New Method for Generation of Alkenylidenecarbenes from Propargylic Methanesulfonates and Its Use in Regioselective C—H Insertion Reactions

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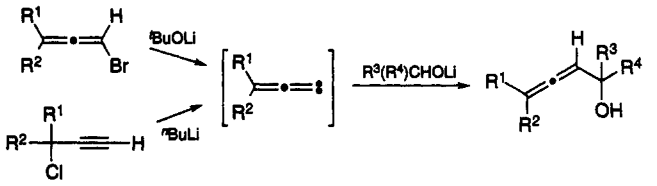
We recently disclosed a novel oxyanionic substituent effect that greatly facilitates regioselective insertion of a variety of carbenes into the α C—H bond of alkoxides.[1,2] The regioselective insertion of carbenes provides a direct method for homologation of alcohols at the α position. The reaction of alkoxides with alkenylidenecarbenes straightforwardly affords allenic alcohols (Scheme 1).[1c] Because the C—H insertion takes place with retention of the configuration of the carbinyl carbon, the reaction affords tertiary allenic alcohols without the loss of enantiomeric integrity of the starting secondary alkoxides. In addition, the reaction proceeds without the formation of propargylic transposition byproducts frequently observed in the reaction of allenic or propargylic organometallics with carbonyl compounds.[3]

Alkenylidenecarbenes are usually generated by interaction of base with propargylic halides or haloallenes.[4] The method, however, is limited to the carbenes with simple structures due to the difficulty in preparation of the corresponding precursors. Development of a new carbene precursor which can tolerate functionalities within the molecule would significantly expand the scope of the regioselective insertion reaction. In connection with our ongoing project on generation of allenic zinc reagents by the reaction of propargylic mesylates with triorganozincates,[5] we had an opportunity to examine generation of alkenylidenecarbenes from the propargylic mesylates. Herein, we wish to report a simple method for generation of alkenylidene carbenes from propargylic mesylates and its application to a transformation of propargylic alcohols to the homologated allenic alcohols by using regioselective insertion of the alkenylidene carbenes, thus generated, into the α C—H bond of alkoxides (Scheme 2).

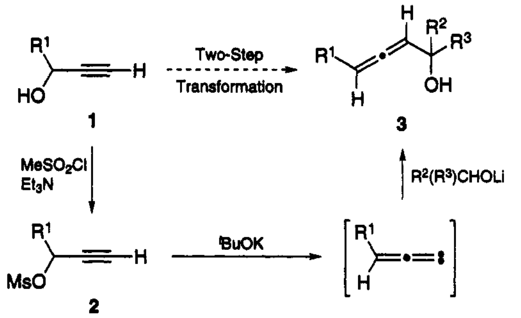
Results and Discussion

The starting mesylates **2** were prepared in quantitative yields by the reaction of propargylic alcohols **1** with methanesulfonyl chloride (1.2 equiv) and triethylamine (1.2 equiv) in CH_2Cl_2 at 0 °C (**2a**; $R^1 = {}^nC_8H_{17}$, 98% yield, **2b**; R^1 = TBDMSO$(CH_2)_5$, 92% yield, **2c**; $R^1 = (Me)_2C{=}CH(CH_2)_2CH(Me)CH_2$, 98% yield, **2d**; R^1 = Me, 93% yield). Treatment of mesylate **2a** with ^{t}BuOK (1.5 equiv) in THF at 0 °C afforded 2-(1,2-undecadienyl)tetrahydrofuran (**4**) in 45% yield (Table 1, entry 1). Formation of **4**, the insertion product of the solvent, clearly demonstrates efficient generation of decenylidenecarbene under these reaction conditions.

Scheme 1



Scheme 2



Mesylate **2a** was treated with ^{t}BuOK in the presence of lithium benzyl oxide (5 equiv)[6] in THF−hexane at 0 °C. The reaction afforded allenic alcohol **3a** in 64% yield with small amount of **4** (<3%) (entry 2). As shown in Table 1, not only lithium benzyl oxide, whose C—H bonds are activated additionally by the adjacent phenyl group,[7] but also a variety of primary and secondary alkoxides underwent a regioselective C—H insertion at the α position to give the corresponding allenic alcohols in moderate yields. Lithium alkoxides were usually prepared in situ by the reaction of the corresponding alcohols with ^{n}BuLi (hexane solution). In entry 3, lithium benzyl oxide, thus prepared, was used after hexane was removed in vacuo. Under these conditions, the yield of insertion product **3a** was improved slightly. Alkenylidenecarbenes bearing the siloxy and alkenyl groups were generated successfully by using propargylic mesylates **2b** and **2c**, respectively. Regioselective insertion of alkoxides with these carbenes furnished the corresponding allenic alcohols **3e**−**j**.

Previously, we demonstrated that alkenylidenecarbenes generated from propargylic chloride underwent C—H insertion stereospecifically with retention of configuration at the carbinyl carbon.[1c] In order to ascertain stereospecificity of the C—H insertion by the alkenylidenecarbenes generated from the mesylates, we examined the reactions of **2d** with *trans*- and *cis*-4-*tert*-butylcyclohexyl oxides. When propargylic mesylate **2d** was treated with ^{t}BuOK in the presence of 5 equiv of lithium *trans*- and *cis*-4-*tert*-butylcyclohexyl oxides, the insertion products *cis*-**3k** and *trans*-**3k** were each obtained in 36% yield (entries 13 and 14). The insertion proceeded again stereospecifically. Careful GC analyses of these reaction

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[1] (a) Harada, T.; Oku, A. *J. Am. Chem. Soc.* **1981**, *103*, 5965. (b) Harada, T.; Akiba, E.; Oku, A. *Ibid.* **1983**, *105*, 2771. (c) Harada, T.; Nozaki, Y.; Oku, A. *Tetrahedron Lett.* **1983**, *24*, 5665. (d) Oku, A.; Yamaura, Y.; Harada, T. *J. Org. Chem.* **1986**, *51*, 3732. (e) Oku, A.; Harada, T.; Hattori, K.; Yamaura, Y.; Nozaki, Y. *Ibid.* **1988**, *53*, 3089.

