of Vinylphosphonates 4, 6, and 7

entry	starting material	Lewis acid	reaction conditions[a] temp/°C	time/h	product (yield/%)[b] 8, 9, or 10	11
1	(*E*)-**4**	$EtAlCl_2$	0	1	(2*S**)-**8** (80)	
2	(*Z*)-**4**	$EtAlCl_2$	0	1	(2*R**)-**8** (74)	
3	(*Z*)-**6**	$EtAlCl_2$	0	1	(2*R**)-**9** (81)	
4	(*Z*)-**6**	$TiCl_2(Oi\text{-}Pr)_2$[c]	0	1	(2*R**)-**9** (88)	
5	(*Z*)-**6**	$SnCl_4$	0	1	(2*R**)-**9** (91)	
6	(*Z*)-**6**	$ZnBr_2$	rt	11	(2*R**)-**9** (92)	
7	(*Z*)-**6**	$TiCl_4$	−78	0.5	(2*R**)-**9** (82)	
8	(*Z*)-**6**	$TiCl_4$	0	1	(2*R**)-**9** (73)	**11** (17)
9	(*Z*)-**6**	$TiCl_4$	rt	23		**11** (76)
10	(*Z*)-**6**	$FeCl_3$	0	1	(2*R**)-**9** (69)	**11** (15)
11	(*Z*)-**7**	$EtAlCl_2$	0	1	(2*R**)-**10** (78)	
12	(*Z*)-**7**	$TiCl_2(Oi\text{-}Pr)_2$[c]	rt	12	(2*R**)-**10** (78)	
13	(*Z*)-**7**	$ZnBr_2$	rt	20	(2*R**)-**10** (94)	
14	(*Z*)-**7**	$SnCl_4$	0	1.5	(2*R**)-**10** (77)	
15	(*Z*)-**7**	$TiCl_4$[d]	0	1	(2*R**)-**10** (81)	
16	(*Z*)-**7**	$FeCl_3$	0	1.5	(2*R**)-**10** (82)	

[a] All reactions were carried out in CH_2Cl_2 in the presence of 1.5 equiv of Lewis acid, unless otherwise noted. [b] Isolated yield by column chromatography. [c] Prepared *in situ* from $TiCl_4$ and $Ti(Oi\text{-}Pr)_4$. [d] In the presence of 1.1 equiv of $TiCl_4$.

$EtAlCl_2$ at 0 °C in CH_2Cl_2 to give exclusively an 80% yield of the (2*S**)-diastereomer **8** with a *trans* relationship between isopropenyl and phosphinylacetate substituents,[8] which is an intramolecular ene product (entry 1 in Table 1).[9] In contrast, similar treatment of the corresponding (*Z*)-vinylphosphonates (*Z*)-**4** and (*Z*)-**6** with $EtAlCl_2$ led to the other diastereomers (2*R**)-**8** and (2*R**)-**9** in 74 and 81% yields, respectively (entries 2 and 3).[8] To ascertain that thus obtained ene products **8** and **9** are each composed of a single diastereomeric isomer, each of the compounds (2*R**)-**8** and (2*R**)-**9** was treated with *t*-BuOK in THF at room temperature for 10 h to undergo a partial epimerization on C-2, resulting in the mixtures of two diastereoisomers (2*R**)-**8** and (2*S**)-**8**, and (2*R**)-**9** and (2*S**)-**9** in ratios of 23:77 and 24:76, respectively. These experimental data clearly indicate that the ene products (2*R**)-**8**, (2*S**)-**8**, and (2*R**)-**9** are diastereomerically pure. Consequently, the $EtAlCl_2$-catalyzed intramolecular ene reaction of the vinylphosphonates can be said to proceed in a stereospecific fashion. In addition, the intramolecular ene reaction of the homologous (*Z*)-vinylphosphonate **7** proceeded with $EtAlCl_2$ under similar conditions to furnish also a single (2*R**)-diastereomer **10** with a *trans* relationship between isopropenyl and phosphinylacetate substituents in 78% yield (Scheme 2).

The stereochemistry of these ene products **8**−**10** was determined by the conversion of the phosphinylacetate substituent into the α-acrylic acid ester group by the Wittig−Horner reaction with paraformaldehyde as mentioned below, because unambiguous assignment of stereochemistry of the products **8**−**10** is difficult to make from their spectral data. Accordingly, the formation of stereospecific ene reaction products may be explained *via* the chairlike transition states T_1 and T_2 with all the methyl, isopropylidene, and phosphinylvinyl groups equatorial. Furthermore, we found that the intramolecular ene reaction of the vinylphosphonates could be effectively catalyzed by a variety of Lewis acids such as $TiCl_4$, $SnCl_4$, $TiCl_2(Oi\text{-}Pr)_2$, $ZnBr_2$, etc.

For instance, the ene reaction of **6** catalyzed by the strong Lewis acids $TiCl_4$ or $FeCl_3$ at 0 °C for 1 h led to a mixture of the expected ene product (2*R**)-**9** (69−73%) and an α-phosphinyl δ-lactone (**11**) (15−17%), while the same reaction at −78 °C for 0.5 h produced exclusively (2*R**)-**9** in 82% yield (entries 7, 8, and 10 in Table 1). When the reaction was carried out at room temperature for a long time (23 h), the vinylphosphonate **6** produced only **11** in 76% yield, but no ene product was obtained (entry 9). In order to examine the formation mechanism of the lactone **11**, the isolated ene product (2*R**)-**9** was treated with $TiCl_4$ at 0 °C for 8 h, which resulted in **11** in 64% yield together with recovered (2*R**)-**9** (30%). This observation suggests that the lactone **11** would be formed *via* Lewis-acid-catalyzed cationic cyclization of initially produced (2*R**)-**9**. However, it might still be difficult to eliminate the possibility that **11** is formed *via* hetero Diels−Alder reaction of the vinylphosphonate **6** into a dihydropyran-2-yl isopropyl ether, followed by hydrolysis.[10] In addition, we attempted to investigate the influence of the acidity of Lewis acids upon the products. Thus, treatment of **6** with rather weak Lewis acids such as $TiCl_2(Oi\text{-}Pr)_2$ and $SnCl_4$ at 0 °C or with $ZnBr_2$ as an even weaker Lewis acid at room temperature led to excellent yields of the single ene product (2*R**)-**9** in all cases (entries 4, and 5 or 6).

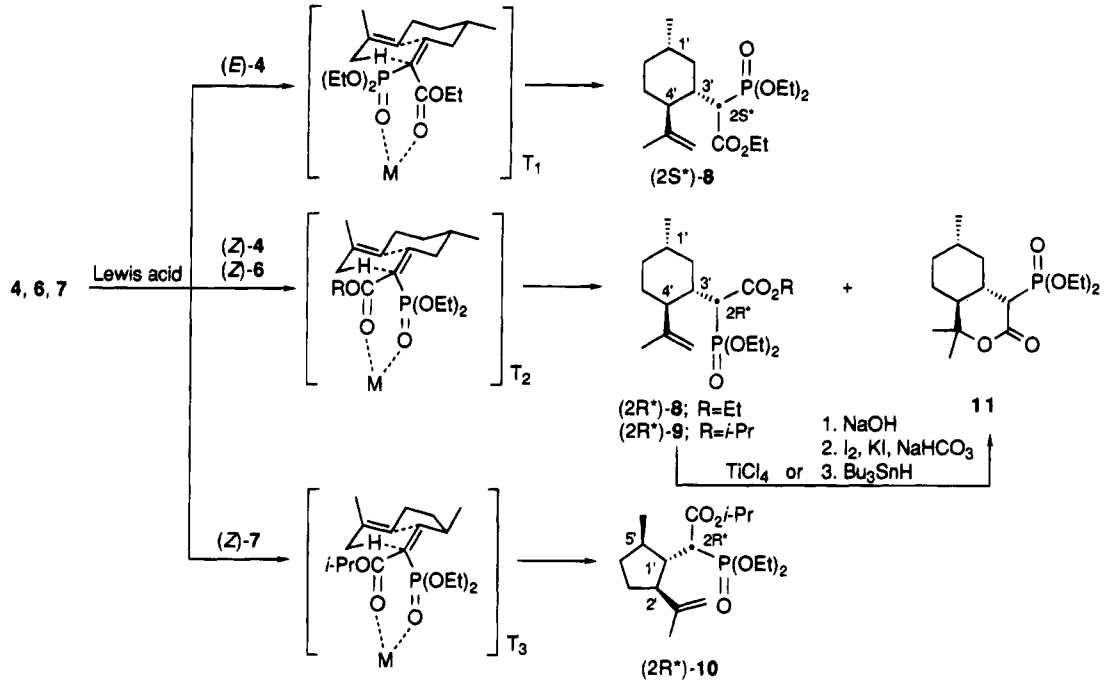
A similar treatment of the (*Z*)-vinylphosphonate (*Z*)-**7** with various Lewis acids [$TiCl_2(Oi\text{-}Pr)_2$, $ZnBr_2$, $SnCl_4$, $TiCl_4$, or $FeCl_3$] produced exclusively the corresponding ene product (2*R**)-**10** in good yields, regardless of the Lewis acid used (entries 11−16).

(8) Configuration at C-2 of **8**−**10** was tentatively assigned on the basis of mechanistic grounds.

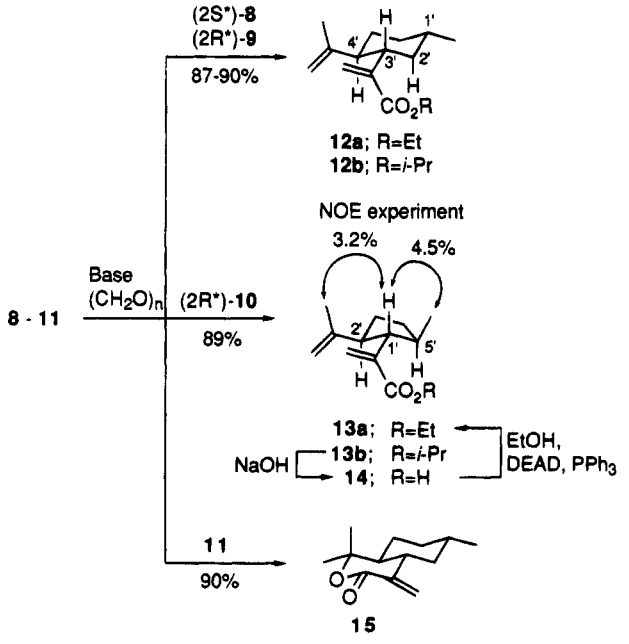
(9) Intramolecular ene reactions of 1,7-dienes with two electron-withdrawing groups such as ester and cyano groups on the terminal carbon of the enophile have been shown to give a mixture of two stereoisomers: see ref 10d.

(10) It has been known that hetero Diels−Alder products are occasionally formed in addition to expected ene products in intramolecular ene reactions using the vinylic ketone or ester moiety as an enophile component. (a) Snider, B. B.; Roush, D. M.; Killinger, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 6023. (b) Narasaka, K.; Hayashi, Y.; Shimada, S. *Chem. Lett.* **1988**, 1609. (c) Tietze, L. F.; Beifuss, U.; Ruther, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1186. (d) Tietze, L. F.; Beifuss, U.; Ruther, M. *J. Org. Chem.* **1989**, *54*, 3120.

