Equatorial Preference in the $GaCl_3$-Promoted Ethenylation of Cyclic Ketones

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Abstract: Silyl enol ethers derived from substituted cyclohexanones are ethenylated with trimethylsilylethyne in the presence of $GaCl_3$. Carbon–carbon bond formation was completed in less than 5 min at room temperature and protodegallation of the organogallium intermediate formed with 6 M sulfuric acid gave β-enones. The reactions exhibit a bias for the equatorial C–C bond formation, which contrasts the axial stereochemistry of enolate alkylation. The origin of this stereoselectivity is discussed.

Key words: α-ethenylation, $GaCl_3$, cyclic ketone, equatorial, silylethyne

The alkylation of enolates is one of the most fundamental carbon-carbon bond formations in organic synthesis and it is used to attach an sp^3-carbon atom to the carbonyl α-carbon atom. Such C–C bond formation between enolates and sp^2-carbon atoms, however, have been problematic, due to the inertness of vinyl halides or acetylenes towards metal enolates. Enolates usually do not undergo S_N1 and S_N2 reactions with vinyl halides and do not add to acetylenes. Another serious problem is that products possessing the β-enone structure can readily isomerize to conjugated α-enones. Of the enolate olefinations,[1,2] ethenylation, i.e. C_2-olefination, is the most undeveloped. Very few examples are known[2] and unfortunately they are applicable only to the synthesis of unenolizable ethenylated products, which do not possess an acidic proton at the carbonyl α-position. Stepwise methods, therefore, have been employed for such enolate ethenylation. Reagents such as vinyl sulfones, ethynyl sulfones, trichloroethylene, α-phenylselenylacetaldehyde, α-trimethylsilylaldehydes or a vinyl ether–iron complex are reacted with enolates and the adducts are subjected to subsequent transformations to generate the ethenyl group.[3]

Previously, we developed an ethenylation reaction of ketones[4] and β-dicarbonyl compounds[5] with trimethylsilylethyne in the presence of $GaCl_3$. The reaction converts silyl enol ethers to an α-ethenylated products in one step. Mechanistically, the ethenylation proceeds via carbogallation of gallium enolate and alkynylgallium generating a bisgallio-intermediate, which is protodegallated under acidic conditions. This novel ethenylation reaction has a wide applicability and provides not only ketones with a quaternary α-carbon but also enolizable products. A limitation of the method, however, was that cyclic ketones with relatively small ring number such as cyclohexanone and cycloheptanone gave considerable amounts of the conjugate α-enones. While in the case of cycloheptanone the amount of the ethenyl product could be increased by careful quenching of the reaction at 0 °C, the α-enone was still the major product in the reaction of cyclohexanone. We now found that several substituted cyclohexanones can be ethenylated in good yield and in addition the reactions exhibit a bias for the equatorial ethenylation.

Trimethylsilylethyne and 1-trimethylsilyloxy-3-butylcyclohexene were reacted with $GaCl_3$ in methylcyclohexane at 0 °C for 5 min. Treatment with THF and 6 M sulfuric acid at 0 °C for 5 min gave *trans*-3-butyl-2-ethenylcyclohexanone and the *cis*-isomer in 51% and 4% yield, respectively (Table, entry 2). The configurations were determined by NMR spectroscopy; coupling constant (*J*), (2-H, 3-H) is 9.4 Hz for the *trans*- and 4.4 Hz for the *cis*-isomer. 3-Isopropyl and 3-methylcyclohexanone derivatives exhibit a similar stereoselectivity (entries 1 and 3). The *trans*-3-butyl-2-ethenylcyclohexanone was insensitive to acid and base and no isomerization was observed when treated with 6 M sulfuric acid in THF or neat triethylamine at room temperature for 1 h. Ethenylation of 2,3-dimethyl-1-trimethylsilyloxycyclohexene and 3-butyl-2-methyl-1-trimethylsilyloxycyclohexene also gave the *trans*-isomers predominantly (entries 4 and 5). The equatorial 2-ethenyl stereochemistry of the major isomer in the former reaction was determined by the presence of a NOE between the 2-methyl protons and the axial 6-proton. The equatorial arrangement of the 3-methyl group is determined from the coupling constant. The *trans*-stereoselectivity (J = 9.0 Hz) was also observed in the reaction of the silyl enol ether derived from β-butylcycloheptanone (entry 6). These stereochemical outcomes are similar to those for the alkylation reactions of alkali metal enolates.[6]

A notable difference between the enolate ethenylation and the alkylation was observed in the reaction of a bicyclic ketone. The ethenylation of the silyl enol ether derived from *trans*-bicyclo[4.4.0]decan-3-one predominantly gave the equatorial diastereomer (J = 11 Hz between the 1-proton and the 2-proton) (entry 7). It is reported that the alkylation of the alkali metal enolate gives the axial isomer.[7] Ethenylation of 2,6-dimethylcyclohexanone silyl enol ether gave two isomers of 2-ethenyl-2,6-dimethylcyclohexanone in 73% and 6% yield (entry 8). The major product was treated with lithium tris(isoamyl)borohydride followed by acetylation giving axial and equatorial acetates. For the equatorial acetate, the 1,6-*trans*-relation was determined by the coupling constant (J = 10 Hz). The