[2] (a) Evans, D. A.; Baillargeon, D. E. *Tetrahedron Lett.* **1978**, 3315, 3319 and references cited therein. (b) Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994. (c) Ritter, R. H.; Cohen, T. *J. Am. Chem. Soc.* **1986**, *108*, 3718.

[3] Moreau, J.-L. *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Eds.; Wiley: New York, 1980; Chapter 10.

[4] (a) Hartler, H. D. *Carbenes*; Moss, R. A.; Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. II, Chapter 2. (b) Stang, P. J. *Chem. Rev.* **1978**, 78, 383.

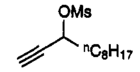
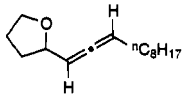
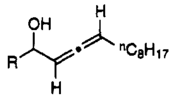
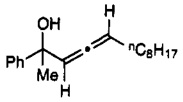
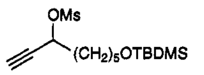
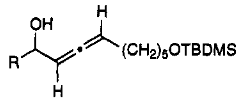
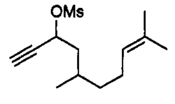
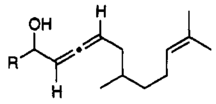
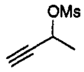
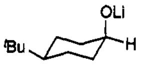
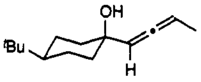
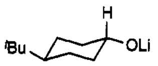
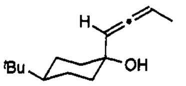
[5] Katsuhira, T.; Harada, T.; Maejima, K.; Osada, A.; Oku, A. *J. Org. Chem.* **1993**, *58*, 6166.

[6] When 2 equiv of lithium benzyl oxide was used, **3a** was obtained in 48% yield.

[7] Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Chapter 7 and references cited therein.

0022-3263/94/1959-4010$04.50/0

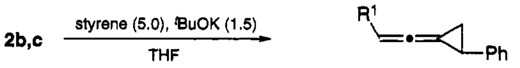
Table 1. C—H Insertion Reactions of Alkenylidenecarbenes Generated from Propargylic Mesylates 2

entry	propargylic mesylate **2**	alkoxide	product	yield (%)
1	 **2a**	*a*	 **4**	45
2	**2a**	$PhCH_2OLi$	 **3a**: R = Ph	64
3[b]	**2a**	$PhCH_2OLi$		80
4	**2a**	$PhCH_2CH_2OLi$	**3b**: R = $PhCH_2$	54
5	**2a**	PrOLi	**3c**: R = Et	57
6	**2a**	$Ph(CH_3)CHOLi$	 **3d**	40
7	 **2b**	$PhCH_2OLi$	 **3e**: R = Ph	64
8	**2b**	$PhCH_2CH_2OLi$	**3f**: R = $PhCH_2$	56
9	**2b**	PrOLi	**3g**: R = Et	58
10	 **2c**	$PhCH_2OLi$	 **3h**: R = Ph	45
11	**2c**	$PhCH_2CH_2OLi$	**3i**: R = $PhCH_2$	42
12	**2c**	PrOLi	**3j**: R = Et	40
13	 **2d**		 *cis*-**3k** (98.5:1.5)[c]	36
14	**2d**		 *trans*-**3k** (3:97)[c]	36

[a] The reaction was carried out in the absence of lithium alkoxides. [b] The reaction was carried out without using hexane as cosolvent. See Experimental Section for details. [c] Ratio of *cis-*:*trans*-**3k** determined by GC analysis.

mixtures indicated that a small amount of the isomerization product was produced in both reactions.[8,9]

Finally, we briefly examined the cyclopropanation by alkenylidenecarbenes generated from the mesylates. Mesylates **2b** and **2c** were treated with ${}^tBuOK$ in the presence of styrene (5 equiv) in THF at 0 °C to rt. These reactions gave cyclopropanes **5a** and **5b** in 68% and 41% yields, respectively (eq 1).


(1)

5a: R^1 = $TBDMSO(CH_2)_5$, 68%

5b: R^1 = $(Me)_2C{=}CH(CH_2)_2CH(Me)CH_2$, 41%

In summary, we have shown that propargylic mesylates, prepared readily and efficiently from the propargylic alcohols, serve as a precursor of alkenylidenecarbenes bearing functional groups such as siloxy and alkenyl. Alkenylidenecarbenes, thus generated, underwent regioselective insertion into the α C—H bond of a variety of lithium alkoxides, providing a simple two-step method for converting propargylic alcohols into the homologated allenic alcohols.

Experimental Section

General Methods. Nuclear magnetic resonance spectra were recorded on a General Electric QE-300 spectrometer (at 300 and 75.6 MHz for ^1H and ^{13}C, respectively). Microanalyses were performed by the Microanalysis Center of Kyoto University. GC analyses were performed with a Shimadzu GC-14B equipped with 20-m PEG-20M and 30-m OV-1 capillary columns. Wakogel C-300 was used for flash chromatography. THF was distilled from sodium benzophenone ketyl. Et_3N, CH_2Cl_2, and DMF were distilled from CaH_2. All the reactions were performed under an argon atmosphere. 6-[(*tert*-Butyldimethylsilyl)oxy]hexanal was prepared from 1,6-hexanediol by monosilylation (imidazole, ${}^tBuMe_2SiCl$ (0.5 equiv), DMF; 57% based on ${}^tBuMe_2SiCl$) followed by PCC oxidation (pyridinium chlorochromate, NaOAc, CH_2Cl_2; 62%). All alcohols used as substrates for C—H insertion reagents were distilled from CaH_2 before use.