Scheme 2



Scheme 3



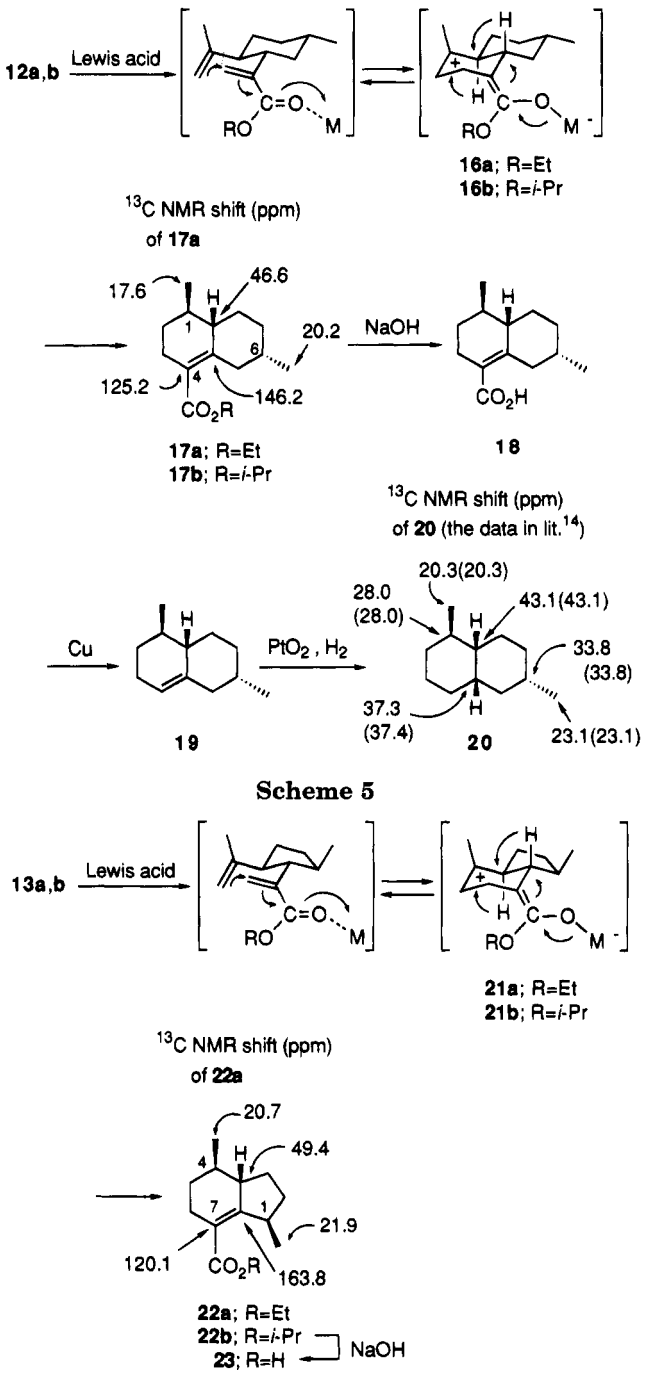
Synthetic Application of the Ene Adducts 8–10. The ene adducts **8–10** containing the phosphinyl group are expected to be versatile building blocks for the synthesis of functionalized cyclic terpenoids. As one of the synthetic applications of the ene adducts, the Wittig–Horner reaction with paraformaldehyde was performed to afford synthetically useful 1,5-dienes, 2-(8′-*p*-menthen-3′-yl)- and 2-(2′-isopropenyl-5′-methylcyclopent-1′-yl)-acrylic acid esters (**12a,b** and **13b**) in high yields (Scheme 3). The coupling constant between H-3′ and H-4′ in the ^{1}H NMR of **12a** was J_{ax-ax} = 11.6 Hz, which indicates that the two tertiary hydrogens are both axial and that the isopropenyl and acrylic acid ester substituents are consequently located *trans*-diequatorial to each other. Furthermore, the methyl chemical shift at δ_C 22.4 was assigned to the equatorial methyl group on the C-1′ by comparison with the corresponding methyl ^{13}C NMR chemical shifts at δ_C 22.9 and at δ_C 18.8 reported for *trans*- and *cis*-8-*p*-menthenes.[11] For the compound **13a** derived from **13b**, the assignment of all *trans* configuration of the substituents on the C-1′, C-2′, and C-5′ of the cyclopentane ring was made by NOE experiments which show the NOE enhancements of 4.5% between H-1′ and CH_3-5′, and of 3.2% between H-1′ and isopropenyl methyl (Scheme 3).

The α-phosphinyl δ-lactone **11** similarly undergoes the Wittig–Horner reaction with paraformaldehyde to afford the 4-methyleneoctahydro-2-benzopyran-3-one **15** in 90% yield.

In further attempts to develop new routes to bicyclic systems, we have studied Lewis-acid- and palladium-catalyzed intramolecular ene reactions of the 1,5-dienes prepared above. For instance, treatment of **12a** with weak Lewis acids such as $TiCl_2(Oi\text{-}Pr)_2$ and Et_2AlCl in CH_2Cl_2 led to none of the expected ene product, but only unreacted **12a** was recovered. However, we found that the use of a stronger Lewis acid, $EtAlCl_2$, in CH_2Cl_2 gave successfully a bicyclic compound, ethyl 1,6-dimethyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-4-carboxylate (**17a**), albeit in low yield (13% yield) (entry 20). To elucidate the relative stereochemistry of **17a**, the compound **17a** was hydrolyzed[12] into a carboxylic acid **18**, and the resulting **18** was decarboxylated on heating in quinoline containing copper[13] to a dimethyloctalin **19**, which was subsequently hydrogenated into a single diastereomeric 1,6-dimethyldecalin **20** (32% yield from **17a**) (Scheme 4). The diastereomer **20** could be unambiguously assigned as (1*R**,4a*S**,6*S**,8a*S**)-1,6-dimethyldecalin by comparison of its ^{13}C chemical shift data with the data in the literature.[14] Accordingly, the ene product **17a** was identified as ethyl (1*R**,6*S**,8a*S**)-1,6-dimethyl-1,2,3,5,6,7,8,-

(11) Pekhk, T. I.; Lippmaa, É. T.; Lysenkov, V. I.; Bardyshev, I. I. *J. Org. Chem. USSR., Engl. Transl.* **1980**, 1694.
(12) Taub, D.; Girotra, N. N.; Hoffsommer, R. D.; Kuo, C. H.; Slates, H. L.; Weber, S.; Wendler, N. L. *Tetrahedron* **1968**, *24*, 2443.
(13) Wiley, R. H.; Smith, N. R. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. 4, p 731.
(14) Pekhk, T. I.; Lakhm, A. Kh.; Musaev, I. A.; Kurashova, E. Kh.; Santsn, P. I. *Neftekhimiya* **1976**, *16* (5), 663.

Scheme 4



Scheme 5

8a-octahydronaphthalene-4-carboxylate. The formation of **17a** would be, therefore, explained by two 1,2-hydride shifts[2f,15] of the zwitterionic intermediate **16a**, which is reversibly formed by complexation of **12a** with excess of $EtAlCl_2$ (Scheme 4). When the reaction was carried out in $ClCH_2CH_2Cl$ instead of CH_2Cl_2, the yield of **17a** was remarkably improved up to 60% yield (entry 21). In contrast to **12a**, similar treatment of **12b** with $EtAlCl_2$ in $ClCH_2CH_2Cl$ gave no bicyclic compound **17b** corresponding to **17a**. The difference in reactivities between **12a** and **12b** would be explained by easier complexation of $EtAlCl_2$ to the carbonyl oxygen of ethyl ester in **12a** than to that of isopropyl ester in **12b**, that is, in terms of bulkiness of ester substituents. However, in the case

(15) Snider, B. B.; van Straten, J. W.; Rodini, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5872.

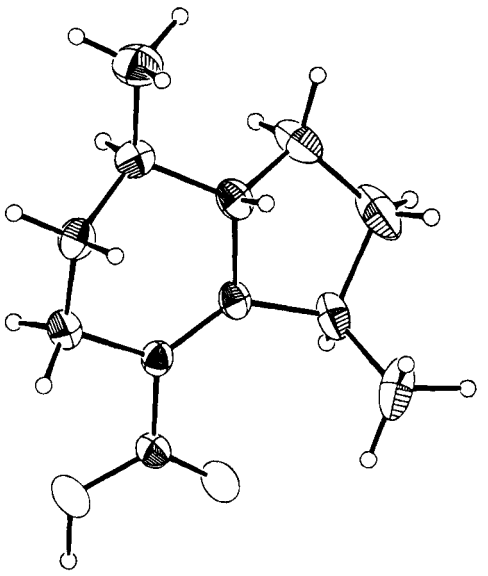


Figure 1. ORTEP diagram of the X-ray structure of **23**. 20% thermal ellipsoids.

using $TiCl_4$ as a Lewis acid, the reaction of **12b** at 0 °C for 1−1.5 h in CH_2Cl_2 and in $ClCH_2CH_2Cl$ successfully produced **17b** in 55 and in 70% yield, respectively (entries 24 and 25).

A similar Lewis-acid-catalyzed intramolecular cyclization of 1,5-dienes **13a,b** led to the corresponding annulated compounds (1*R**,3a*S**,4*R**)-1,4-dimethyl-2,3,3a,4,5,6-hexahydroindene-7-carboxylic acid esters **22a,b** in 55−80% yields (entries 26 and 28) (Scheme 5). Although the relative arrangement of the substituents on the hexahydroindene ring in **22a,b** can be expected to be on the same face on the basis of the results of the ene reaction using **12a,b**, determination of the relative stereochemistries of **22a,b** was similarly unsuccessful by analysis of proton−proton coupling constants and NOE experiments. Finally, the stereochemistry of **22a,b** was confirmed by X-ray analysis[16] (Figure 1) of the corresponding carboxylic acid **23** derived from **22b**. As expected, the structures of **22a,b** were concluded as (1*R**,3a*S**,4*R**)-1,4-dimethyl-2,3,3a,4,5,6-hexahydroindene-7-carboxylic acid esters.

In general, it has been found that in the ene reaction with alkenes, α,β-unsaturated carbonyl compounds such as acrolein, methyl vinyl ketone, etc. undergo preferably an olefin-ene reaction rather than a carbonyl-ene reaction to form δ,ϵ-unsaturated carbonyl compounds.[17] Since it is of interest to examine whether α,β-unsaturated aldehydes **25** and **27**, derived from **12b** and **13b**, undergo an olefin-ene type of cyclization by analogy to the reaction of the esters **12a,b** and **13a,b**, or give a carbonyl-ene reaction, we have further investigated the Lewis-acid-

(16) X-ray crystallographic analysis of **23**. $C_{12}H_{18}O_2$, M = 194.27, monoclinic, space group $P2_1/c$, a = 8.232(6), b = 9.107(6), c = 15.478(6) Å, β = 103.98(4)°, V = 1126(1) Å^3, Z = 4, D_{calc} = 1.146 g cm^{-3}, graphite monochromated radiation λ(Mo K$_\alpha$) = 0.71069 Å, μ = 0.76 cm^{-1}, T = 20.0 °C. Data collected on a Rigaku AFC7R diffractometer. Structure solved by direct methods. Final agreement statistics are: R = 0.046, R_w = 0.050. The authors have deposited the atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

(17) (a) Kruk, C.; Velzen, J. C. v.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 139. (b) Snider, B. B. *J. Org. Chem.* **1974**, *39*, 255. (c) Snider, B. B.; Deutsch, E. A. *J. Org. Chem.* **1983**, *48*, 1822. (d) Moore, L.; Gooding, D.; Wolinsky, J. *J. Org. Chem.* **1983**, *48*, 3750. (e) Kato, N.; Wu, X.; Tanaka, S.; Takeshita, H. *Chem. Lett.* **1989**, 91.

Table 2. Lewis Acid-Promoted Cyclization of 12a,b and 13a,b

entry	starting material	Lewis acid	solvent	reaction conditions[a] temp/°C	time/h	product (yield/%)[b]
17	**12a**	$TiCl_2(Oi\text{-}Pr)_2$[c]	CH_2Cl_2	rt	48	
18	**12a**	Et_2AlCl	CH_2Cl_2	rt	12	
19	**12a**	$SnCl_4$	CH_2Cl_2	rt	12	
20	**12a**	$EtAlCl_2$	CH_2Cl_2	rt	12	**17a** (13)
21	**12a**	$EtAlCl_2$	$ClCH_2CH_2Cl$	rt	12	**17a** (60)
22	**12a**	$TiCl_4$[d]	CH_2Cl_2	0	4	**17a** (33)
23	**12b**	$EtAlCl_2$	$ClCH_2CH_2Cl$	rt	12	
24	**12b**	$TiCl_4$	CH_2Cl_2	0	1	**17b** (55)
25	**12b**	$TiCl_4$	$ClCH_2CH_2Cl$	0	1.5	**17b** (70)
26	**13a**	$EtAlCl_2$	$ClCH_2CH_2Cl$	rt	12	**22a** (55)
27	**13b**	$EtAlCl_2$	$ClCH_2CH_2Cl$	rt	12	
28	**13b**	$TiCl_4$	$ClCH_2CH_2Cl$	0	2	**22b** (80)

[a] All reactions were carried out in the presence of 1.5 equiv of Lewis acid, unless otherwise noted. [b] Isolated yield by column chromatography. [c] Prepared *in situ* from $TiCl_4$ and $Ti(Oi\text{-}Pr)_4$. [d] In the presence of 1.2 equiv of $TiCl_4$.