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NOE between the 2-methyl protons and the 6-proton showed the axial arrangement of the 2-methyl group. It is again in contrast to the stereochemistry of the sodium enolate alkylation derived from 2,6-dimethylcyclohexanone.[8] The enolate alkylation and ethenylation appear to prefer the axial stereochemistry and the equatorial stereochemistry, respectively. The reaction of 2,3,6-trimethylcyclohexanone silyl enol ether was conducted using a 1: 1 mixture of isomers giving three products in 45%, 32% and 10% yield. The axial 2-methyl and the equatorial 3,6-dimethyl stereochemistry of the major isomer were determined by the presence of a NOE between the 2-methyl protons and the 6-proton as well as the coupling constant at the 3-proton. The second major product showed a NOE between the 2-methyl protons and the 6-proton, and therefore should possess the 3-axial methyl group. The minor product exhibited a NOE between the vinyl proton and the 6-proton as well as the 3-methyl proton and the 5-axial proton. Based on these observations it can be concluded that the *trans*-silyl enol ether exclusively gives the (2*S**, 3*R**,6*R**)-isomer with the equatorial ethenyl group in 90% yield (entry 9). The (2*S**,3*S**,6*R**)- and (2*R**,3*S**,6*R**)- isomers were obtained by the ethenylation of the *cis*-isomer in 64% and 20% yield, respectively (entry 11). These results were again interpreted by the equatorial preference in the enolate ethenylation. The conformationally rigid 3,5-*trans*-isomer reacts at the equatorial site, and the flexible 3,5-*cis*-isomer gives an isomer mixture. 3-Butyl-2,6-dimethylcyclohexanone silyl enol ether gave essentially the same results (entries 10 and 12). A single isomer of the ethenylated product was obtained from *trans*-2-methyl-3,5-diisopropyl-1-trimethylsilyloxycyclohexene in 64% yield (entry 13). The stereochemistry was determined by conversion to the alcohol.

As described before, the present reaction involves carbogallation of gallium enolate with ethynyl gallium.[4,9] The formation of the gallium enolate **1** was confirmed spectroscopically by reacting $GaCl_3$ and 1-trimethylsilyloxy-3-butylcyclohexene in cyclohexane-d_{12}: ^{13}C NMR (C_6D_{12}) δ 125.0, 150.6. Since no carbonyl absorption was observed by IR in methylcyclohexane, α-galliocarbonyl

Biographical Sketches

Masahiko Yamaguchi is a professor of Tohoku University. He was born in Fukuoka in 1954, and recieived his BSc. (1977) and Ph.D. degrees (1982) from The University of Tokyo. He joined the Department of Industrial Chemistry, Kyushu Institute of Technology, in 1982 as Assistant Professor and was promoted to Associate Professor in 1985. He moved to the Department of Chemistry at Tohoku University in 1991. During 1987 to 1988 he worked as a postdoctorate fellow at Yale University with Professor S. Danishefsky. In 1997, he was appointed Professor in the Faculty of Pharmaceutical Sciences of Tohoku University. He received the Chemical Society of Japan Award for Young Chemists in 1986. His research interests are in the area of synthetic methodology and functionally interesting compounds.

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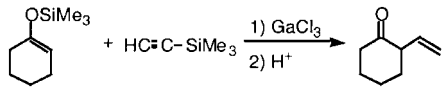
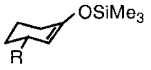
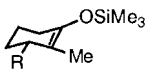
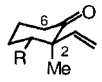
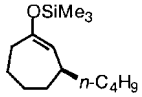
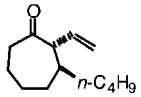
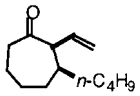
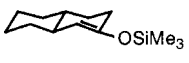
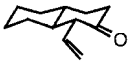
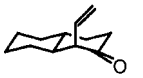
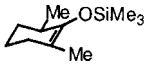
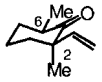
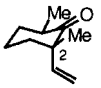
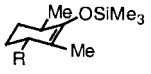
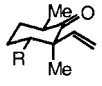
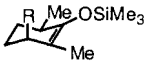
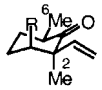
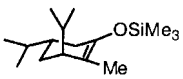
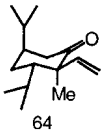
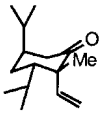
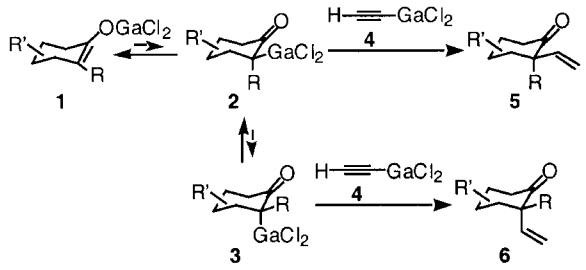
Table α-Ethenylation of Silyl Enol Ethers Derived from Cyclic Ketones