Propargylic Alcohols 1a–c. The preparation of 1-undecyn-3-ol (**1a**) is given as a representative example. To a solution of (trimethylsilyl)acetylene (2.70 g, 27.5 mmol) in 19 mL of THF under argon at 0 °C was added ${}^nBuLi$ (1.62 M in hexane) (17.0 mL, 27.5 mmol). The mixture was stirred at −85 °C for 15 min. 1-Nonanal (3.56 g, 4.32 mL, 25.0 mmol) was then added into the resulting solution of lithium (trimethylsilyl)acetylide. After

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[8] *trans*- and *cis*-4-*tert*-butylcyclohexyl oxides of >99% diastereopurities were used in these reactions.

[9] C—H insertion of alkoxides by cyclopropylidenes and alkylidenecarbenes proceeds without stereospecificity.[1d,e]

being allowed to warm to 0 °C over a period of 2 h, the mixture was poured into water and extracted three times with ethyl acetate (50 mL). The combined organic layers were dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was dissolved in 60 mL of methanol solution containing 6 mL of aqueous 3 N NaOH. After being stirred for 1.5 h, the mixture was neutralized with aqueous 1 N HCl and then concentrated *in vacuo* to one fourth of its original volume. Brine (100 mL) was added into the concentrate. The mixture was extracted three times with ethyl acetate (100 mL), and the combined extracts were dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by flash chromatography (5% ethyl acetate in hexane) affording **1a** (>98% pure by GC analysis) in 97% yield. **1a**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.7 Hz), 1.18–1.39 (10H, m), 1.45 (2H, m), 1.71 (3H including OH, m), 2.46 (1H, d, J = 2.1 Hz), 4.37 (1H, dt, J = 2.1 and 6.6 Hz); IR (liquid film) 3330 (br), 3310 (s), 2110 (m), 1465 (s), 1455 (s), 1025 (s), 650 (s), 625 (s) cm^{-1}; MS (CI) m/z (relative intensity) 151 (MH$^+$ − H_2O, 5), 121 (7), 109 (62), 95 (100), 81 (94). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.22; H, 12.02.

The isolated yields and spectral data of **1b** and **1c** are as follows.

8-[(*tert*-Butyldimethylsilyl)oxy]-1-octyn-3-ol (1b): 86% yield, isolated by flash column chromatography (5–20% ethyl acetate in hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.04 (6H, s), 0.89 (9H, s), 1.30–1.58 (6H, m), 1.67–1.76 (2H, m), 1.91 (1H (OH), br d, J = 5.6 Hz), 2.46 (1H, d, J = 2.1 Hz), 3.60 (2H, t, J = 6.4 Hz), 4.37 (1H, br dq, J = 2.1 and 6.2 Hz); ^{13}C-NMR (75.6 MHz, $CDCl_3$) δ 85.0, 72.8, 63.1, 62.2, 37.6, 32.7, 26.0, 25.4, 24.8, 18.4, −5.3; IR (liquid film) 3370 (br), 3300 (s), 2110 (w), 1255 (s), 1100 (s), 835 (s), 775 (s) cm^{-1}; MS (CI) m/z (relative intensity) 257 (MH$^+$, 8), 239 (3), 133 (11), 107 (82), 79 (100); HRMS (CI) calcd for $C_{14}H_{29}O_2Si$ 257.1938, found 257.1943. Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.00. Found: C, 65.27; H, 11.13.

5,9-Dimethyl-8-decen-1-yn-3-ol (1c) (a mixture of diastereomers): 87% yield, isolated by flash column chromatography (10–20% ethyl acetate in hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.92, 0.94 (3H, d, J = 6.5 Hz), 1.12–1.26 (1H, m), 1.29–1.44 (1H, m), 1.47–1.80 (9H, m, including s (3H) at 1.60 and s (3H) at 1.68), 1.82, 1.87 (1H (OH), d, J = 5.8 Hz), 1.88–2.08 (2H, m), 2.464, 2.460 (1H, d, J = 2.1 Hz), 4.40–4.47 (1H, m), 5.090, 5.095 (1H, sept t, J = 1.4 and 7.1 Hz); IR (liquid film) 3350 (br), 3310 (s), 2120 (m), 1380 (s), 1060 (s), 1025 (s) cm^{-1}; MS (CI) m/z (relative intensity) 181 (MH$^+$, 1), 163 (4), 147 (8), 135 (8), 121 (26), 107 (79), 95 (53), 81 (69), 69 (100). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.03; H, 11.16.

General Procedure for Preparation of Propargylic Methanesulfonates 2a–d. To a solution of propargylic alcohol (10 mmol) in CH_2Cl_2 (30 mL) at 0 °C were added Et_3N (1.67 mL, 12 mmol) and methanesulfonyl chloride (0.93 mL, 12 mmol). After being stirred for 15 min, the mixture was poured into aqueous 1 N HCl (50 mL) and extracted three times with ether. The combined organic extracts were washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by flash chromatography gave the pure propargylic methanesulfonates. The isolated yields and spectral data are as follows.

1-Undecyn-3-yl methanesulfonate (2a): 98% yield, isolated by flash chromatography (25–40% ether in hexane); mp 46.5–47.0 °C (recrystallized from hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.87 (3H, br t, J = *ca.* 7 Hz), 1.20–1.38 (10H, m), 1.44–1.54 (2H, m), 1.80–1.98 (2H, m), 2.70 (1H, d, J = 2.1 Hz), 3.12 (3H, s), 5.15 (1H, dt, J = 2.1 and 6.6 Hz); ^{13}C-NMR (75.6 MHz, $CDCl_3$) δ 79.4, 76.8, 71.3, 39.1, 35.5, 31.8, 29.3, 29.1, 28.8, 24.6, 22.6, 14.1; IR (KBr) 3260 (s), 2125 (s), 1345 (s), 1325 (s), 1170 (s), 985 (s), 955 (s), 920 (s), 865 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_3S$: C, 58.50; H, 9.00; S, 13.01. Found: C, 58.45; H, 8.73; S, 13.17.