Table 3. Lewis Acid-Promoted Cyclization of 25 and 27

entry	starting material	Lewis acid	reaction conditions[a] temp/°C	time/h	product (yield/%)[b] 28, 29	30, 31
29	**25**	$ZnBr_2$	rt	0.5	**28** (54)	**30** (3)
30	**25**	$ZnCl_2$	rt	0.5	**28** (40)	
31	**25**	Et_2AlCl	rt	0.5	**28** (12)	**30** (56)
32	**25**	Et_2AlCl	−78	0.5	**28** (20)	**30** (63)
33	**25**	$BF_3{\cdot}OEt_2$	−78	0.5		**30** (54)
34	**25**	$SnCl_4$	−78	0.5		**30** (71)
35	**27**	$ZnBr_2$	rt	1	**29** (59)	
36	**27**	Et_2AlCl	−78	3	**29** (28)	
37	**27**	$BF_3{\cdot}OEt_2$	−78	1	**29** (21)	
38	**27**	$SnCl_4$	−78	1	**29** (18)	

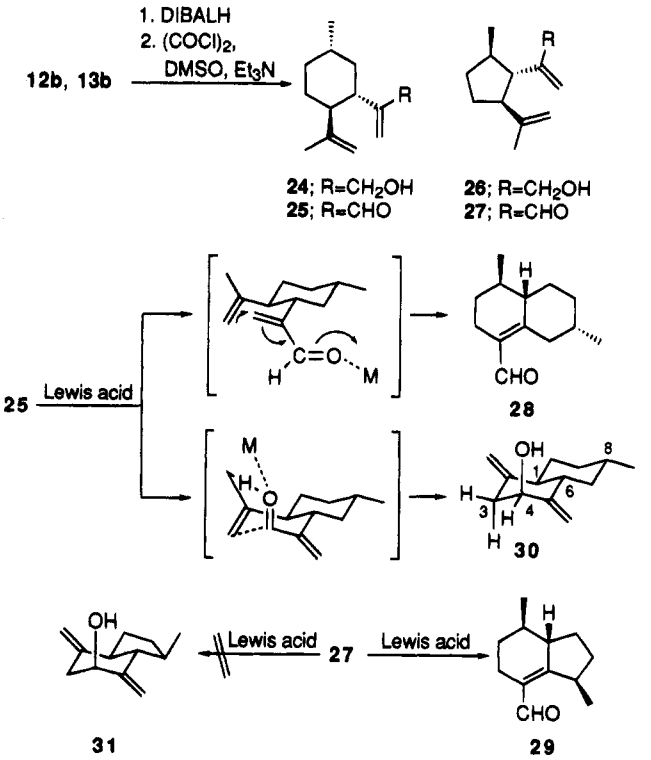
[a] All reactions were carried out in CH_2Cl_2 in the presence of 1.5 equiv of Lewis acid. [b] Isolated yield by chromatography.

catalyzed reaction of the aldehydes **25** and **27** under various conditions. For instance, treatment of **25** with $ZnCl_2$ at room temperature led to the olefin-ene type of cyclization product **28** (40%) as a single product, while the $ZnBr_2$-catalyzed reaction gave a mixture of **28** (54%) and the carbonyl-ene product **30** (3%) (entries 29 and 30 in Table 3). In contrast, using Et_2AlCl instead of $ZnCl_2$ and $ZnBr_2$ under similar conditions, the carbonyl-ene product **30** (56%) was predominantly formed accompanying a small amount of **28** (12%) (entry 31). Also, upon treatment with Et_2AlCl, $BF_3{\cdot}OEt_2$, or $SnCl_4$ at −78 °C, the aldehyde **25** underwent selectively the carbonyl-ene reaction to afford **30** in 54−71% yields (entries 32−34).

These results have demonstrated that the ene reaction is controlled by the strength of Lewis acid; that is, strong Lewis acids cause the carbonyl-ene reaction, while weak Lewis acids give rise to the olefin-ene type of cyclization. The *S** stereochemistry of C-4 for **30**, namely the axial orientation of the hydroxyl group, was confirmed on the basis of the axial−equatorial coupling constant J_{ax-eq} = 3.1 Hz between H^{ax}-3 and H^{eq}-4 in the ^1H NMR (Scheme 6). Unlike aldehyde **25**, the Lewis-acid-induced cyclization of the aldehyde **27** under similar conditions led to only the olefin-ene type of cyclization product **29** in lower yields, regardless of variation of Lewis acid (entries 35−38) (Scheme 6). This result suggests that, in the case using **27**, the formation of the olefin-ene type of cyclization product **29** is sterically more favorable than that of the carbonyl-ene reaction product **31**.

We have been also interested in the possibility of the application of the 1,5-dienes to palladium-catalyzed metallo-ene reaction[18] for the construction of bicyclic systems. Heating the acetate **32** prepared from **24** with $Pd_2(dba)_3{\cdot}CHCl_3$ (0.07 equiv) and PPh_3 (0.2 equiv) in AcOH at 110 °C for 10 h furnished a 48% yield of 2,5,8-trimethyl-1,2,3,4-tetrahydronaphthalene (**34**) as a single product. The formation of **34** can be easily rationalized in terms of aromatization of the initially formed palladium-ene adduct **33** (Scheme 7).

Scheme 6



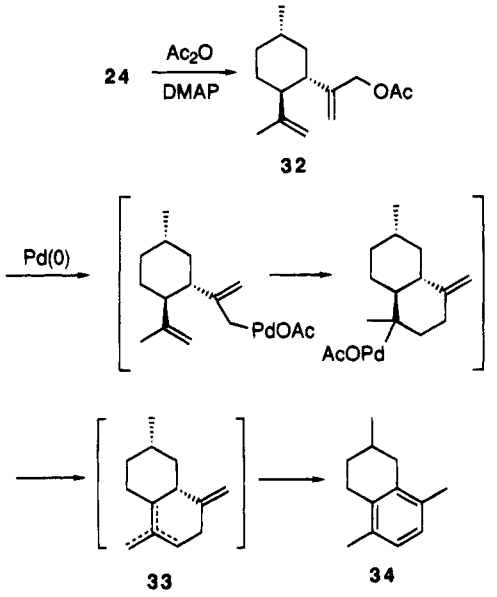
Synthesis of Cadalane and Valerenic Acid Sesquiterpenoids. The cadalane[19] series of sesquiterpenes, which are represented with β-cadinene (**35**), are isolated from high-boiling hydrocarbon fractions of numerous essential oils of *Mentha piperita*,[20] *Pinus silivestris*,[21] *Shorea robusta*,[22] etc. They are used as an ingredient of perfumery preparations, etc., and characterized to be

(18) For a review, see: Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38.

(19) (a) Iwasaki, S.; Nozoe, S. *Natural Products Chemistry*; Nakanishi, K., Goto, T., Ito, S., Natori, S., Nozoe, S., Eds.; Kodansha LTD: Tokyo; Academic Press, Inc.: New York and London, 1974; Vol. 1, Chap. 3. (b) Bryant, R. *Rodd's Chemistry of Carbon Compounds*; Coffey, S., Ed.; Elsevier Publishing Co.: Amsterdam, London, New York, 1969; Vol. 2, Chap. 13.

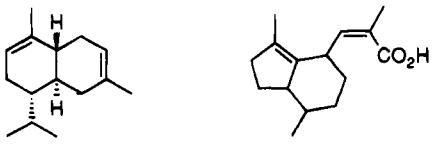
(20) Vlahov, R.; Holub, M.; Ognjanov, I.; Herout, V. *Collect. Czech. Chem. Commun.* **1967**, *32*, 808. Vlahov, R.; Holub, M.; Herout, V. *Collect. Czech. Chem. Commun.* **1967**, *32*, 822.

Scheme 7



natural substances having a 4-isopropyl-1,6-dimethylnaphthalene skeleton.

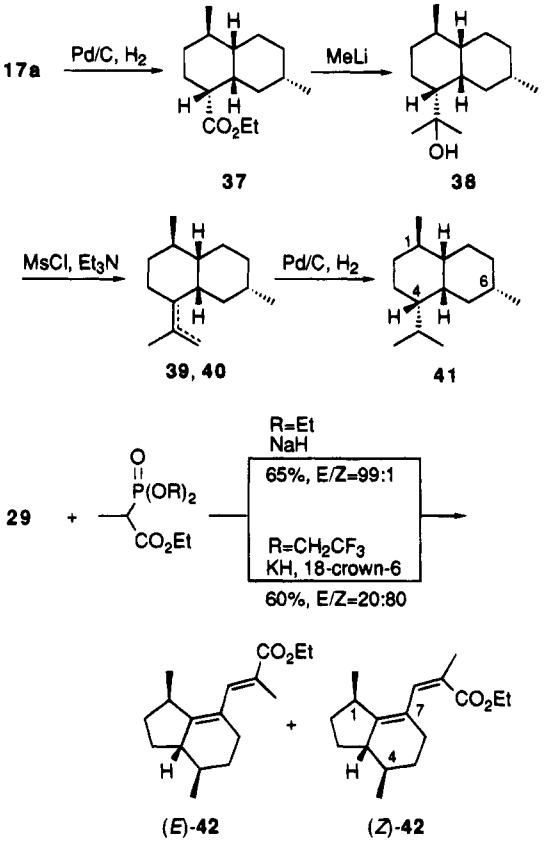
Valerenic acid (**36**), showing the spasmolytic effects, was isolated from *Valeriana officinals* L. roots and is characterized to be a sesquiterpene containing a novel type of carbon skeleton.[19b,23]



β-Cadinene (**35**) Valerenic acid (**36**)

Accordingly, as an extension of this work, we have been interested in development of a convenient route to cadalane and valerenic acid sesquiterpenoids, *via* the above-mentioned Lewis-acid-catalyzed cyclization products **17a** and **29**. Hydrogenation of **17a** over Pd/C at low hydrogen pressure (3 atm) easily gave the compound **37** (95%),[24] which was treated with 2 equiv of MeLi in THF to lead to dihydroveticadinol[25] (**38**) (63%) having the cadalane skeleton. Mesylation of **38** with MsCl, followed by hydrogenation over Pd/C afforded the desired (1*R**,6*S**)-amorphane (**41**),[19a] a *cis*-fused diastereomer of decahydrocadalenes, in 64% yield (Scheme 8). Furthermore, we sought to investigate approaches to building the valerenic acid derivatives. For the introduction of a methacrylate moiety at the C-7 position of a hexahydroindene ring, the compound **29** was treated with an ethyl diethylphosphonopropionate carbanion, generated from treatment of ethyl 2-diethylphosphonopropionate with NaH, to give

Scheme 8



stereoselectively valerenic acid analogue (*E*)-**42** in 65% yield (*E*/*Z* = 99:1). Since the naturally occurring valerenic acid possesses the (*Z*)-acrylic acid moiety, an ethyl bis(trifluoroethyl)phosphonopropionate carbanion[26] was used in the reaction with **29** to result in predominantly (*Z*)-**42** in good yield (60%, *E*/*Z* = 20:80) as expected (Scheme 8).

In conclusion, we note the following results of this investigation: (1) the vinylphosphonates **4**, **6**, **7** have been proven to act as very useful enophiles in intramolecular ene reactions; (2) the resulting ene products were applied to the synthesis of various bicyclic compounds; (3) an effective method for the synthesis of cadalane and valerenic acid sesquiterpenoids was provided.