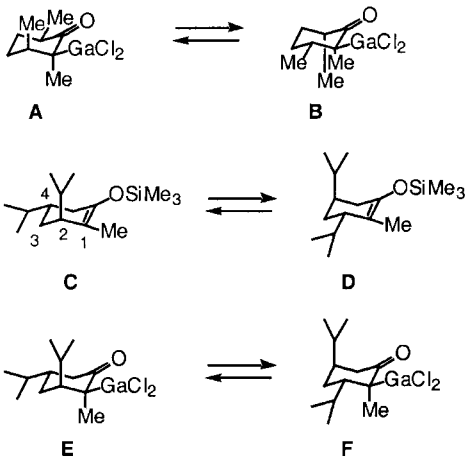
Entry	Substrate	Product/Yield (%)	
			
1	R = Me	36	trace
2	R = *n*-C_4H_9	51	4
3	R = *i*-C_3H_7	47	trace
			
4	R = Me	74	6
5	R = *n*-C_4H_9	68	9
			
6		73	13
			
7		52	trace
			
8		73	6
			
9 [a]	R = Me	90	trace
10 [a]	R = *n*-C_4H_9	85	trace
			
11 [a]	R = Me	64	20
12 [a]	R = *n*-C_4H_9	63	22
			
13		64	trace

[a] The reaction was conducted using a 1:1 diastereomer mixture of the silyl enol ether.

intermediates **2** and **3** may not be the major compound. It is widely accepted for the enolate alkylation that the electrophile approaches from the axial site of the enolate plane. Strong equatorial preferences observed in the present ethenylation (entries 6–10) suggest involvement of quite a different mechanism. A possible explanation can be provided taking into account the C-metallospecies as the intermediate (Scheme 1). Gallium enolate can equilibrate with a small amount of carbon-gallium intermediate, which may exist either as axial or equatorial compound **2** and **3**. It is reasonably assumed that **2** having the bulky gallium group at the equatorial position is more stable than **3**. Then, carbogallation of **2** and **4** with retention of configuration gives the product **5**. The mechanism is consistent with the *trans*-stereochemistry in the reactions of β-substituted cyclohexanones (entries 1–5), in which the equatorial α-gallioketone are considered to be the reactive species. In the reaction of 3,6-*cis*-dimethylcyclohexanone derivatives (entries 11 and 12), the α-gallioketone can adopt two conformations **A** and **B** (Scheme 2). If the equatorial mechanism also applies in this case, **A** should be the major reactive species. As for the diisopropyl derivative (entry 13), NMR studies indicate that the silyl enol ether possesses the conformation **C** rather than **D**. The coupling constant of the 5-axial proton and the 4-proton (J = 8.0 Hz) confirms the equatorial orientation of the 4-isopropyl group**.** The reactive species, however, may be **F** rather than **E** based on the equatorial mechanism (Scheme 2).



Scheme 1



Scheme 2

^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian Mercury (400 MHz). Chemical shift values are given in ppm relative to internal Me_4Si. IR spectra were recorded on an ASI REACT-IR 1000 or

a JASCO FT/IR-410. MS spectra were taken with a JEOL JMS-DX303 or a JEOL JMS-AX500. Elemental analyses were conducted with a Yanaco CHN CORDER MT-5.

Synthesis of Silyl Enol Ethers

Synthesized by the conjugate addition of organocuprates to 2-cyclohexenones in the presence of TMSCl according to the literature (entries 1–5, 8–13).[10] 3-(Trimethylsilyloxy)bicyclo[4.4.0]dec-2-ene was synthesized according to the literature (entry 6).[11] 1-Trimethylsilyloxy-2,6-dimethylcyclohexene was synthesized from 2,6-dimethylcyclohexanone, LDA and TMSCl by usual procedures (entry 7).

***trans*-3,5-Diisopropyl-2-methyl-1-(trimethylsilyloxy)-cyclohexene**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.17 (9 H, s), 0.78 (3 H, d, *J* = 6.4 Hz), 0.88 (3 H, d, *J* = 6,4 Hz), 0.89 (3 H, d, *J* = 6.8 Hz), 0.95 (3 H, d, *J* = 6.4 Hz), 1.21 (1 H, ddd, *J* = 13.2, 10.4, 6.0 Hz, 4ax), 1.41 (1 H, quintet, *J* = 6.8 Hz), 1.46–1.51 (1 H, m, 5ax), 1.62 (1 H, dt, J = 13.2, 2.8 Hz, 4eq), 1.80 (1 H, ddt, *J* = 16.8, 8.0, 2.0 Hz, 6ax), 1.89–1.94 (2 H, m), 2.02 (1 H, dd, *J* = 17.6, 5.2 Hz, 6eq).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.72, 15.3, 18.9, 20.1, 20.3, 21.8, 26.6, 29.9, 31.4, 34.2, 38.1, 43.8, 114.5, 144.3.