8-[(*tert*-Butyldimethylsilyl)oxy]-1-octyn-3-yl methanesulfonate (2b): 92% yield, isolated by flash chromatography (30% ether in hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.04 (6H, s), 0.88 (9H, s), 1.32–1.43 (2H, m), 1.44–1.57 (4H, m), 1.82–1.98 (2H, m), 2.70 (1H, d, J = 2.2 Hz), 3.12 (3H, s), 3.60 (2H, t, J = 6.3 Hz), 5.15 (1H, dt, J = 2.2 and 6.6 Hz); ^{13}C-NMR (75.6 MHz, $CDCl_3$) δ 79.3, 76.9, 71.2, 62.9, 39.1, 35.5, 32.5, 25.9, 25.2, 24.4, 18.3, −5.3; IR (liquid film) 3275 (s), 2125 (s), 1365 (s), 1255 (s), 1180 (s), 1095 (s), 920 (s), 840 (s) cm^{-1}; MS (CI) m/z (relative intensity) 335 (MH$^+$, 3), 239 (9), 153 (42), 107 (100), 79 (76); HRMS (CI) calcd for $C_{15}H_{31}O_4SSi$ 335.1713, found 335.1707.

5,9-Dimethyl-8-decen-1-yn-3-yl methanesulfonate (2c) (a mixture of diastereomers): 98% yield, isolated by flash chromatography (30–40% ether in hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.95, 0.96 (3H, d, J = 6.4 Hz), 1.15–1.46 (2H, m), 1.57–2.06 (11H, m, including s (3H) at 1.60 and d (3H, J = 0.9 Hz) at 1.68), 2.709, 2.710 (1H, d, J = 2.2 Hz), 3.122, 3.124 (3H, s), 5.04–5.12 (1H, m), 5.18–5.24 (1H, m); IR (liquid film) 3275 (s), 2125 (s), 1365 (s), 1330 (s), 1175 (s), 970 (s), 920 (s), 890 (s) cm^{-1}; MS (CI) m/z (relative intensity) 163 (MH$^+$ − CH_3SO_3H, 12), 147 (19), 121 (39), 107 (100), 69 (97).

1-Butyn-3-yl methanesulfonate (2d): 93% yield, isolated by flash chromatography (30–50% ether in hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.64 (3H, d, J = 6.8 Hz), 2.69 (1H, d, J = 2.2 Hz), 3.11 (3H, s), 5.27 (1H, dq, J = 2.2 and 6.8 Hz); ^{13}C-NMR (75.6 MHz, $CDCl_3$) δ 80.1, 76.3, 67.5, 39.1, 22.4; IR (liquid film) 3280 (s), 2125 (s), 1360 (s), 1335 (s), 1175 (s), 915 (s) cm^{-1}.

2-(1,2-Undecadienyl)tetrahydrofuran (4). To a solution of ^{t}BuOK (121 mg, 1.08 mmol) in THF (7 mL) at 0 °C was added a solution of the mesylate **2a** (178 mg, 0.723 mmol) in THF (1 mL). After being stirred at ambient temperature for 5 min, the mixture was poured into water and extracted three times with ether. The dried ($MgSO_4$) and concentrated organic extracts were purified by flash chromatography (10–20% ether in hexane) to give **4** (72.4 mg, 0.326 mmol, 45% yield). **4** (a mixture of diastereomers): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.87 (3H, t, J = 6.7 Hz), 1.15–1.45 (12H, m), 1.67–1.78 (1H, m), 1.82–2.07 (5H, m), 3.72–3.81 (1H, m), 3.83–3.92 (1H, m), 4.37 (1H, dq, J = 2.2 and 6.4 Hz), 5.12–5.27 (2H, m); IR (liquid film) 1965 (s), 1460 (s), 1055 (s), 920 (s), 870 (s) cm^{-1}; MS (CI) m/z (relative intensity) 223 (MH$^+$, 3), 205 (3), 135 (8), 123 (15), 107 (9), 95 (11), 81 (15), 71 (100); HRMS (CI) calcd for $C_{15}H_{27}O$ 223.2063, found 223.2065.

Reaction of Propargylic Methanesulfonates 2 with Lithium Alkoxides. The reaction of methanesulfonate **2a** with lithium benzyl oxide is given as a representative example (entry 2). To a solution of benzyl alcohol (378 mg, 3.5 mmol) in THF (1 mL) at 0 °C was added slowly ^{n}BuLi (1.62 M in hexane) (2.2 mL, 3.5 mmol), and the mixture was stirred for 5 min. Immediately after addition of the solution of ^{t}BuOK (118 mg, 1.05 mmol) in THF (0.8 mL), a solution of mesylate **2a** (172 mg, 0.70 mmol) in THF (1 mL) was added dropwise to the resulting suspension of alkoxides at 0 °C with vigorous stirring. After being stirred at rt for 5 min, the mixture was poured into water and extracted with ether. The dried ($MgSO_4$) and concentrated residue was purified by flash chromatography (15–20% ether in hexane) to give 116 mg (0.448 mmol, 64% yield) of 1-phenyl-2,3-dodecadien-1-ol (**3a**). **3a** (a mixture of the diastereomers): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 6.5 Hz), 1.22–1.46 (12H, m), 2.03, 2.05 (2H, dq, J = 3.2 and 6.8 Hz), 2.15 (1H (OH), br d, J = *ca.* 3 Hz), 5.20–5.27 (1H, m), 5.34–5.46 (2H, m), 7.26–7.42 (5H, m); IR (liquid film) 3350 (br), 1965 (s), 1450 (s), 740 (s), 700 (s) cm^{-1}; MS m/z (relative intensity) 258 (M$^+$, 2), 216 (2), 159 (2), 107 (100), 79 (34); HRMS calcd for $C_{18}H_{26}O$ 258.1985, found 258.1978. Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.47; H, 10.15.