Experimental Section

Materials. $TiCl(O\textit{i}\text{-}Pr)_3$ and $TiCl(OEt)_3$ were prepared according to the reported procedure.[7] $TiCl_2(O\textit{i}\text{-}Pr)_2$ was prepared *in situ* from $TiCl_4$ and $Ti(O\textit{i}\text{-}Pr)_4$. Commercial 0.93 M solution of $EtAlCl_2$ and Et_2AlCl in hexane were used. Ethyl bis(trifluoroethyl)phosphonopropionate was prepared according to the literature procedure.[26]

General. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a JEOL JNM-FX-60, JEOL JNM-EX-270, or Bruker AMX-400 spectrometer, operating ^1H NMR at 59.8 or 270 MHz, and ^{13}C NMR at 15.0, 67.8, or 101 MHz, with Me_4Si as an internal standard. DEPT, NOESY, 2D proton–proton and proton–carbon correlations were used when necessary, to assign ^1H and ^{13}C NMR spectra. IR spectra were recorded with a Shimadzu IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer. Melting points were measured in open capillary tubes and are uncorrected. Gas chromato-

(21) Zabza, A.; Romanuk, M.; Herout, V. *Collect. Czech. Chem. Commun.* **1966**, *31*, 3373. Westfelt, L. *Acta Chem. Scand.* **1966**, *20*, 2852.

(22) Paknikar, S. K.; Bhattacharyya, S. C. *Perfum. Essent. Oil Rec.* **1961**, *52*, 233.

(23) Büchi, G.; Popper, T. L.; Stauffacher, D. *J. Am. Chem. Soc.* **1960**, *82*, 2962. Krepinsky, J.; Sykora, V.; Zvonkova, E.; Herout, V. *Collect. Czech. Chem. Commun.* **1965**, *30*, 553.

(24) Stereochemistry of the hydrogenation product **37** was assigned as the cis-fused decalin structure **37** (see Scheme 8) on the basis of the result of hydrogenation of **19**.

(25) The stereochemistries of naturally occurring veticadinol and dihydroveticadinol have not been reported, see: Chiurdoglu, G.; Delsemme, A. *Bull. Soc. Chim. Belg.* **1961**, *70*, 5.

(26) The Wittig–Horner reaction of the ethyl bis(trifluoroethyl)-phosphonopropionate carbanion with aldehydes is well-known to produce (*Z*)-unsaturated esters stereoselectively, see: Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405.

graphic results were obtained with a Shimadzu GC-8A instrument system equipped with a Hicap CBP 10 (Shimadzu capillary column).

Synthesis of Vinylphosphonates. Procedure A. To a solution of citronellal **1** (1.54 g, 10.0 mmol) and triethyl phosphonoacetate **3** (2.24 g, 10.0 mmol) in EtOH (20 mL) was added a catalytic amount of piperidine at room temperature, and then the mixture was stirred under reflux for 30 h. After removal of solvent ethanol, the residue was chromatographed on silica gel (AcOEt:hexane = 1:1) to give (*E*)-**4** and **5**. The compounds (*E*)-**4** and **5** had the following properties.

Ethyl (*E*)-2-(diethoxyphosphinyl)-5,9-dimethyldeca-2,8-dienoate [(*E*)-4]: yield 1.28 g (3.55 mmol, 35.5%); colorless oil; R_f 0.43 [AcOEt−hexane (1:1)]; IR (neat) 1620, 1720 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.92 (3 H, d, J = 6.3 Hz, CH_3-5), 1.00−2.20 (5 H, m, CH and CH_2), 1.33 (9 H, t, J = 6.9 Hz, OCH_2CH_3), 1.60 (3 H, brs, CH=CCH_3), 1.69 (3 H, brs, CH=CCH_3), 2.20−2.60 (2 H, m, PC=CHCH_2), 3.76−4.48 (6 H, m, OCH_2CH_3), 4.80−5.24 (1 H, m, CH=CCH$_3$), 7.11 (1 H, dt, $^3J_{P-H}$ = 23.0 Hz, J = 7.5 Hz, PC=CH); MS m/z 360 (M^+). Anal. Calcd for $C_{18}H_{33}O_5P$: C, 59.98; H, 9.23%. Found: C, 59.89; H, 9.34%.

Ethyl 2-(diethoxyphosphinyl)-5,9-dimethyldeca-3,8-dienoate (5): yield 1.28 g (3.55 mmol, 35.5%); colorless oil; R_f 0.38 [AcOEt−hexane (1:1)]; IR (neat) 1740 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.82−2.64 (5 H, m, CH and CH_2), 0.99 (3 H, d, J = 6.6 Hz, CH_3-5), 1.28 (3 H, t, J = 7.1 Hz, $COCH_2CH_3$), 1.32 (6 H, t, J = 7.0 Hz, $POCH_2CH_3$), 1.59 (3 H, brs, CH=CCH_3), 1.68 (3 H, d, J = 1.0 Hz, CH=CCH_3), 3.66 (1 H, dd, $^2J_{P-H}$ = 23.6 Hz, J = 8.6 Hz, PCH), 4.06 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 4.15 (4 H, dq, $^3J_{P-H}$ = 7.0 Hz, J = 7.0 Hz, $POCH_2CH_3$), 4.82−5.28 (1 H, m, CH=CCH$_3$), 5.44−5.64 (2 H, m, PCHCH=CH); HRMS calcd for $C_{18}H_{33}O_5P$, 360.2028 (M^+), found 360.2074.

Procedure B. To a suspension of NaH (60% dispersion in mineral oil, 0.19 g, 4.8 mmol) in THF (15 mL) was added **3** (1.12 g, 5.00 mmol) in THF (5 mL) at room temperature and the mixture was stirred until an almost clear solution formed. The solution was cooled to −78 °C and treated with $ClTi(OEt)_3$ (8.06 mL of 0.62 M in THF, 5.0 mmol) or $ClTi(O\text{-}i\text{-}Pr)_3$ (3.33 mL of 1.50 M in THF, 5.00 mmol). After the mixture was stirred at room temperature for 1.5 h, an aldehyde **1** or **2** (5.00 mmol) was added to the solution, and the reaction mixture was stirred at this temperature for 4 h. The reaction mixture was poured on 4% aqueous HCl and extracted with Et_2O, and the extract was washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on silica gel to afford (*Z*)-**4**, (*Z*)-**6**, or (*Z*)-**7**. The compounds (*Z*)-**4**, (*Z*)-**6**, (*Z*)-**7** had the following physical properties.

Ethyl (*Z*)-2-(diethoxyphosphinyl)-5,9-dimethyldeca-2,8-dienoate [(*Z*)-4]: yield 0.92 g (2.6 mmol, 52%); colorless oil; R_f 0.50 [AcOEt−hexane (1:1)]; IR (neat) 1615, 1725 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.95 (3 H, d, J = 6.2 Hz, CH_3-5), 1.10−2.24 (5 H, m, CH and CH_2), 1.33 (9 H, t, J = 7.3 Hz, OCH_2CH_3), 1.61 (3 H, brs, CH=CCH_3), 1.69 (3 H, brs, CH=CCH_3), 2.73 (2 H, ddd, J = 7.6, 7.6 Hz, $^4J_{P-H}$ = 2.9 Hz, PC=CHCH_2), 4.15 (4 H, dq, $^3J_{P-H}$ = 7.3 Hz, J = 7.3 Hz, $POCH_2CH_3$), 4.25 (2 H, q, J = 7.3 Hz, OCH_2CH_3), 4.82−5.26 (1 H, m, CH=CCH$_3$), 7.51 (1 H, dt, $^3J_{P-H}$ = 46.1 Hz, J = 7.6 Hz, PC=CH); MS m/z 360 (M^+). Anal. Calcd for $C_{18}H_{33}O_5P$: C, 59.98; H, 9.23%. Found: C, 59.85; H, 9.29%.

Isopropyl (*Z*)-2-(diethoxyphosphinyl)-5,9-dimethyldeca-2,8-dienoate [(*Z*)-6]: yield 1.61 g (4.30 mmol, 86.0%); colorless oil; R_f 0.49 [AcOEt−hexane (1:1)]; IR (neat) 1610, 1720 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.94 (3 H, d, J = 6.3 Hz, CH_3-5), 1.04−2.22 (5 H, m, CH and CH_2), 1.30 (6 H, d, J = 6.3 Hz, $OCH(CH_3)_2$), 1.33 (6 H, t, J = 7.3 Hz, $POCH_2CH_3$), 1.60 (3 H, brs, CH=CCH_3), 1.69 (3 H, brs, CH=CCH_3), 2.68 (2 H, ddd, J = 7.6, 7.6 Hz, $^4J_{P-H}$ = 3.1 Hz, PC=CHCH_2), 4.14 (4 H, dq, $^3J_{P-H}$ = 7.3 Hz, J = 7.3 Hz, $POCH_2CH_3$), 4.84−5.52 (1 H, m, CH=CCH$_3$), 5.10 (1 H, septet, J = 6.3Hz, OCH(CH$_3$)$_2$), 7.49 (1 H, dt, $^3J_{P-H}$ = 46.3 Hz, J = 7.6 Hz, PC=CH); MS m/z 374 (M^+). Anal. Calcd for $C_{19}H_{35}O_5P$: C, 60.95; H, 9.42%. Found: C, 60.88; H, 9.48%.

Isopropyl (*Z*)-2-(diethoxyphosphinyl)-4,8-dimethylnona-2,7-dienoate [(*Z*)-7]: yield 0.97 g (2.7 mmol, 54%); colorless oil; R_f 0.39 [AcOEt−hexane (1:2)]; IR (neat) 1615, 1715 cm^{-1}; ^1H NMR (59.8 MHz) δ 1.06 (3 H, d, J = 6.6 Hz, CH_3-4), 1.10−1.50 (5 H, m, CH and CH_2), 1.30 (6 H, d, J = 6.3 Hz, $OCH(CH_3)_2$), 1.33 (6 H, t, J = 7.0 Hz, $POCH_2CH_3$), 1.57 (3 H, brs, CH=CCH_3), 1.67 (3 H, brs, CH=CCH_3), 4.15 (4 H, dq, $^3J_{P-H}$ = 7.0 Hz, J = 7.0 Hz, $POCH_2CH_3$), 4.84−5.48 (1 H, m, CH=CCH$_3$), 5.09 (1 H, septet, J = 6.3 Hz, OCH(CH$_3$)$_2$), 7.49 (1 H, dt, $^3J_{P-H}$ = 46.1 Hz, J = 10.9 Hz, PC=CH); MS m/z 360 (M^+). Anal. Calcd for $C_{18}H_{33}O_5P$: C, 59.98; H, 9.23%. Found: C, 59.78; H, 9.20%.

General Procedure for Intramolecular Ene Reaction of Vinylphosphonates 4, 6, and 7. To a stirred solution of a vinylphosphonate **4**, **6**, or **7** (2.0 mmol) in CH_2Cl_2 (16 mL) was added a Lewis acid (3.0 mmol) under a nitrogen atmosphere. After the reaction mixture was stirred for 0.5−20 h, the reaction was quenched by the slow addition of 4% aqueous HCl. The mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated *in vacuo*. Column chromatography of the residue on silica gel gave (2*S**)-**8**, (2*R**)-**8**, (2*R**)-**9**, and/or **11** or (2*R**)-**10**. The yields of the products and reaction conditions were summarized in Table 1. The compounds **8**−**11** had the following properties.

Ethyl (2*S,1′*S**,3′*S**,4′*S**)-2-(diethoxyphosphinyl)-2-(8′-*p*-menthen-3′-yl)acetate [(2*S**)-8]**: colorless oil; R_f 0.43 [AcOEt−hexane (1:1)]; IR (neat) 1640, 1730 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.90 (3 H, d, J = 5.4 Hz, CH_3-1′), 1.06−2.40 (9 H, m, CH and CH_2), 1.29 (9 H, t, J = 7.0 Hz, OCH_2CH_3), 1.66 (3 H, s, CH_2=CCH_3), 3.25 (1 H, d, J_{P-H} = 21.7 Hz, PCH), 4.10 (2 H, q, J = 7.0 Hz, OCH_2CH_3), 4.13 (4 H, dq, $^3J_{P-H}$ = 7.0 Hz, J = 7.0 Hz, $POCH_2CH_3$), 4.68−4.90 (2 H, m, CH_2=CCH$_3$); MS m/z 360 (M^+). Anal. Calcd for $C_{18}H_{33}O_5P$: C, 59.98; H, 9.23%. Found: C, 59.74; H, 9.32%.