The *trans*-configuration of this compound can be deduced from the results in the literature[12] and was confirmed as will be described later.

(2*R,3*S**)-3-Butyl-2-ethenylcyclohexanone and (2*S**,3*S**)-3-Butyl-2-ethenylcyclohexanone; Typical Procedure**

Under an Ar atmosphere, a solution of $GaCl_3$ (1.0 M, 2.0 mmol) in methylcyclohexane (2.0 mL) was added to a mixture of 1-trimethylsilyloxy-3-butylcyclohexene (0.5 mmol, 113 mg) and trimethylsilylethyne (1.0 mmol, 0.14 mL) in methylcyclohexane (2.0 mL) at r.t. The mixture was stirred at r.t. for 5 min, when THF (5.0 mL) was added to dissolve insoluble materials. Sulfuric acid (6 M, 5.0 mL) was added at 0 °C and stirring was continued for another 5 min. The organic materials were then extracted with Et_2O. The organic layer was washed with water, brine, dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography (hexene: EtOAc 50:1) to give (2*R**,3*S**)-2-ethenyl-3-butylcyclohexanone (45.9 mg, 51%) and (2*S**,3*S**)-2-ethenyl-3-butylcyclohexanone (3.6 mg, 4%).

(2*R,3*S**)-3-Butyl-2-ethenylcyclohexanone**

IR (neat): 3076, 1714, 1644, 1457, 990, 914 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 6.4 Hz), 1.12–1.46 (6 H, m), 1.48–1.55 (1 H, m), 1.60–1.73 (2 H, m), 1.98–2.10 (2 H, m), 2.30 (1 H, dt, *J* = 13.2, 5.6 Hz, 6eq), 2.43 (1 H, dt, *J* = 14.0, 4.4 Hz, 6ax), 2.73 (1 H, dd, *J* = 9.4, 9.2 Hz, 2ax), 5.00 (1 H, d, *J* = 17.6, 1.6 Hz), 5.23 (1 H, d, *J* = 10.0, 1.2 Hz), 5.74 (1 H, ddd, *J* = 18.2, 10.0, 8.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.8, 25.7, 28.5, 29.7, 33.7, 41.5, 43.6, 61.4, 118.1, 135.0, 211.3.

MS (EI) *m/z*: 180 (M^+, 18%), 123 (M^+–57, 100%).

HRMS calcd for $C_{12}H_{20}O$, 180.1514; found: 180.1511.

Anal. calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.33; H, 10.94.

(2*S,3*S**)-3-Butyl-2-ethenylcyclohexanone**

IR (neat): 3078, 1712, 1458, 993, 919 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–0.90 (3 H, m), 1.19–1.34 (6 H, m), 1.63–1.76 (2 H, m), 1.84–1.94 (1 H, m), 1.97–2.06 (1 H, m), 2.22–2.32 (1 H, m), 2.38–2.48 (1 H, m), 3.12 (1 H, dd, *J* = 8.8, 4.4 Hz, 2eq), 5.16 (1 H, d, *J* = 16.8 Hz), 5.18 (1 H, d, *J* = 10 Hz), 5.60 (1 H, ddd, *J* = 16.8, 10.0, 8.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 22.8, 25.3, 27.3, 29.1, 31.3, 39.6, 42.8, 60.3, 118.8, 132.1, 211.2.

MS (EI) *m/z*: 180 (M^+, 31%), 95 (M^+-85, 100%).

HRMS calcd for $C_{12}H_{20}O$, 180.1514; found: 180.1523.

(2*R,3*R**)-2-Ethenyl-3-methylcyclohexanone**

IR (neat): 3078, 1712, 1643, 1455, 990, 916 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (3 H, d, *J* = 6.4 Hz), 1.40–1.50 (1 H, m), 1.56–1.78 (2 H, m), 1.93 (1 H, ddq, *J* = 13.2, 3.6, 1.6 Hz), 2.02–2.10 (1 H, m), 2.31 (1 H, dt, *J* = 13.2, 6.0 Hz, 6eq), 2.40–2.46 (1 H, m, 6ax), 2.61 (1 H, t, J = 9.6 Hz, 2ax), 5.00 (1 H, dd, *J* = 16.8, 1.2 Hz), 5.23 (1 H, dd, *J* = 10.4, 1.2 Hz), 5.75 (1 H, ddd, *J* = 17.6, 10.0, 8.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 26.0, 33.5, 39.2, 41.6, 63.1, 118.2, 134.9, 211.2.

MS (EI) *m/z*: 138 (M^+, 54%), 79 (M^+–59, 100%).

HRMS calcd for $C_9H_{14}O$, 138.1045; found, 138.1032.

Anal. calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.80; H, 10.24.