In entry 3, a THF–hexane solution of lithium benzyl oxide (3.5 mmol), prepared by a similar procedure described above, was concentrated *in vacuo* at rt. The resulting white solid of lithium benzyl oxide was dissolved in 1.8 mL of THF and used for the C–H insertion reaction.

The other reactions (entries 4–14) were carried out by a procedure similar to that described above except that, in the preparation of lithium alkoxides (3.5 mmol), phenethyl alcohol and *cis*- and trans-4-*tert*-butylcyclohexanol were dissolved in 4, 5, and 7 mL of THF, respectively. The spectral data of allenic alcohols **3b–k** are as follows.

1-Phenyl-3,4-tridecadien-2-ol (3b) (less polar diastereomer): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 6.6 Hz), 1.20–1.41 (12H, br s), 1.73 (1H (OH), br s), 1.93–2.02 (2H, m), 2.84 (1H, dd, J = 7.2 and 13.6 Hz), 2.91 (1H, dd, J = 5.5 and 13.6 Hz), 4.38 (1H, dddd, J = 3.4, 4.7, 5.5, and 7.2 Hz), 5.25–5.34 (2H, m), 7.20–7.34 (5H, m); ^{13}C-NMR (75.6 MHz, $CDCl_3$) δ 201.9, 137.8, 129.6, 128.3, 126.4, 95.1, 94.9, 70.2, 44.0, 31.9, 29.4, 29.3, 29.09, 29.07, 28.6, 22.7, 14.1; IR (liquid film) 3550 (sh), 3380 (br), 1965 (s), 1455 (s), 740 (s), 700 (s) cm^{-1}; MS (CI) m/z (relative intensity) 273 (MH$^+$, 1.7), 255 (18), 181 (14), 157 (25), 143 (22), 129 (19), 117 (58), 91 (100); HRMS (CI) calcd for

$C_{19}H_{29}O$ 273.2220, found 273.2214. 3b (more polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.89 (3H, t, J = 6.6 Hz), 1.20–1.42 (12H, br s), 1.76 (1H (OH), br s), 1.90–1.99 (2H, m), 2.88 (2H, d, J = 6.6 Hz), 4.37 (1H, ddt, J = 2.8, 5.6, and 6.6 Hz), 5.21–5.32 (2H, m), 7.21–7.34 (5H, m); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 202.3, 137.9, 129.6, 128.4, 126.4, 94.9, 94.4, 71.0, 44.1, 31.9, 29.4, 29.3, 29.1, 29.0, 28.6, 22.7, 14.1; IR (liquid film) 3540 (sh), 3360 (br), 1965 (s), 1455 (s), 1030 (s), 745 (s), 700 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 273 (MH$^+$, 1.7), 255 (21), 181 (13), 157 (30), 143 (25), 129 (24), 117 (68), 91 (100); HRMS (CI) calcd for $C_{19}H_{29}O$ 273.2220, found 273.2223. Anal. (a mixture of diastereomers) Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.68; H, 10.38.

4,5-Tetradecadien-3-ol (3c): bp (a mixture of diastereomers) 110 °C/0.03 mmHg (Kugelrohr) (less polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.88 (3H, t, J = 6.7 Hz), 0.95 (3H, t, J = 7.4 Hz), 1.17–1.46 (12H, m), 1.54–1.64 (3H, m, including br s (OH) at 1.63), 2.02 (2H, dq, J = 3.0 and 7.0 Hz), 4.06 (1H, m), 5.21 (1H, tt, J = 3.0 and 6.0 Hz), 5.30 (1H, dq, J = 2.5 and 6.6 Hz); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 202.0, 95.5, 94.5, 71.0, 31.9, 30.4, 29.4, 29.3, 29.13, 29.10, 28.8, 22.7, 14.1, 9.6; IR (liquid film) 3340 (br), 1965 (s), 1455 (s), 1100 (s), 1050 (s), 1010 (s), 965 (s), 870 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 211 (MH$^+$, 1.2), 193 (14), 181 (4), 151 (5), 137 (14), 123 (40), 109 (44), 95 (100); HRMS (CI) calcd for $C_{14}H_{27}O$ 211.2063, found 211.2049. **3c** (more polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.88 (3H, t, J = 6.7 Hz), 0.95 (3H, t, J = 7.4 Hz), 1.17–1.44 (12H, m), 1.54–1.64 (3H, m, including OH), 2.01 (2H, dq, J = 3.0 and 7.0 Hz), 4.06 (1H, m), 5.19 (1H, tt, J = 3.0 and 6.1 Hz), 5.29 (1H, dq, J = 2.2 and 6.6 Hz); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 202.3, 95.3, 94.1, 71.5, 31.9, 30.4, 29.4, 29.3, 29.11, 29.08, 28.8, 22.7, 14.1, 9.7; IR (liquid film) 3340 (br), 1965 (s), 1460 (s), 1105 (s), 1055 (s), 1010 (s), 965 (s), 875 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 211 (MH$^+$, 1.2), 193 (12), 181 (3), 151 (4), 137 (12), 123 (35), 109 (40), 95 (100); HRMS (CI) calcd for $C_{14}H_{27}O$ 211.2063, found 211.2074. Anal. (a mixture of diastereomers) Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.85; H, 12.40.