Ethyl (2*R,1′*S**,3′*S**,4′*S**)-2-(diethoxyphosphinyl)-2-(8′-*p*-menthen-3′-yl)acetate [(2*R**)-8]**: colorless oil; R_f 0.35 [AcOEt:hexane (1:2)]; IR (neat) 1645, 1740 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.93 (3 H, d, J = 4.5 Hz, CH_3-1′), 1.08−2.76 (9 H, m, CH and CH_2), 1.27 (3 H, t, J = 7.1 Hz, OCH_2CH_3), 1.33 (6 H, t, J = 7.1 Hz, $POCH_2CH_3$), 1.62 (3 H, s, CH_2=CCH_3), 3.16 (1 H, dd, $^2J_{P-H}$ = 26.1 Hz, J = 2.2 Hz, PCH), 4.13 (4 H, dq, $^3J_{P-H}$ = 7.1 Hz, J = 7.1 Hz, $POCH_2CH_3$), 4.16 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 4.68−4.92 (2 H, m, CH_2=CCH$_3$); HRMS calcd for $C_{18}H_{33}O_5P$, 360.2064 (M^+), found 360.2078. Anal. Calcd for $C_{18}H_{33}O_5P$: C, 59.98; H, 9.23%. Found: C, 59.75; H, 9.16%.

Isopropyl (2*R,1′*S**,3′*S**,4′*S**)-2-(diethoxyphosphinyl)-2-(8′-*p*-menthen-3′-yl)acetate [(2*R**)-9]**: colorless oil; R_f 0.39 [AcOEt−hexane (1:2)]; IR (neat) 1640, 1720 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.93 (3 H, d, J = 4.1 Hz, CH_3-1′), 1.04−2.68 (9 H, m, CH and CH_2), 1.25 (6 H, d, J = 6.3 Hz, $OCH(CH_3)_2$), 1.30 (6 H, t, J = 7.3 Hz, $POCH_2CH_3$), 1.60 (3 H, s, CH_2=CCH_3), 3.13 (1 H, dd, $^2J_{P-H}$ = 24.9 Hz, J = 1.9 Hz, PCH), 4.12 (4 H, dq, $^3J_{P-H}$ = 7.3 Hz, J = 7.3 Hz, $POCH_2CH_3$), 4.66−4.88 (2 H, m, CH_2=CCH$_3$), 5.01 (1 H, septet, J = 6.3 Hz, OCH(CH$_3$)$_2$); MS m/z 374 (M^+). Anal. Calcd for $C_{19}H_{35}O_5P$: C, 60.95; H, 9.42%. Found: C, 60.57; H, 9.19%.

Isopropyl (2*R,1′*S**,2′*S**,5′*R**)-2-(diethoxyphosphinyl)-2-(2′-isopropenyl-5′-methylcyclopent-1′-yl)acetate [(2*R**)-10]**: colorless oil; R_f 0.34 [AcOEt−hexane (1:2)]; IR (neat) 1640, 1720 cm^{-1}; ^1H NMR (59.8 MHz) δ 1.09 (3 H, d, J = 6.6 Hz, CH_3-5′), 1.16−2.60 (7 H, m, CH and CH_2), 1.27 (6 H, d, J = 6.3 Hz, $OCH(CH_3)_2$), 1.33 (6 H, t, J = 7.1 Hz, $POCH_2CH_3$), 1.70 (3 H, s, CH_2=CCH_3), 3.07 (1 H, dd, $^2J_{P-H}$ = 22.7 Hz, J = 3.8 Hz, PCH), 4.15 (4 H, dq, $^3J_{P-H}$ = 7.1 Hz, J = 7.1 Hz, $POCH_2CH_3$), 4.64−4.82 (2 H, m, CH_2=CCH$_3$), 5.07 (1 H, septet, J = 6.3 Hz, OCH(CH$_3$)$_2$); HRMS calcd for $C_{18}H_{33}O_5P$ 360.2028 (M^+), found 360.2064.

(4a*S,6*S**,8a*S**)-4-(Diethoxyphosphoryl)-1,1,6-trimethyl-3,4,4a,5,6,7,8,8a-octahydro-1*H*-2-benzopyran-3-one (11)**: colorless oil; R_f 0.29 [AcOEt−hexane (1:1)]; IR (neat) 1720 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.91 (3 H, d, J = 5.6 Hz, CH_3-6), 1.06−2.62 (9 H, m, CH and CH_2), 1.33 (3 H, t, J = 7.1 Hz, $POCH_2CH_3$), 1.37 (3 H, t, J = 7.1 Hz, $POCH_2CH_3$), 1.37 (6 H, brs, CH_3-1), 2.68 (1 H, dd, $^2J_{P-H}$ = 36.9 Hz, J = 8.2 Hz, PCH), 4.21 (4 H, dq, $^3J_{P-H}$ = 7.1 Hz, J = 7.1 Hz, $POCH_2CH_3$); ^{13}C NMR (15.0 MHz) δ 16.1 ($^3J_{P-C}$ = 6.0 Hz), 21.8, 21.9, 27.3, 28.5, 31.9, 34.4, 34.6 ($^2J_{P-C}$ = 4.3 Hz), 42.5, 46.6 ($^1J_{P-C}$ = 130.7 Hz), 47.5 ($^3J_{P-C}$ = 9.5 Hz), 62.6 ($^2J_{P-C}$ = 6.9 Hz), 63.2 ($^2J_{P-C}$ = 7.7

Hz), 85.2, 165.8 ($^2J_{P-C}$ = 5.2 Hz); HRMS calcd for $C_{16}H_{29}O_5P$ 332.1751, found 332.1719 (M^+). Anal. Calcd for $C_{16}H_{29}O_5P$: C, 57.82; H, 8.79%. Found: C, 57.38; H, 8.83%.

Preparation of Authentic 11. The iodolactonization reaction of 2-(diethoxyphosphinyl)-2-(8′-*p*-menthen-3′-yl)acetic acid, prepared from hydrolysis of (2*R**)-**9** (1.00 g, 2.67 mmol), was carried out, according to the reported procedure,[27] to give an iodo lactone in 71% yield (0.86 g, 1.9 mmol): yellow oil; R_f 0.37 [AcOEt–hexane (1:1)]; IR (neat) 1725 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 0.92 (3 H, d, J = 5.4 Hz, CH_3-6), 1.10–2.68 (9 H, m, CH and CH_2), 1.33 (3 H, t, J = 7.3 Hz, $POCH_2CH_3$), 1.37 (3 H, t, J = 7.3 Hz, $POCH_2CH_3$), 1,58 (3 H, s, CH_3-1), 2.72 (1 H, dd, $^2J_{P-H}$ = 36.6 Hz, J = 7.9 Hz, PCH), 3.32–3.56 (2 H, m, CH_2I), 4.21 (4 H, dq, $^3J_{P-H}$ = 7.9 Hz, J = 7.3 Hz, $POCH_2CH_3$); MS m/z 458 (M^+). Anal. Calcd for $C_{16}H_{28}O_5PI$: C, 41.93; H, 6.16%. Found: C, 41.85; H, 6.35%. Reduction of the iodo lactone (0.55 g, 1.2 mmol) with Bu_3SnH (0.70 g, 2.4 mmol) and AIBN (0.04 g, 0.2 mmol) in THF at 65 °C for 2 h produced **11** in 0.39 g (1.2 mmol, 100%). The spectral data of authentic **11** was consistent with those of **11** obtained in the above experiment.

Epimerization of (2*R)-8 and (2*R**)-9.** To a solution of (2*R**)-**8** or (2*R**)-**9** (0.50 mmol) in THF (10 mL) was added potassium *tert*-butoxide (0.07 g, 0.6 mmol). After the reaction mixture was stirred at room temperature for 10 h, the reaction was quenched by the addition of water. The mixture was extracted with AcOEt, washed with brine, dried over Na_2SO_4, and evaporated in *vacuo*. The residue was chromatogrphed on silica gel to afford (2*R**)-**8** (21%) and (2*S**)-**8** (71%), or (2*R**)-**9** (24%) and (2*S**)-**9** (76%).

Isopropyl (2*S,1′*S**,3′*S**,4′*S**)-2-(diethoxyphosphinyl)-2-(8′-*p*-menthen-3′-yl)acetate [(2*S**)-9]**: colorless oil; R_f 0.29 [AcOEt–hexane (1:2)]; IR (neat) 1645, 1725 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 0.90 (3 H, d, J = 5.1 Hz, CH_3-1′), 1.06–2.42 (9 H, m, CH and CH_2), 1.27 (6 H, d, J = 6.5 Hz, $OCH(CH_3)_2$), 1.33 (6 H, t, J = 6.9 Hz, $POCH_2CH_3$), 1.66 (3 H, s, CH_2=CCH_3), 3.22 (1 H, d, $^2J_{P-H}$ = 22.7 Hz, PCH), 4.16 (4 H, dq, $^3J_{P-H}$ = 6.9 Hz, J = 6.9 Hz, $POCH_2CH_3$), 4.66–4.90 (2 H, m, CH_2=CCH_3), 5.06 (1 H, septet, J = 6.5 Hz, $OCH(CH_3)_2$); MS m/z 374 (M^+). Anal. Calcd for $C_{19}H_{35}O_5P$: C, 60.95; H, 9.42%. Found: C, 60.73; H, 9.45%.

Synthesis of 1,5-Dienes 12a,b and 13b. General Procedure. To a solution of an *in situ*-generated carbanion from a phosphinylacetate, (2*S**)-**8**, (2*R**)-**9**, or (2*R**)-**10** (5.00 mmol), and NaH (60% dispersion in mineral oil, 0.22 g, 5.5 mmol) in THF (20 mL) at room temperature during 0.5 h was added paraformaldehyde (0.30 g, 10 mmol). After the reaction mixture was stirred at room temperature for 2 h, the reaction was quenched with the addition of aqueous NH_4Cl. The mixture was extracted with AcOEt, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel to give **12a,b** and **13b**. The compounds **12a,b**, **13b** had the following properties.

Ethyl (1′*S,3′*S**,4′*S**)-2-(8′-*p*-menthen-3′-yl)acrylate (12a)**: yield 1.06 g (4.50 mmol, 90.0%); colorless oil, R_f 0.21 [AcOEt–hexane (1:24)]; IR (neat) 1620, 1640, 1710 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.89 (3 H, d, J = 6.2 Hz, CH_3-1′), 0.94–1.08 (2 H, m, H^{ax}-2′ and H^{ax}-6′), 1.29 (3 H, t, J = 7.3 Hz, OCH_2CH_3), 1.32–1.55 (2 H, m, H^{ax}-1′ and H^{ax}-5′), 1.56–1.59 (3 H, m, CH_2=CCH_3), 1.66–1.84 (3 H, m, H^{eq}-2′, H^{eq}-5′, and H^{eq}-6′), 2.18 (1 H, ddd, J_{ax-ax} = 11.6, J_{ax-ax} = 11.6, J_{ax-eq} = 3.4 Hz, H^{ax}-4′), 2.62 (1 H, ddd, J_{ax-ax} = 11.6, J_{ax-ax} = 11.6, J_{eq-eq} = 3.4 Hz, H-3′), 4.18 (2 H, q, J = 7.3 Hz, OCH_2CH_3), 4.60–4.63 (1 H, m, one H of CH_2=CCH_3), 4.63–4.66 (1 H, m, one H of CH_2=CCH_3), 5.45–5.47 (1 H, m, one H of C(O)C=CH_2), 6.12 (1 H, d, J = 1.1 Hz, one H of C(O)C=CH_2); ^{13}C NMR (15.0 MHz) δ 14.2, 19.2, 22.4, 32.6, 32.9, 35.0, 42.6, 49.7, 60.4, 111.2, 123.6, 144.3, 148.2, 169.2; MS m/z 236 (M^+). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23%. Found: C, 76.33; H, 10.30%.

Isopropyl (1′*S,3′*S**,4′*S**)-2-(8′-*p*-menthen-3′-yl)acrylate (12b)**: yield 1.09 g (4.36 mmol, 87.2%); colorless oil, R_f 0.23 [AcOEt–hexane (1:24)]; IR (neat) 1620, 1640, 1715 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 0.89 (3 H, d, J = 5.1 Hz, CH_3-1′), 0.96–2.84 (9 H, m, CH and CH_2), 1.26 (6 H, t, J = 6.3 Hz, $OCH(CH_3)_2$), 1.54–1.62 (3 H, m, CH_2=CCH_3), 4.56–4.66 (2 H, m, CH_2=CCH_3), 5.04 (1 H, septet, J = 6.3 Hz, $OCH(CH_3)_2$), 5.38–5.44 (1 H, m, one H of C(O)C=CH_2), 6.08 (1 H, d, J = 1.3 Hz, one H of C(O)C=CH_2); MS m/z 250 (M^+). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.56%. Found: C, 76.66; H, 10.56%.