(2*R,3*R**)-2-Ethenyl-3-isopropylcyclohexanone**

IR (neat): 3075, 1714, 1459, 1425, 991, 909 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (3 H, d, *J* = 7.2 Hz), 0.94 (3 H, d, *J* = 7.6 Hz), 1.43 (1 H, dq, *J* = 12.4, 3.6 Hz), 1.45–1.69 (1 H, m), 1.78–1.85 (2 H, m), 2.07–2.15 (1 H, m), 2.29 (1 H, dt, *J* = 13.2, 6.4 Hz, 6eq), 2.41–2.45 (1 H, m, 6ax), 2.89 (1 H, t, *J* = 10.4 Hz, 2ax), 5.01 (1 H, dd, *J* = 17.6, 1.2 Hz), 5.23 (1 H, dd, *J* = 10.0, 1.2 Hz), 5.72 (1 H, ddd, *J* = 17.6, 9.6, 9.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0, 21.4, 23.5, 25.9, 28.1, 41.8, 49.3, 59.7, 117.9, 135.0, 211.8. MS (EI) *m/z*: 166 (M^+, 46%), 95 (M^+–71, 100%).

HRMS calcd for $C_{11}H_{18}O$, 166.1378; found, 166.1358.

Anal. calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.19; H, 10.93.

(2*R,3*S**)-2,3-Dimethyl-2-ethenylcyclohexanone**

IR (neat) 2933, 1707, 1455, 1248, 1092, 914 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, d, *J* = 6.8 Hz), 1.14 (3 H, s), 1.57 (1 H, dtd, *J* = 13.2, 9.6, 3.6 Hz, 4ax), 1.69–1.77 (1 H, m), 1.86 (1 H, *J* = 11.2, 6.4, 4.4 Hz, 4eq), 1.92–2.01 (2 H, m, 3ax), 2.43 (2 H, m, 6ax,eq), 5.00 (1 H, d, *J* = 17.6 Hz), 5.20 (1 H, d, *J* = 10.4 Hz), 5.92 (1 H, dd, *J* = 17.6, 10.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.7, 16.7, 24.5, 28.9, 38.2, 40.9, 55.7, 114.5, 142.5, 214.1.

MS (EI) *m/z*: 152 (M^+, 48%), 109 (M^+–43, 100%).

HRMS calcd for $C_{10}H_{16}O$, 152.1202; found, 152.1228.

The equatorial configuration of the 3-methyl group was determined by observing the 3-proton with irradiation at the 3-methyl group. *J* (^{3}H-^{4}H) = ca 4.8 Hz. The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ = 1.14) and the 6-axial proton (δ 2.43).

(2*S,3*S**)-2,3-Dimethyl-2-ethenylcyclohexanone**

IR (neat): 2931, 1710, 1456, 1249, 1048, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (3 H, d, J = 6.0 Hz), 1.19 (3 H, s), 1.62–1.69 (4 H, m), 1.99–2.05 (1 H, m), 2.29 (1 H, dt, *J* = 11.2, 2.4 Hz, 6eq), 2.55–2.63 (1 H, m, 6ax), 5.03 (1 H, d, *J* = 16.4 Hz), 5.20 (1 H, d, *J* = 11.2 Hz), 6.18 (1 H, dd, *J* = 17.6, 11.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2, 19.8, 26.1, 30.2, 38.9, 43.6, 56.1, 116.9, 137.1, 212.2.

MS (EI) *m/z*: 152 (M^+, 57%), 109 (M^+–43, 100%).

HRMS calcd for $C_{10}H_{16}O$,152.1202; found, 152.1219.

The equatorial configuration of the 2-methyl group was determined by NOE between the 2-ethenyl proton (δ 6.18) and the 6-axial proton (δ 2.55–2.63).

(2*R,3*S**)-3-Butyl-2-ethenyl-2-methylcyclohexanone**
IR (neat): 2932, 2861, 1707, 1458, 961, 913 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, brt, *J* = 7.6 Hz), 1.15 (3 H, s), 1.18–1.44 (6 H, m), 1.48–1.58 (1 H, m), 1.62–1.73 (2 H, m), 1.91–2.01 (2 H, m), 2.37–2.52 (2 H, m), 5.00 (1 H, d, *J* = 17.6 Hz), 5.22 (1 H, d, *J* = 11.2 Hz), 5.88 (1 H, dd, *J* = 17.6, 10.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 16.6, 22.8, 24.7, 25.4, 28.9, 30.3, 38.3, 46.1, 56.0, 114.5, 142.5, 214.1.

MS (EI) *m/z*: 194 (M^+, 51%), 109 (M^+–85, 100%).

HRMS calcd for $C_{13}H_{22}O$, 194.1671; found, 194.1684.

Anal. calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 79.99; H, 11.42.

Configuration was determined by analogy to the methyl derivative. The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ 1.15) and the 6-axial proton (δ 2.37–2.52).