2-Phenyl-3,4-tridecadien-2-ol (3d) (less polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.89 (3H, t, J = 6.7 Hz), 1.17–1.44 (12H, m), 1.64 (3H, s), 2.04 (2H, dq, J = 3.0 and 7.0 Hz), 2.13 (1H (OH), s), 5.40 (1H, q, J = 6.6 Hz), 5.52 (1H, td, J = 3.0 and 6.1 Hz), 7.22–7.27 (1H, m), 7.31–7.37 (2H, m), 7.49–7.53 (2H, m); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 200.9, 147.4, 128.1, 126.8, 125.0, 101.1, 96.0, 73.3, 31.9, 30.4, 29.4, 29.2, 29.17, 29.16, 28.8, 22.7, 14.1; IR (liquid film) 3550 (sh), 3400 (br), 1965 (s), 1450 (s), 1095 (s), 1065 (s), 740 (s), 880 (s), 765 (s), 700 (s) cm^{-1}; MS *m/z* (relative intensity) 272 (M$^+$, 0.3), 254 (2.5), 155 (11), 141 (7), 121 (100); HRMS calcd for $C_{19}H_{28}O$ 272.2141, found 272.2146. **3d** (more polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.89 (3H, t, J = 6.7 Hz), 1.17–1.46 (12H, m), 1.64 (3H, s), 2.06 (2H, dq, J = 3.0 and 7.0 Hz), 2.13 (1H (OH), s), 5.39 (1H, q, J = 6.5 Hz), 5.52 (1H, td, J = 3.0 and 6.3 Hz), 7.22–7.28 (1H, m), 7.31–7.37 (2H, m), 7.49–7.53 (2H, m); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 200.8, 147.4, 128.1, 126.8, 124.9, 101.0, 96.0, 73.2, 31.9, 30.5, 29.4, 29.2, 29.14, 29.10, 28.8, 22.7, 14.1; IR (liquid film) 3550 (sh), 3400 (br), 1965 (s), 1045 (s), 1095 (s), 1070 (s), 935 (s), 880 (s), 765 (s), 700 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 273 (MH$^+$, 1.3), 255 (19), 171 (3), 157 (5), 143 (13), 131 (8), 121 (100); HRMS (CI) calcd for $C_{19}H_{29}O$ 273.2220, found 273.2233. Anal. (a mixture of diastereomers) Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.68; H, 10.56.

9-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyl-2,3-nonadien-1-ol (3e) (a mixture of the diastereomers): bp 230 °C/0.03 mmHg (Kugelrohr); ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.048, 0.053 (6H, s), 0.90 (9H, s), 1.26–1.58 (6H, m), 2.04, 2.06 (2H, dq, J = 3.1 and 7.0 Hz), 2.18, 2.26 (1H (OH), br d, J = 4.0 Hz), 3.59, 3.61 (2H, t, J = 6.4 Hz), 5.20–5.26 (1H, m), 5.33–5.45 (2H, m), 7.25–7.42 (5H, m); IR (liquid film) 3370 (br), 1965 (s), 1255 (s), 1100 (s), 835 (s), 775 (s), 740 (s), 695 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 347 (MH$^+$, 0.4), 329 (10), 271 (3), 197 (76), 141 (100), 117 (77), 75 (82). Anal. Calcd for $C_{21}H_{34}O_2Si$: C, 72.78; H, 9.89. Found: C, 72.58; H, 9.79.

10-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyl-3,4-decadien-2-ol (3f) (less polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.051 (6H, s), 0.90 (9H, s), 1.26–1.44 (4H, m), 1.51 (2H, quint, J = 6.6 Hz), 1.84 (1H (OH), br d, J = 4.3 Hz), 1.94–2.02 (2H, m), 2.84 (1H, dd, J = 7.1 and 13.6 Hz), 2.91 (1H, dd, J = 5.5 and 13.6 Hz), 3.60 (2H, t, J = 6.5 Hz), 4.38 (1H, m), 5.24–5.33 (2H, m), 7.20–7.34 (5H, m); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 202.0, 137.8, 129.6, 128.3, 126.4, 95.1, 94.6, 70.3, 63.2, 43.9, 32.6, 28.8, 28.5, 26.0, 25.3, 18.4, −5.3; IR (liquid film) 3550 (sh), 3400 (br), 1965 (s), 1255 (s), 1100 (s), 835 (s), 775 (s), 740 (s), 700 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 361 (MH$^+$, 0.1), 343 (9), 285 (6), 269 (11), 211 (32), 141 (100), 91 (99). **3f** (more polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.049 (6H, s), 0.90 (9H, s), 1.26–1.41 (4H, m), 1.43–1.55 (2H, m), 1.83 (1H (OH), br d, J = 4.1 Hz), 1.89–1.98 (2H, m), 2.87 (2H, d, J = 6.6 Hz), 3.60 (2H, t, J = 6.5 Hz), 4.37 (1H, m), 5.24 (1H, tt, J = 3.3 and 6.3 Hz), 5.28 (1H, dq, J = 2.4 and 6.3 Hz), 7.20–7.33 (5H, m); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 202.3, 137.9, 129.6, 128.3, 126.4, 94.9, 94.2, 71.0, 63.2, 44.1, 32.6, 28.8, 28.5, 26.0, 25.2, 18.3, −5.3; IR (liquid film) 3360 (br), 1965 (s), 1255 (s), 1100 (s), 835 (s), 775 (s), 745 (s), 700 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 361 (MH$^+$, 0.2), 343 (5), 285 (5), 269 (6), 211 (22), 141 (100), 91 (52). Anal. (a mixture of diastereomers) Calcd for $C_{22}H_{36}O_2Si$: C, 73.28; H, 10.06. Found: C, 73.23; H, 10.03.