Isopropyl (1′*S,2′*S**,5′*R**)-2-(2′-isopropenyl-5′-methylcyclopent-1′-yl)acrylate (13b)**: yield 1.05 g (4.45 mmol, 89.0%); colorless oil, R_f 0.46 [AcOEt–hexane (1:24)]; IR (neat) 1620, 1640, 1710 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 0.94 (3 H, d, J = 5.6 Hz, CH_3-5′), 1.26 (6 H, t, J = 6.3 Hz, $OCH(CH_3)_2$), 1.44–2.88 (7 H, m, CH and CH_2), 1.60–1.70 (3 H, m, CH_2=CCH_3), 4.56–4.66 (2 H, m, CH_2=CCH_3), 5.05 (1 H, septet, J = 6.3 Hz, $OCH(CH_3)_2$), 5.47 (1 H, d, J = 1.3 Hz, one H of C(O)C=CH_2), 6.13 (1 H, d, J = 1.3 Hz, one H of C(O)C=CH_2); MS m/z 236 (M^+). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23%. Found: C, 76.12; H, 10.27%.

Preparation of (1′*S,2′*S**,5′*R**)-2-(2′-Isopropenyl-5′-methylcyclopent-1′-yl)acrylic acid (14).** A solution of **13b** (0.47 g, 2.0 mmol) in EtOH–water (1:1, 6 mL) containing NaOH (0.4 g, 10 mmol) was stirred at reflux for 6 h. After evaporation of the solvent under reduced pressure, the mixture was acidified with 4% aqueous HCl and extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on preparative TLC (silica gel, AcOEt:hexane = 1:6) to give the acid **14**: yield 0.28 g (1.4 mmol, 70%); colorless oil; R_f 0.70 [AcOEt–hexane (1:6)]; IR (neat) 1610, 1640, 1700, 2900 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 0.94 (3 H, d, J = 5.6 Hz, CH_3-5′), 1.04–2.92 (7 H, m, CH and CH_2), 1.67 (3 H, s, CH_2=CCH_3), 4.52–4.71 (2 H, m, CH_2=CCH_3), 5.62 (1 H, s, one H of C(O)C=CH_2), 6.32 (1 H, s, one H of C(O)C=CH_2), 10.37 (1 H, brs, CO_2H); MS m/z 194 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%. Found: C, 73.90; H, 9.26%.

Preparation of Ethyl (1′*S,2′*S**,5′*R**)-2-(2′-isopropenyl-5′-methylcyclopent-1′-yl)acrylate (13a).**[28] To a solution of triphenylphosphine (0.53 g, 2.0 mmol), EtOH (0.13 mL), and an acid **14** (0.39 g, 2.0 mmol) in 5 mL of benzene was added diethyl azodicarboxylate (0.35 g, 2.0 mmol) at room temperature. After stirring for 0.5 h, the solvent was removed *in vacuo*, and the residue was chromatographed on preparative TLC (silica gel, AcOEt:hexane = 1:24) to afford **13a**: yield 0.41 g (1.8 mmol, 90%); colorless oil; R_f 0.48 [AcOEt–hexane (1:24)]; IR (neat) 1620, 1640, 1715 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.95 (3 H, d, J = 6.2 Hz, CH_3-5′), 1.29 (3 H, t, J = 7.2 Hz, OCH_2CH_3), 1.50–2.12 (5 H, m, H-5′ and CH_2), 1.65–1.68 (3 H, m, CH_2=CCH_3), 2.38 (1 H, dd, J = 10.4, J = 10.4 Hz, H-1′), 2.61–2.75 (1 H, m, H-2′), 4.19 (2 H, q, J = 7.2 Hz, OCH_2CH_3), 4.62–4.64 (2 H, m, CH_2=CCH_3), 5.49–5.51 (1 H, m, one H of C(O)C=CH_2), 6.17 (1 H, d, J = 1.1 Hz, one H of C(O)C=CH_2); ^{13}C NMR (67.8 MHz) δ 14.2, 18.9, 19.2, 29.4, 32.9, 41.0, 53.8, 53.9, 60.4, 110.3, 124.2, 142.5, 147.1, 167.5; MS m/z 222 (M^+). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98%. Found: C, 75.48; H, 10.12%.

Reaction of 11 with Paraformaldehyde. To a solution of **11** (0.100 g, 0.301 mmol) in THF (6 mL) was added potassium *tert*-butoxide (0.037 g, 0.33 mmol). After the mixture was stirred for 0.5 h, paraformaldehyde (0.045 g, 1.5 mmol) was added at room temperature. The reaction mixture was stirred at this temperature for 0.5 h, and then quenched with water. After similar workup, the residue was chromatographed on preparative TLC (silica gel, AcOEt:hexane = 1:9) to give (4a*S**,6*S**,8a*S**)-1,1,6-trimethyl-4-methylene-3,4,-4a,5,6,7,8,8a-octahydro-1*H*-2-benzopyran-3-one (**15**): yield 0.056 g (0.27 mmol, 90%); colorless oil; R_f 0.19 [AcOEt–hexane (1:9)]; IR (neat) 1620, 1720 cm^{-1}; ^{1}H NMR (59.8 MHz) δ 1.08–2.64 (9 H, m, CH and CH_2), 0.98 (3 H, d, J = 5.6 Hz, CH_3-6), 1.31 (3 H, s, CH_3-1), 1.41 (3 H, s, CH_3-1), 5.62–5.69 (1 H, m, one H of C=CH_2), 6.49–6.56 (1 H, m, one H of C=CH_2); ^{13}C NMR (15.0 MHz) δ 22.2, 27.4, 28.2, 31.8, 33.8, 36.8, 39.4, 46.4, 83.6, 126.0, 138.5, 165.4; MS m/z 208 (M^+). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%. Found: C, 74.70; H, 9.82%.

Lewis-Acid-Catalyzed Cyclization of the 1,5-dienes 12a,b and 13a,b. General Procedure. Lewis-acid-catalyzed

(27) Minami, T.; Hirakawa, K.; Koyanagi, S.; Nakamura, S.; Yamaguchi, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2385.

(28) Mitsunobu, O.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380.

cyclization of 1,5-diene was carried out according to the intramolecular ene reaction procedure as described above to give **17a,b** and **22a,b**. The yields of the products and reaction conditions were summarized in Table 2. The compounds **17a,b**, **22a,b** had the following properties.

Ethyl (1*R,6*S**,8a*S**)-1,6-dimethyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-4-carboxylate (17a)**: colorless oil; R_f 0.40 [Et_2O–hexane (1:30)]; IR (neat) 1710 cm^{-1}; ^1H NMR (270 MHz) δ 0.85 (3 H, d, J = 6.9 Hz, CH_3-1), 0.93 (3 H, d, J = 6.3 Hz, CH_3-6), 1.04–1.31 (3 H, m, H-6 and CH_2), 1.24 (3 H, t, J = 7.1 Hz, OCH_2CH_3), 1.40–1.71 (4 H, m, H-8a and CH_2), 1.79–2.30 (5 H, m, H-1 and CH_2), 2.95 (1 H, ddd, J_{gem} = 13.5 Hz, J = 2.4 Hz, J = 2.4 Hz, one H of H-3), 4.13 (2 H, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR (67.8 MHz) (DEPT) δ 14.3 (CH_3), 17.6 (CH_3), 20.2 (CH_3), 26.2 (CH_2), 28.2 (CH_2), 29.6 (CH_2 and CH), 31.8 (CH_2), 35.1 (CH), 37.2 (CH_2), 46.6 (CH), 59.8 (CH_2), 125.2 (C), 146.2 (C), 169.9 (C); MS m/z 236 (M^+). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23%. Found: C, 76.34; H, 10.49%.

Isopropyl (1*R,6*S**,8a*S**)-1,6-dimethyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-4-carboxylate (17b)**: colorless oil; R_f 0.45 [Et_2O–hexane (1:37)]; IR (neat) 1710 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.80–1.06 (6 H, m, CH_3-1 and CH_3-6), 1.06–2.42 (12 H, m, CH and CH_2), 1.26 (6 H, d, J = 6.3 Hz, $OCH(CH_3)_2$), 2.70–3.16 (1 H, m, one H of H-3), 5.09 (1 H, septet, J = 6.3 Hz, $OCH(CH_3)_2$); ^{13}C NMR (15.0 MHz) δ 17.7, 20.3, 21.9, 26.3, 28.2, 29.7, 29.7, 31.9, 35.2, 37.1, 46.6, 67.0, 125.7, 145.1, 169.4; HRMS calcd for $C_{16}H_{26}O_2$ 250.1931, found 250.1936.

Ethyl (1*R,3a*S**,4*R**)-1,4-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-7-carboxylate (22a)**: colorless oil; R_f 0.45 [AcOEt–hexane (1:24)]; IR (neat) 1710 cm^{-1}; ^1H NMR (270 MHz) δ 0.93–1.30 (4 H, m, H-4 and CH_2), 0.97 (3 H, d, J = 5.6 Hz, CH_3-4), 1.09 (3 H, d, J = 6.9 Hz, CH_3-1), 1.26 (3 H, t, J = 7.2 Hz, OCH_2CH_3), 1.71 (1 H, ddd, J_{gem} = 10.4 Hz, J = 6.1, 1.3 Hz, one H of H-6), 1.89–2.46 (5 H, m, H-3a and CH_2), 3.30 (1 H, dq, J = 7.0, 7.0 Hz, H-1), 4.14 (2 H, q, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR (67.8 MHz) (DEPT) δ 14.2 (CH_3), 20.7 (CH_3), 21.9 (CH_3), 26.7 (CH_2), 30.4 (CH_2), 31.2 (CH_2), 32.3 (CH_2), 34.0 (CH), 37.3 (CH), 49.4 (CH), 59.6 (CH_2), 120.1 (C), 163.8 (C), 167.8 (C); MS m/z 222 (M^+). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98%. Found: C, 75.45; H, 10.22%.

Isopropyl (1*R,3a*S**,4*R**)-1,4-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-7-carboxylate (22b)**: colorless oil; R_f 0.44 [AcOEt–hexane (1:24)]; IR (neat) 1712 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.94–2.50 (16 H, m, CH_3-1, CH_3-4, CH, and CH_2), 1.27 (6 H, d, J = 6.3 Hz, $CH(CH_3)_2$), 2.90–3.64 (1 H, m, H-1), 5.06 (1 H, septet, J = 6.3 Hz, $OCH(CH_3)_2$); ^{13}C NMR (15.0 MHz) δ 20.7, 21.8, 22.0, 26.8, 30.4, 31.3, 32.4, 34.1, 37.3, 49.3, 66.7, 120.5, 162.9, 167.1; MS m/z 236 (M^+). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23%. Found: C, 75.88; H, 9.89%.

Preparation of (1*R,4a*S**,6*S**,8a*S**)-1,6-dimethyldecahydronaphthalene (20).** A solution of **17a** (8.00 g, 33.9 mmol) in DMSO–water (5:3, 160 mL) containing NaOH (15.0 g, 380 mmol) was stirred at 110 °C for 3 h. After the reaction mixture was acidified with 4% aqueous HCl, the mixture was extracted with AcOEt and dried over Na_2SO_4. After evaporation of the solvent *in vacuo*, the residue gave the crude acid **18** (6.95 g, 33.4 mmol, 98.5%). To a solution of **18** (4.00 g, 19.2 mmol) in quinoline (30 mL) was added copper powder (0.40 g, 6.3 mmol) at room temperature. The mixture was heated at 220–237 °C for 3 h, and then copper powder (0.40 g, 6.3 mmol) was added again. After being additionally heated for 3.5 h, the reaction mixture was poured into 4% aqueous HCl, extracted with Et_2O, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was passed through a short silica gel column with hexane as eluant to give a crude compound **19** (2.45 g, 14.9 mmol, 77.6%). Hydrogenation of the crude compound **19** (0.40 g, 2.4 mmol) obtained above was accomplished at 3 atm hydrogen pressure for 75 min in EtOH (12 mL) over PtO_2 (0.080 g, 0.35 mmol) to give **20**: yield 0.17 g (1.0 mmol, 42%; 32% overall yield from **17a**); IR (neat) 1380, 1450, 2900 cm^{-1}; colorless oil; ^1H NMR (59.8 MHz) δ 0.70–2.06 (22 H, m, CH, CH_2, and CH_3); ^{13}C NMR (15.0 MHz) δ 20.3, 21.9, 23.1, 28.0, 28.6, 29.7, 33.1, 33.8, 36.1, 36.8, 37.3, 43.1. The ^{13}C NMR spectral data was consistent with those of a reported (1*R**,-4a*S**,6*S**,8a*S**)-1,6-dimethyldecahydronaphthalene;[14] MS m/z 166 (M^+). Anal. Calcd for $C_{12}H_{22}$: C, 86,67; H, 13.33%. Found: C, 86.36: H, 13.48%.