(2*S,3*S**)-3-Butyl-2-ethenyl-2-methylcyclohexanone**
IR (neat): 3083, 1710, 1631, 1458, 994, 917 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (3 H, t, *J* = 7.2 Hz), 1.16–1.66 (9 H, m), 1.21 (3 H, s), 1.85–1.88 (1 H, m), 2.01–2.07 (1 H, m), 2.27–2.33 (1 H, m), 2.59 (1 H, dt, *J* = 13.2, 6.4 Hz, 6ax), 5.01 (1 H, d, *J* = 17.6 Hz), 5.17 (1 H, d, *J* = 10.8 Hz), 6.16 (1 H, dd, *J* = 17.6, 11.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 19.8, 23.0, 26.1, 27.0, 30.2, 30.6, 39.1, 49.0, 56.4, 116.5, 137.8, 212.2.

MS (EI) *m/z*: 194 (M^+, 43%), 109 (M^+–85, 100%).

HRMS calcd for $C_{13}H_{22}O$, 194.1671; found, 194.1676.

Configuration was determined by analogy to the methyl derivative. The equatorial configuration of the 2-methyl group was determined by a NOE between the 2-ethenyl proton (δ 6.16) and the 6-axial proton (δ 2.59).

(2*R,3*S**)-3-Butyl-2-ethenylcycloheptanone**
IR (neat): 2930, 2859, 2360, 1707, 1448, 1321, 1237, 1180, 1084, 990 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (3 H, t, *J* = 7.6 Hz), 1.08–1.62 (10 H, m), 1.77–1.94 (3 H, m), 2.35 (1 H, m), 2.58 (1 H, dt, *J* = 11.6, 3.6 Hz), 2.85 (1 H, t, *J* = 9.0 Hz), 5.14 (1 H, d, *J* = 18.4 Hz), 5.15 (1 H, d, J = 9.6 Hz), 5.77 (1 H, ddd, *J* = 8.0, 10.4, 8.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 22.9, 26.4, 28.8, 28.9, 32.2, 33.4, 40.3, 41.1, 64.5, 117.8, 135.7, 212.8.

MS (EI) *m/z*: 194 (M^+, 98%), 95 (M^+–99, 100%).

HRMS calcd for $C_{13}H_{22}O$, 194.1670; found, 194.1669.

Anal. calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.27; H, 11.50.

(2*S,3*S**)-3-Butyl-2-ethenylcycloheptanone**
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.92 (3 H, m), 1.08–1.34 (7 H, m), 1.55–1.58 (2 H, m), 1.64–1.71 (2 H, m), 1.73–1.83 (2 H, m), 2.46 (1 H, m), 2.55 (1 H, m), 3.33 (1 H, dd, *J* = 8.8, 2.8 Hz), 5.07 (1 H, d, *J* = 17.6, Hz), 5.18 (1 H, d, *J* = 10.0 Hz), 6.08 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4, 24.0, 25.0, 27.7, 31.05, 31.14, 32.6, 34.0, 41.8, 44.3, 62.5, 118.8, 135.5, 214.5.

IR (neat): 2926, 2856, 1700, 1457, 1378, 1260, 1098, 915 cm^{-1}.

MS (EI) *m/z*: 194 (M^+, 51%), 95 (M^+-99, 100%).

HRMS calcd for $C_{13}H_{22}O$, 194.1670; found, 194.1671.

(1*S,2*R**,5*R**)-2-Ethenylbicyclo[4.4.0]deca-3-one**
IR (neat) 3075, 1713, 1643, 989, 913 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89–1.05 (2 H, m), 1.10–1.34 (3 H, m), 1.39–1.50 (2 H, m), 1.73–1.86 (4 H, m), 1.95–1.99 (1 H, m), 2.35–2.46 (2 H, m), 2.66 (1 H, dd, *J* = 11.6, 9.2 Hz, 2ax), 4.96 (1 H, dd, *J* = 17.6, 2.4 Hz), 5.23 (1 H, dd, *J* = 10.0, 2.4 Hz), 5.69 (1 H, ddd, *J* = 17.6, 9.6, 9.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.8, 26.1, 32.3, 33.2, 34.3, 41.7, 41.8, 47.7, 61.4, 118.3, 134.5, 211.1.

MS (EI) *m/z*: 178 (M^+, 66%), 95 (M^+–83, 100%).

HRMS calcd for $C_{12}H_{18}O$, 178.1358; found, 178.1322.

Anal. calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.64; H, 10.32.

(2*R,6*R**)-2-Ethenyl-2,6-dimethylcyclohexanone**
IR (neat): 1932, 1704, 1457, 1002 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (3 H, d, *J* = 6.0 Hz), 1.26 (1 H, m), 1.31 (3 H, s), 1.38 (1 H, dq, *J* = 12.4, 3.6 Hz), 1.72–1.77 (1 H, m), 1.78–1.81 (2 H, m), 1.84–1.97 (1 H, m), 2.02–2.09 (1 H, m), 2.69 (1 H, septet, *J* = 8.0 Hz, 6ax), 5.00 (1 H, d, *J* = 17.6 Hz), 5.09 (1 H, d, *J* = 11.2 Hz), 6.19 (1 H, q, *J* = 17.6, 11.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4, 21.2, 22.8, 22.8, 36.0, 38.8, 41.2, 50.8, 112.0, 143.1, 216.3. MS (EI) *m/z*: 152 (M^+, 43%), 68 (M^+084, 100%).