11-[(*tert*-Butyldimethylsilyl)oxy]-4,5-undecadien-3-ol (3g): bp (a mixture of diastereomers) 160 °C/0.03 mmHg (Kugelrohr) (less polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.042 (6H, s), 0.89 (9H, s), 0.95 (3H, t, J = 7.4 Hz), 1.30–1.63 (8H, m), 1.69 (1H (OH), br d, J = 4.6 Hz), 2.03 (2H, dq, J = 3.0 and 6.9 Hz), 3.60 (2H, t, J = 6.4 Hz), 4.05 (1H, m), 5.21 (1H, tt, J = 3.0 and 6.0 Hz), 5.29 (1H, dq, J = 2.5 and 6.5 Hz); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 202.1, 95.6, 94.2, 71.1, 63.2, 32.6, 30.4, 28.8, 28.7, 26.0, 25.3, 18.4, 9.6, −5.3; IR (liquid film) 3360 (br), 1965 (s), 1255 (s), 1100 (s), 1005 (s), 835 (s), 775 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 299 (MH$^+$, 0.4), 281 (15), 241 (3), 223 (2), 149 (100), 75 (78). 3g (more polar diastereomer): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.039 (6H, s), 0.89 (9H, s), 0.94 (3H, t, J = 7.4 Hz), 1.29–1.63 (8H, m), 1.67 (1H (OH), br s), 2.02 (2H, dq, J = 3.1 and 6.9 Hz), 3.59 (2H, t, J = 6.5 Hz), 4.05 (1H, br q, J = *ca.* 6 Hz), 5.18 (1H, tt, J = 3.1 and 6.2 Hz), 5.28 (1H, dq, J = 2.1 and 6.5 Hz); ^{13}C-NMR (75.6 MHz, CDCl$_3$) δ 202.4, 95.4, 93.9, 71.5, 63.2, 32.6, 30.4, 28.9, 28.7, 26.0, 25.3, 18.4, 9.7, −5.3; IR (liquid film) 3360 (br), 1965 (s), 1255 (s), 1100 (s), 1005 (s), 835 (s), 775 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 299 (MH$^+$, 0.3), 281 (13), 223 (3), 149 (100), 75 (92). Anal. (a mixture of diastereomers) Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48. Found: C, 68.41; H, 11.67.

6,10-Dimethyl-1-phenyl-2,3,9-undecatrien-1-ol (3h) (a mixture of four diastereomers): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.907, 0.913, 0.917 (3H, d, J = 6.6 Hz), 1.10–1.26 (1H, m), 1.32–1.45 (1H, m), 1.47–1.64 (4H, m, including br s (3H) at 1.61), 1.69 (3H, br s), 1.83–2.22 (5H, m, including br d (OH, J = 3.7 Hz) at 2.17, 2.18), 5.07–5.13 (1H, m), 5.21–5.43 (3H, m), 7.25–7.42 (5H, m); IR (liquid film) 3440 (sh), 3340 (br), 1965 (s), 1450 (s), 1375 (s), 1010 (s), 870 (s), 760 (s), 740 (s), 700 (s) cm^{-1}.

7,11-Dimethyl-1-phenyl-3,4,10-dodecatrien-2-ol (3i) (a mixture of two less polar diastereomers): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.89, 0.90 (3H, d, J = 6.6 Hz), 1.09–2.06 (14H, m, including s (3H) at 1.61, s (3H) at 1.69, and br d (OH, J = 4.6 Hz) at 1.73), 2.84 (1H, dd, J = 7.2 and 13.6 Hz), 2.92 (1H, dd, J = 5.4 and 13.6 Hz), 4.34–4.43 (1H, m), 5.06–5.13 (1H, m), 5.19–5.28 (2H, m), 7.21–7.34 (5H, m); IR (liquid film) 3550 (sh), 3390 (br), 2000 (s), 1960 (s), 1450 (s), 1370 (s), 1030 (s), 740 (s), 700 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 285 (MH$^+$, 0.4), 267 (8), 211 (11), 175 (21), 157 (18), 141 (60), 91 (82), 69 (100). **3i** (a mixture of more polar two diastereomers): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.873, 0.878 (3H, d, J = 6.6 Hz), 1.07–2.05 (14H, m, including s (3H) at 1.61 and s (3H) at 1.69), 2.88 (2H, d, J = 6.6 Hz), 4.33–4.42 (1H, m), 5.06–5.12 (1H, m), 5.20–5.25 (2H, m), 7.20–7.34 (5H, m); IR (liquid film) 3550 (sh), 3380 (br), 2000 (s), 1965 (s), 1450 (s), 1375 (s), 1030 (s), 745 (s), 700 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 285 (MH$^+$, 0.3), 267 (9), 211 (12), 175 (22), 157 (25), 141 (77), 91 (92), 69 (100). Anal. (a mixture of diastereomers) Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.23; H, 9.94.

2,6-Dimethyl-2,8,9-tridecatrien-11-ol (3j) (a mixture of two less polar diastereomers): ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.92 (3H, d, J = 6.5 Hz), 0.95 (3H, t, J = 7.4 Hz), 1.11–1.27 (1H, m), 1.32–1.45 (1H, m), 1.47–1.64 (6H, m, including br s (3H) at 1.60), 1.68 (3H, d, J = 0.9 Hz), 1.83–2.12 (5H, m, including OH), 4.02–4.11 (1H, m), 5.06–5.13 (1H, m), 5.14–5.28 (2H, m); IR (liquid film) 3340 (br), 1965 (s), 1455 (s), 1375 (s), 1100 (s), 1010 (s), 965 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 223 (MH$^+$, 0.1), 205 (13), 175 (12), 163 (12), 149 (43), 135 (40), 123 (32), 109 (52), 95 (97), 69 (100). **3j** (a mixture of more polar two diastereomers): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.91 (3H, d, J = 6.8 Hz), 0.95 (3H, t, J = 7.4 Hz), 1.10−1.25 (1H, m), 1.31−1.44 (1H, m), 1.47−1.65 (6H, m, including br s (3H) at 1.60), 1.68 (3H, d, J = 0.9 Hz), 1.80−2.11 (5H, m, including OH), 4.06 (1H, br dq, J = 1.6 and 6.2 Hz), 5.06−5.12 (1H, m), 5.13−5.27 (2H, m); IR (liquid film) 3350 (br), 1965 (s), 1460 (s), 1375 (s), 1105 (s), 1010 (s), 965 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 223 (MH$^+$, 0.7), 205 (15), 175 (11), 163 (11), 149 (45), 135 (37), 123 (31), 109 (49), 95 (100), 69 (94). Anal. (a mixture of diastereomers) Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.86; H, 11.83.