Preparation of (1*R,3a*S**,4*R**)-1,4-Dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-7-carboxylic Acid (23).**[12] A solution of **22b** (0.357 g, 1.51 mmol) in DMSO–water (5:3, 7.1 mL) containing NaOH (0.68 g, 17 mmol) was stirred at 110 °C for 1 h. After the reaction mixture was acidified with 4% aqueous HCl, the mixture was extracted with AcOEt, and the extract was dried over Na_2SO_4 and evaporated *in vacuo*. The residue was chromatographed on preparative TLC (silica gel, AcOEt:hexane = 1:2) to give the acid **23**: yield 0.203 g (1.05 mmol, 69.5%); mp 116.0–117.0 °C; R_f 0.42 [AcOEt–hexane (1:4)]; IR (KBr) 1640, 1695 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.91–2.70 (16H, m, CH_3-1, CH_3-4, CH, and CH_2), 3.02–3.93 (1H, m, H-1), 9.74 (1H, brs, CO_2H); ^{13}C NMR (15.0 MHz) δ 20.7, 22.0, 26.6, 30.3, 31.2, 32.3, 34.0, 37.7, 49.8, 119.5, 168.0, 173.6; MS m/z 194 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%. Found: C, 73.94; H, 9.40%.

Reduction of Acrylic Acid Esters 12b and 13b. General Procedure. Diisobutylaluminum hydride (13.4 mL, 0.93 M in hexane 12 mmol) was added to the solution of an acrylic acid ester (5.00 mmol) in CH_2Cl_2 (15 mL) at −78 °C. The solution was stirred for 0.5 h at −40 °C and then quenched with MeOH (0.8 mL) at this temperature. The mixture was stirred for 0.5 h at room temperature, filtered through Celite pad, washed with water, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel (AcOEt:hexane = 1:11) to give alcohols **24** and **26**.

(1′*S,2′*S**,5′*S**)-2-(8′-*p*-Menthen-3′-yl)-2-propenol (24)**: yield 0.92 g, (4.7 mmol, 94%); colorless oil; R_f 0.27 [AcOEt–hexane (1:11)]; IR (neat) 1645, 3300 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.89 (3 H, d, J = 5.0 Hz, CH_3-1′), 0.98–2.42 (10 H, m, CH, CH_2 and OH), 1.57–1.70 (3 H, m, CH_2=CCH_3), 3.96–4.08 (2 H, m, CH_2OH), 4.56–4.72 (2 H, m, CH_2=CCH_3), 4.78–4.90 (1 H, m, one H of CH_2=CCH_2OH), 5.02 (1 H, d, J = 1.5 Hz, one H of CH_2=CCH_2OH); MS m/z 194 (M^+). Anal. Calcd for $C_{13}H_{22}O$: C, 80.36; H, 11.41%. Found: C, 80.22; H, 11.47%.

(1′*S,2′*S**,5′*R**)-2-(2′-Isopropenyl-5′-methylcyclopent-1′-yl)-2-propenol (26)**: yield 0.85 g, (4.7 mmol, 94%); colorless oil; R_f 0.39 [AcOEt:hexane (1:6)]; IR (neat) 1648, 3330 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.95 (3 H, d, J = 5.4 Hz, CH_3-5′), 1.32–2.65 (8 H, m, CH, CH_2, and OH), 1.64–1.74 (3 H, m, CH_2=CCH_3), 3.94–4.08 (2 H, m, CH_2OH), 4.58–4.74 (2 H, m, CH_2=CCH_3), 4.80–4.92 (1 H, m, one H of CH_2=CCH_2OH), 5.02–5.14 (1 H, m, one H of CH_2=CCH_2OH); MS m/z 180 (M^+). Anal. Calcd for $C_{12}H_{20}O$: C, 79.95; H, 11.18%. Found: C, 79.75; H, 11.38%.

Oxidation of 24 and 26. General Procedure. To a stirred solution of oxalyl chloride (0.95 g, 7.5 mmol) in CH_2Cl_2(40 mL) was added DMSO (1.18 g, 15.0 mmol) at −78 °C. After the mixture was stirred for 10 min, a CH_2Cl_2 solution (10 mL) of an alcohol **24** or **26** (5.00 mmol) was added to the mixture at this temperature. The reaction mixture was stirred for 1 h at −40 °C and Et_3N (2.8 mL) was added. The reaction mixture was warmed to room temperature and then stirred for 20 min. The reaction was quenched by the addition of aqueous NH_4Cl, and the mixture was extracted with CH_2Cl_2 and dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on silica gel to afford **25** or **27**.

(1′*S,2′*S**,5′*S**)-2-(8′-*p*-Menthen-3′-yl)acrylaldehyde (25)**: yield 0.76 g (4.0 mmol, 80%); colorless oil; R_f 0.58 [AcOEt–hexane (1:11)]; IR (neat) 1640, 1690 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.88 (3 H, d, J = 5.1 Hz, CH_3-1′), 0.96–1.96 (7 H, m, CH and CH_2), 1.48–1.58 (3 H, m, CH_2=CCH_3), 2.18 (1 H, ddd, J_{ax-ax} = 10.7 Hz, J_{ax-ax} = 10.7 Hz, J_{ax-eq} = 2.5 Hz, H-4′), 2.70 (1 H, ddd, J_{ax-ax} = 10.7 Hz, J_{ax-ax} = 10.7 Hz, J_{ax-eq} = 3.2 Hz, H-3′), 4.50–4.66 (2 H, m, CH_2=CCH_3), 5.94 (1 H, s, one H of C(O)C=CH_2), 6.18 (1 H, s, one H of C(O)C=CH_2), 9.43 (1 H, s, CHO); ^{13}C NMR (15.0 MHz) δ 19.0, 22.3, 32.4, 32.7, 34.9, 38.8, 42.0, 49.5, 111.3, 133.8, 147.7, 153.5, 194.0; MS m/z 192 (M^+). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48%. Found: C, 81.47; H, 10.65%.

(1′*S,2′*S**,5′*R**)-2-(2′-Isopropenyl-5′-methylcyclopent-1′-yl)acrylaldehyde (27)**: yield 0.77 g (4.3 mmol, 86%); colorless oil; R_f 0.57 [AcOEt:hexane (1:8)]; IR (neat) 1645, 1690 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.89 (3 H, d, J = 5.9 Hz, CH_3-5′),

1.07–2.77 (7 H, m, CH and CH_2), 1.56–1.66 (3 H, m, CH_2=CCH_3), 4.50–4.62 (2 H, m, CH_2=CCH$_3$), 6.03 (1 H, d, J = 0.6 Hz, one H of C(O)C=CH_2), 6.24 (1 H, s, one H of C(O)C=CH_2), 9.60 (1 H, s, CHO); MS m/z 178 (M^+). 2,4-Dinitrophenylhydrazone (2,4-DNP) derivative: mp 126.0–127.0 °C (EtOH). Anal. Calcd for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63%. Found: C, 59.99; H, 6.02; N, 15.47%.

Intramolecular Cyclization of 25 and 27. General Procedure. To a stirred solution of an aldehyde **25** or **27** (1.00 mmol) in 10 mL of CH_2Cl_2 was added a Lewis acid (1.50 mmol) under a nitrogen atmosphere. The mixture was stirred for 0.5–12 h, quenched with saturated $NaHCO_3$, extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (gradient elution, AcOEt:hexane = 1:11–1:6) to give the compounds **28–30**. The yields of the products and reaction conditions were summarized in Table 3. The compounds **28–30** had the following properties.

(1*R,6*S**,8a*S**)-1,6-Dimethyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-4-carbaldehyde (28)**: colorless oil; R_f 0.54 [AcOEt–hexane (1:9)]; IR (neat) 1670 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.75–1.10 (6 H, m, CH_3-1 and CH_3-6), 1.10–2.72 (12 H, m, CH and CH_2), 3.00–3.52 (1 H, m, one H of H-3), 10.11 (1 H, s, CHO); ^{13}C NMR (15.0 MHz) δ 17.8, 20.4, 21.9, 28.7, 29.0, 30.2, 31.5, 34.7, 35.2, 48.3, 134.6, 160.2, 190.3; HRMS calcd for $C_{13}H_{20}O$ 192.1513, found 192.1494. 2,4-DNP derivative: mp 205.5–206.5 °C (EtOH). Anal. Calcd for $C_{19}H_{24}N_4O_4$: C, 61.28; H, 6.50; N, 15.04%. Found: C, 61.38; H, 6.51; N, 14.98%.

(1*R,3a*S**,4*R**)-1,4-Dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-7-carbaldehyde (29)**: colorless oil; R_f 0.45 [AcOEt–hexane (1:8)]; IR (neat) 1670 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.91–2.70 (16 H, m, CH_3-1, CH_3-4, CH, and CH_2), 3.07–3.75 (1 H, m, H-1), 10.04 (1 H, s, CHO); ^{13}C NMR (15.0 MHz) δ 20.6, 22.6, 24.7, 30.5, 30.7, 32.8, 34.2, 34.8, 49.7, 129.7, 171.6, 191.2; MS m/z 178 (M^+). 2,4-DNP derivative: mp 228.0–229.0 °C (EtOH). Anal. Calcd for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63%. Found: C, 60.15; H, 6.14; N, 15.59%.

(1*S,4*S**,6*S**,8*S**)-8-Methyl-2,5-dimethylenebicyclo[4.4.0]-decan-4-ol (30)**: mp 53–54 °C; IR (KBr) 1650, 3350 cm^{-1}; ^1H NMR (270 MHz) δ 0.96 (3 H, d, J = 5.1 Hz, CH_3-8), 1.35–2.11 (10 H, m, CH, CH_2 and OH), 2.41 (1 H, dm, J_{gem} = 13.7 Hz, H^{ax}-3), 2.54 (1 H, dd, J_{gem} = 13.7 Hz, J_{eq-eq} = 3.1 Hz, H^{eq}-3), 4.36 (1 H, dd, J_{eq-eq} = 3.1 Hz, J_{eq-ax} = 3.1 Hz, H^{eq}-4) 4.75 (1 H, dd, J = 1.7 Hz, J = 1.7 Hz, olefinic H), 4.85–4.89 (2 H, m, olefinic H), 4.94 (1 H, dd, J = 1.7 Hz, J = 1.7 Hz, olefinic H); ^{13}C NMR (67.8 MHz) δ 22.95, 29.09, 32.29, 34.58, 37.89, 42.12, 44.70, 47.04, 74.02, 107.91, 109.34, 147.12, 152.55; MS m/z 192 (M^+). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48%. Found: C, 80.86; H, 10.47%.

Preparation of (1′*S,2′*S**,5′*S**)-2-(8′-*p*-Menthen-3′-yl)-2-propenyl Acetate (32).** After a mixture of alcohol **24** (0.97 g, 5.0 mmol), acetic anhydride (1.02 g, 10.0 mmol), dry pyridine (0.79 g, 10 mmol), and catalytic amount of 4-(dimethylamino)-pyridine was stirred for 15 min at room temperature, aqueous $KHSO_4$ was added to the reaction mixture. The mixture was extracted with AcOEt, washed with aqueous $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was chromatographed on preparative TLC (silica gel, AcOEt:hexane = 1:22) to give **32**: yield 0.99 g (4.2 mmol, 84%); colorless oil; R_f 0.42 [AcOEt–hexane (1:22)]; IR (neat) 1645, 1740 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.90 (3 H, d, J = 4.8 Hz, CH_3-1′), 0.96–2.24 (9 H, m, CH and CH_2), 1.52–1.68 (3 H, m, CH_2=CCH_3), 2.07 (3 H, s, $COCH_3$), 4.51 (2 H, brs, OCH_2), 4.56–4.72 (2 H, m, CH_2=CCH$_3$), 4.92 (1 H, brs, one H of OCH_2C=CH_2), 5.02 (1 H, d, J = 1.3 Hz, one H of OCH_2C=CH_2); MS m/z 236 (M^+). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23%. Found: C, 75.99; H, 10.39%.