HRMS calcd for $C_{10}H_{16}O$,152.1201; found,152.1190.

(2*S,6*R**)-2-Ethenyl-2,6-dimethylcyclohexanone**
IR (neat): 2930, 2856, 1711, 1632, 1451, 1374, 1259, 1036, 918 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (1 H, d, *J* = 6.4 Hz), 1.13 (1 H, s), 1.30–1.43 (1 H, m), 1.52–1.69 (1 H, m), 1.90 (1H, tq, *J* = 13.2, 3.6 Hz), 2.01–2.08 (2 H, m), 2.70 (1 H, septet, *J* = 6.4 Hz, 6ax), 4.97, (1 H, d, *J* = 17.6 Hz), 5.13 (1 H, d, *J* = 10.0 Hz), 5.96 (1 H, dd, *J* = 17.8, 10.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0, 22.1, 24.6, 37.0, 40.9, 42.1, 52.4, 77.2, 115.1, 142.7, 214.1. MS (EI) *m/z*: 152 (M^+, 55%), 94 (M^+–58, 100%).

HRMS calcd for $C_{10}H_{16}O$, 152.1201; found, 152.1194.

Anal. calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.57; H, 10.51.

(1*S,2*R**,6*R**)-1-Acetoxy-2,6-dimethyl-2-ethenylcyclohexane**
Under an Ar atmosphere, to a lithium tris(isoamyl)borohydride solution in THF (2.1 mL, 2.1 mmol) was added (2*R**,6*R**)-2-ethenyl-2,6-dimethylcyclohexanone (274 mg, 1.8 mmol) in THF (14 mL) at –78 °C. The resulting mixture was stirred vigorously for 2 h at –78 °C and then allowed to warm to room temperature for 1 h. The reaction mixture was hydrolyzed with H_2O and EtOH, and the organoborane compound was oxidized by treatment with sodium hydroxide (6 M) and hydrogen peroxide (30%). The aq phase was sat. with K_2CO_3 and the organic phase was separated. The aq phase was extracted with Et_2O–THF. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography to give (1*S**,2*R**,6*R**)-2,6-dimethyl-2-ethenyl-1-cyclohexanol (136 mg, 49%) and (1*R**,2*R**,6*R**)-2,6-dimethyl-2-ethenyl-1-cyclohexanol (127 mg, 46%).

Pyridine (5 mL) and Ac_2O (1 mL) were added to (1*S**,2*R**,6*R**)-2,6-dimethyl-2-ethenyl-1-cyclohexane (136 mg, 0.88 mmol) in Et_2O (5 mL), and the mixture was stirred at r.t. for 1 h. After addition of sat. $NaHCO_3$ the organic materials were extracted with Et_2O, washed with sat. $KHSO_4$, brine, dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography (hexene: EtOAc 50:1) to give (1*S**,2*R**,6*R**)-1-acetoxy-2,6-dimethyl-2-ethenylcyclohexane (131 mg, 76%).

IR (neat): 2928, 2857, 1769, 1463, 1072 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.83 (3 H, d, *J* = 6.8 Hz), 1.07 (3 H, s), 1.02–1.07 (1 H, m), 1.42–1.53 (4 H, m), 1.69–1.83 (2 H, m, 6ax), 2.01 (3 H, s), 4.53 (1 H, d, *J* = 10.4 Hz, 1ax), 4.92 (1 H, d, *J* = 9.6 Hz), 4.96 (1 H, d, *J* = 17.6 Hz), 5.72 (1 H, dd, *J* = 17.6, 11.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6, 18.7, 20.9, 21.0, 32.5, 33.9, 37.6, 41.7, 81.5, 111.6, 146.9, 170.5.

MS (EI) *m/z*: 196 (M^+, 3%), 43 (M^+–153, 100%).

HRMS calcd for $C_{12}H_{22}O_2$: 196.1463; found: 196.1463.

The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ 1.07) and the 6-axial proton (δ 1.69-1.83).

(1*S,2*R**,6*R**)-1-Acetoxy-2,6-dimethyl-2-ethenylcyclohexane**
IR (neat): 2934, 1741, 1245 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.81 (3 H, d, *J* = 7.6 Hz), 1.06 (3 H, s), 1.23 (1 H, td, *J* = 12.4, 4.4 Hz), 1.27–1.32 (1 H, m), 1.40–1.45 (1H, m), 1.54 (1 H, td, *J* = 13.2, 3.6 Hz), 1.61–1.67 (1 H, m), 1.71 (1 H, td, *J* = 13.2, 4.4 Hz), 1.87–1.96 (1 H, m), 2.01 (3 H, s), 4.78 (1 H, br. s), 4.92 (1 H, dd, *J* = 10.8, 1.6 Hz), 4.93 (1 H, dd, *J* = 17.6, 1.6 Hz), 5.75 (1 H, dd, *J* = 11.2, 17.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4, 21.0, 21.2, 22.4, 28.6, 29.3, 30.4, 30.8, 40.7, 111.2, 146.3, 170.5.