***cis*-4-*tert*-Butyl-1-(1,2-butadienyl)-1-cyclohexanol (*cis*-3k):** ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.87 (9H, s), 0.96 (1H, m), 1.32−1.51 (5H, m), 1.57−1.63 (2H, m), 1.67−1.78 (5H, m, including dd (3H, J = 3.4 and 6.8 Hz) at 1.69), 5.23 (1H, qd, J = 3.4 and 6.6 Hz), 5.28 (1H, quint, J = 6.7 Hz); ^{13}C-NMR (75.6 MHz, $CDCl_3$) δ 201.4, 101.2, 89.5, 69.7, 47.6, 38.5, 32.4, 27.6, 22.6, 14.5; IR (liquid film) 3375 (br), 1965 (s), 1365 (s), 950 (s), 870 (s) cm^{-1}; MS *m/z* (relative intensity) 208 (M$^+$, 1), 191 (3), 175 (2), 155 (100), 137 (13), 109 (15), 95 (21), 81 (44), 57 (78); HRMS calcd for $C_{14}H_{24}O$ 208.1828, found 208.1817. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.96; H, 11.60.

***trans*-4-*tert*-Butyl-1-(1,2-butadienyl)-1-cyclohexanol (*trans*-3k):** mp 60.5 °C (recrystallized from hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.85 (9H, s), 0.97−1.22 (3H, m), 1.49 (1H, td, J = 3.9 and 12.5 Hz), 1.53 (1H, td, J = 3.8 and 12.7 Hz), 1.63−1.73 (6H, m, including dd (3H, J = 3.3 and 6.9 Hz) at 1.70), 1.84 (1H, qd, J = 3.1 and 12.5 Hz), 1.91 (1H, qd, J = 3.0 and 12.3 Hz), 5.19 (1H, qd, J = 3.4 and 6.6 Hz), 5.25 (1H, quint, J = 6.8 Hz); ^{13}C-NMR (75.6 MHz, $CDCl_3$) δ 203.8, 97.1, 88.7, 71.9, 47.4, 39.3, 38.9, 32.3, 27.6, 24.7, 24.6, 14.3; IR (KBr disk) 3285 (br), 1965 (s), 1445 (s), 1365 (s), 1070 (s), 1060 (s), 980 (s), 880 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 209 (MH$^+$, 1), 191 (100), 155 (72), 135 (9), 121 (6), 109 (7), 95 (14), 81 (25), 67 (17). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.28; H, 11.41.

General Procedure for Cyclopropanation Reaction of Styrene. To a solution of ^{t}BuOK (118 mg, 1.05 mmol) and styrene (365 mg, 0.40 mL, 3.51 mmol) in THF (2 mL) at 0 °C was added a solution of mesylate **2** (0.702 mmol) in THF (1 mL). After being stirred at rt for 5 min, the mixture was poured into water, extracted three times with ether, dried with $MgSO_4$, and then concentrated *in vacuo*. After removal of volatile compounds by Kugelrohr distillation (100−130 °C/0.03 mmHg), the residue was purified by flash chromatography affording pure cyclopropane.

7-[(*tert*-Butyldimethylsilyl)oxy]-1-(2-phenylcyclopropylidene)-1-heptene (5a) (a mixture of diastereomers): 68% yield, isolated by flash chromatography (3−5% ether/benzene in hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.049, 0.058 (6H, s), 0.90 (9H, s), 1.32−1.65 (7H, m), 2.02−2.16 (3H, m, including br q (2H, J = 6.8 Hz) at 2.13), 2.89−2.98 (1H, m), 3.58, 3.62 (2H, t, J = 6.4 Hz), 5.35−5.43 (1H, m), 7.16−7.32 (5H, m); IR (liquid film) 2005 (s), 1945 (w), 1605 (s), 1250 (s), 1100 (s), 835 (s), 770 (s), 750 (s), 695 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 343 (MH$^+$, 1.3), 285 (17), 211 (37), 155 (50), 141 (70), 129 (55), 75 (100); HRMS (CI) calcd for $C_{22}H_{35}OSi$ 343.2459, found 343.2461. Anal. Calcd for $C_{22}H_{34}OSi$: C, 77.13; H, 10.00. Found C, 76.93; H, 9.99.

4,9-Dimethyl-1-(2-phenylcyclopropylidene)-1,7-nonadiene (5b) (a mixture of four diastereomers): 41% yield, isolated by flash chromatography (1−2% benzene in hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.91, 0.92, 0.945, 0.948 (3H, d, J = 6.6 Hz), 1.13−1.26 (1H, m), 1.34−1.50 (1H, m), 1.53−1.70 (8H, m, including br s (3H) at 1.60, 1.61 and br s (3H) at 1.68, 1.69), 1.91−2.22 (5H, m), 2.90−2.97 (1H, m), 5.05−5.15 (1H, m), 5.29−5.39 (1H, m), 7.16−7.31 (5H, m); IR (liquid film) 2005 (s), 1945 (w), 1605 (s), 1450 (s), 1375 (s), 750 (s), 695 (s) cm^{-1}; MS (CI) *m/z* (relative intensity) 267 (MH$^+$, 1.2), 251 (14), 223 (26), 175 (25), 155 (47), 141 (39), 91 (83), 69 (100); HRMS (CI) calcd for $C_{20}H_{27}$ 267.2114, found 267.2112. Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.39; H, 9.82.

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Supplementary Material Available: High-field ^{1}H NMR spectra of **2b–d**, **4**, and **3h** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.