Palladium-Catalyzed Metallo-Ene Reaction of 32. A mixture of the acetate **32** (0.30 g, 1.3 mmol), $Pd_2(dba)_3$·$CHCl_3$ (0.092 g, 0.090 mmol) and triphenylphosphine (0.067 g, 0.26 mmol) in AcOH (4.7 mL) was heated at 110 °C for 10 h. After addition of water, the mixture was filtered through a Celite pad. The organic layer was separated from the filtrate and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was chromatographed on preparative TLC (silica gel, hexane) to give 2,5,8-trimethyl-1,2,3,4-tetrahydronaphthalene (**34**): yield 0.11 g (0.63 mmol, 48%); colorless oil; R_f 0.54 (hexane); IR (neat) 1460, 2900 cm^{-1}; ^1H NMR (59.8 MHz) δ 1.08 (3 H, d, J = 5.3 Hz, CH_3-2), 1.16–2.96 (7 H, m, CH and CH_2), 2.18 (6 H, s, CH_3-5 and CH_3-8), 6.88 (2 H, s, H-6 and H-7); MS m/z 174 (M^+). Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41%. Found: C, 89.27; H, 10.63%.

Hydrogenation of 17a. Hydrogenation of the compound **17a** (0.90 g, 3.8 mmol) was accomplished at 3 atm hydrogen pressure for 6 h in EtOH (30 mL) over Pd–C (10%; 0.90 g). After evaporation of the solvent, the residue was filtered through a Celite pad and chromatographed on silica gel (Et_2O: hexane = 1:30) to give ethyl (1*R**,4*R**,4a*S**,6*S**,8a*S**)-1,2,3,4,-4a,5,6,7,8,8a-decahydro-1,6-dimethylnaphthalene-4-carboxylate (**37**): yield 0.86 g (3.6 mmol, 95%); colorless oil; R_f 0.40 (Et_2O:hexane = 1:30); IR (neat) 1735, 2900 cm^{-1}; ^1H NMR (270 MHz) δ 0.84 (3 H, d, J = 6.3 Hz, CH_3-6), 0.87 (3 H, d, J = 6.3 Hz, CH_3-1), 0.90–1.05 (2 H, m, CH_2), 1.06–1.53 (6 H, m, H-1, H-8a, and CH_2), 1.25 (3 H, t, J = 7.2 Hz, OCH_2CH_3), 1.53–1.79 (4 H, m, H-6 and CH_2), 1.91 (1 H, dm, J = 14.0 Hz, one H of H-8), 2.08–2.19 (1 H, m, H-4a), 2.42–2.52 (1 H, m, H-4), 4.13 (2 H, q, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR (67.8 MHz) (DEPT) δ 14.3 (CH_3), 19.7 (CH_3), 22.8 (CH_3 and CH_2), 27.0 (CH), 28.2 (CH_2), 29.2 (CH_2), 31.2 (CH_2), 33.0 (CH), 34.9 (CH_2), 39.4 (CH), 43.1 (CH), 47.6 (CH), 60.0 (CH_2), 175.2 (C); MS (m/z) 238 (M^+). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00%. Found: C, 75.59; H, 11.10%.

Preparation of (1*R,4*R**,4a*S**,6*S**,8a*S**)-α,α,1,6-Tetramethyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-4-naphthalenemethanol (38).** To a solution of **37** (0.65 g, 2.7 mmol) in THF (20 mL) was added dropwise methyllithium (4.95 mL of a 1.10 M Et_2O solution, 5.45 mmol). The mixture was stirred at −78 °C for 1 h and then poured into saturated aqueous ammonium chloride. The organic layer was extracted with Et_2O, washed with brine, and dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on silica gel (AcOEt: hexane = 1:5) to afford **38**: yield 0.39 g (1.7 mmol, 63%); mp 88.5–89.5 °C; IR (KBr) 1370, 1455, 3250 cm^{-1}; ^1H NMR (59.8 MHz) δ 0.74–0.96 (6 H, m, CH_3-1 and CH_3-6), 1.22 (6 H, s, C(CH_3)$_2$OH), 0.74–2.16 (16 H, m, CH, CH_2, and OH); ^{13}C NMR (15.0 MHz) δ 19.8, 22.2, 23.3, 27.7, 28.1, 28.8, 29.0, 29.4, 31.6, 33.3, 36.6, 39.2, 44.6, 52.5, 73.1; MS m/z 166 [M^+ − $(CH_3)_2$-CO], CIMS m/z 207 (M^+ − OH). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58%. Found: C, 80.17; H, 12.27%.

Preparation of (1*R,4*R**,4a*S**,6*S**,8a*S**)-4-Isopropenyl-1,6-dimethyl-1,2,3,4,4a,5,6,7,8,8a-decahydronaphthalene (39) and (1*R**,4a*S**,6*S**,8a*S**)-4-Isopropylidene-1,6-dimethyl-1,2,3,4,4a,5,6,7,8,8a-decahydronaphthalene (40).** To a stirred solution of **38** (0.45 g, 2.0 mmol) and Et_3N (0.64 mL, 6.6 mmol) in Et_2O (20 mL) was added MsCl (0.31 mL, 4.0 mmol) at room temperature. After stirring for 7 days at this temperature, the reaction mixture was poured into water. The mixture was extracted with Et_2O, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was passed through a short silica gel column with hexane. Kugelrohr distillation (75 °C, 3 mmHg) of the crude product gave a 4:1 mixture of **39** and **40:** yield 0.29 g (1.4 mmol, 70%); colorless oil; IR (neat) 1380, 1450, 1645, 2900 cm^{-1}; ^1H NMR (for a mixture of **39** and **40**) (59.8 MHz) δ 0.74–0.98 (6 H, m, CH_3-1 and CH_3-6), 0.98–2.88 (15 H × 0.8, m, CH and CH_2 of **39**, and 14 H × 0.2, m, CH and CH_2 of **40**), 1.64–1.70 (3 H × 0.8, m, CH_2=CCH_3 of **39**, and 6 H × 0.2, m, C=C(CH_3)$_2$ of **40**), 4.42–4.82 (2 H × 0.8, m, CH_2=CCH$_3$ of **39**); ^{13}C NMR (for a mixture of **39** and **40**) (15.0 MHz) δ 20.0, 20.3, 22.7, 23.2, 25.5, 26.0, 27.8, 28.1, 28.6, 28.9, 29.5, 30.0, 30.1, 30.3, 33.7, 36.0, 36.4, 36.9, 39.5, 41.1, 43.4, 44.3, 48.5, 109.3, 120.0, 136.0, 148.3, **39**/**40** = 4/1; HRMS calcd for $C_{15}H_{26}$ 206.2033 (M^+), found 206.2015.

Synthesis of 4-Isopropyl-(1*R,4*S**,4a*R**,6*S**,8a*S**)-1,6-dimethyl-1,2,3,4,4a,5,6,7,8,8a-decahydronaphthalene (41).** Hydrogenation of the mixture of **39** and **40** (0.27 g, 1.3 mmol) was accomplished as described above using Pd-C (10%; 0.3 g) in EtOH (20 mL). After similar workup, Kugelrohr distillation (100 °C, 4 mmHg) of the residue gave **41**: yield 0.24 g (1.2 mmol, 92%); colorless oil; IR (neat) 1380, 1455, 2925 cm^{-1}; ^1H

NMR (270 MHz) δ 0.81 (3 H, d, J = 6.3 Hz, CH_3), 0.86 (3 H, d, J = 7.3 Hz, CH_3), 0.87 (3 H, d, J = 6.6 Hz, CH_3), 0.89 (3 H, d, J = 6.6 Hz, CH_3), 0.92–1.14 (3 H, m, CH and CH_2), 1.20–1.45 (6 H, m, CH and CH_2), 1.52–1.94 (7 H, m, CH and CH_2); ^{13}C NMR (101 MHz) (DEPT) δ 19.9 (CH_3), 20.8 (CH_3), 21.6 (CH_3), 23.2 (CH_3), 25.2 (CH_2), 27.4 (CH), 28.7 (CH_2), 29.0 (CH), 29.7 (CH_2), 29.9 (CH_2), 33.4 (CH), 36.6 (CH_2), 39.0 (CH), 44.2 (CH), 49.1 (CH); MS m/z 208 (M^+), 165, 109. Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54%. Found: C, 86.48; H, 13.35%.

Reaction of 29 with Ethyl Bis(trifluoroethyl)phosphonopropionate. To a suspension of KH (35% dispersion in mineral oil, 0.17 g, 1.5 mmol) in THF (8 mL) was added 18-crown-6 (0.396 g, 1.50 mmol) and ethyl bis(trifluoroethyl)-phosphonopropionate[26] (0.519 g, 1.50 mmol) in THF (4 mL) under a nitrogen atmosphere. After the mixture was stirred for 5.5 h at room temperature, the aldehyde **29** (0.089 g, 0.50 mmol) was added to the mixture and the reaction mixture was stirred for 1.7 h at room temperature. After conventional workup, the residue was chromatographed on preparative TLC (silica gel, AcOEt:hexane = 1:24) to give a 20:80 mixture of (*E*)- and (*Z*)-ethyl 3-[(1*R**,3aS*,4*R**)-1,4-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-inden-7-yl]methacrylate (**42**) [GC, 180 °C, t_R-(*Z*) = 9.9 min and t_R(*E*) = 15.1 min]: yield 0.079 g (0.30 mmol, 60%); colorless oil; R_f 0.43 [AcOEt:hexane (1:24)]; IR (neat) 1630, 1715, 1725 cm^{-1}; ^1H NMR [for a mixture (*Z*)- and (*E*)-**42**] (59.8 MHz) δ 0.92–1.14 (6 H, m, CH_3-1 and CH_3-4), 1.14–3.08 (11 H, m, CH and CH_2), 1.28 (3 H, t, J = 7.2 Hz, OCH_2CH_3), 1.97 (3 H, m, J = 1.6 Hz, $C{=}CCH_3$), 4.17 (2 H, q, J = 7.2 Hz, OCH_2CH_3), 6.34 (1 H × 0.80, brs, *Z*-vinylic H), 7.38 (1 H × 0.20, brs, *E*-vinylic H); ^{13}C NMR [for a mixture (*Z*)- and (*E*)-**42**] (15.0 MHz) δ 13.9, 14.3, 20.8, 21.5, 21.7, 28.1, 29.0, 31.5, 31.8, 33.1, 34.8, 35.8, 36.3, 48.3, 48.6, 60.3, 60.5, 124.6, 124.8, 125.7, 126.9, 135.0, 139.2, 147.5, 151.8, 169.1, 169.9; MS m/z 262 (M^+). Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99%. Found [for a mixture of (*Z*)- and (*E*)-**42**]: C, 77.54; H, 9.68%.

Reaction of 29 with Ethyl 2-(Diethylphosphono)propionate. A solution of the aldehyde **29** (0.55 g, 3.1 mmol) in 7 mL of THF was added to the carbanion generated *in situ* from ethyl 2-(diethylphosphono)propionate (0.80 g, 3.4 mmol) and NaH (60% dispersion in mineral oil, 0.13 g, 3.3 mmol) in THF (15 mL). The reaction was stirred for 32.5 h at room temperature. After workup similar to that described above, the crude product was chromatographed on preparative TLC (silica gel, AcOEt:hexane = 1:24) to give a 0.53 g (2.0 mmol, 65%) of 99:1 of (*E*)- and (*Z*)-**42**. The physical data was consistent with those of (*E*)- and (*Z*)-**42** obtained in the above experiment.

Acknowledgment. We are grateful for financial support of this work by a Grant-in-Aid for Scientific Research (05650861) and (06651011), and by a Grant-in-Aid for Scientific Research on Priority Areas (04217227) from the Japan Ministry of Education, Science and Culture. We also thank the Center for Instrumental Analysis KIT for the use of their facilities.