MS (EI) *m/z*: 196 (M^+, 0.7%), 43 (M^+–153, 100%).

HRMS calcd for $C_{12}H_{22}O_2$, 196.1463; found, 196.1427.

(2*S,3*R**,6*R**)-2-Ethenyl-2,3,6-trimethylcyclohexanone**
IR (neat): 3091, 1704, 1639, 1455, 1414, 985 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (3 H, d, *J* = 6.4 Hz), 0.99 (3 H, d, *J* = 6.4 Hz), 1.17 (3 H, s), 1.30–1.41 (1 H, m), 1.67–1.72 (2 H, m), 1.73–1.83 (1 H, m, 3ax), 2.00–2.06 (1 H, m), 2.68 (1 H, septet, *J* = 6.2 Hz, 6ax), 5.01 (1 H, d, *J* = 17.6 Hz), 5.22 (1 H, d, *J* = 11.2 Hz), 5.87 (1 H, dd, *J* = 17.6, 11.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 15.1, 15.9, 29.5, 35.1, 40.4, 41.4, 55.2, 113.7, 142.0, 215.3.

MS (EI) *m/z*: 166 (M^+, 60%), 67 (M^+–99, 100%).

HRMS calcd for $C_{11}H_{18}O$, 166.1358; found, 166.1346.

The equatorial 3-methyl stereochemistry was determined by observing the 3-proton with irradiation of the 3-methyl protons, *J* (^3H-^4H) = ca 9.6 Hz. The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ 1.17) and the 6-axial proton (δ 2.68).

(2*S,3*S**,6*R**)-2-Ethenyl-2,3,6-trimethylcyclohexanone**
IR (neat): 1707, 1612 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (3 H, d, *J* = 6.8 Hz), 1.03 (3 H, d, *J* = 6.4 Hz), 1.35 (3 H, s), 1.49–1.56 (1 H, m), 1.57–1.65 (1 H, m), 1.91–2.03 (2 H, m), 2.04–2.15 (1 H, m, 3eq), 2.72 (1 H, ddq, *J* = 11.6, 6.4, 6.4 Hz, 6ax), 5.06 (1H, d, *J* = 17.2 Hz), 5.16 (1H, dd, *J* = 10.8, 1.2 Hz), 6.27 (1H, dd, *J* = 17.6, 10.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.8, 16.4, 22.6, 27.6, 30.2, 40.4, 41.8, 54.3, 114.1, 139.5, 215.5.

MS (EI) *m/z*: 166 (M^+, 57%), 67 (M^+–99, 100%).

HRMS calcd for $C_{11}H_{18}O$, 166.1358; found, 166.1356.

Since this compound possesses *trans*-2,6-dimethyl group, the 3-methyl should be axial. The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ 1.35) and the 6-axial proton (δ 2.72).

(2*R,3*S**,6*R**)-2-Ethenyl-2,3,6-trimethylcyclohexanone**
IR (neat): 1711, 1601, 1260, 1453, 1384 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (3 H, d, *J* = 7.2 Hz), 0.99 (3 H, d, *J* = 6.4 Hz), 1.08 (3 H, s), 1.43–1.51 (1H, m, 4ax), 1.54–1.62 (1 H, m, 5ax), 1.88–1.95 (1 H, m, 5eq), 2.18–2.25 (2 H, m, 3eq,4eq), 2.80 (1 H, ddq, *J* = 12.4, 6.4, 6.0 Hz, 6ax), 4.93 (1 H, d, *J* = 17.6 Hz), 5.11 (1 H, d, *J* = 10.0 Hz), 6.06 (1 H, dd, *J* = 17.6, 10.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0, 15.5, 21.5, 28.6, 31.5, 41.2, 41.6, 56.1, 114.8, 144.6, 214.8. IR (neat) 1711, 1601, 1260, 1453, 1384 cm^{-1}.

MS (EI) m/z 166 (M^+, 48%), 93 (M^+-73, 100%).

HRMS calcd for $C_{11}H_{18}O$, 166.1358; found,166.1343.

The axial configuration of the 3-methyl group was determined by NOE between the 3-methyl protons (δ 0.87) and the 5-axial proton (δ 1.54-1.62). The equatorial configuration of the 2-methyl group was determined by NOE between the 2-ethenyl proton (δ 6.06) and the 6-axial proton (δ 2.80).

(2*S,3*R**,6*R**)-3-Butyl-2-ethenyl-2,6-dimethylcyclohexanone**
IR (neat): 3083, 1705, 1640, 1456, 996 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (3 H, t, *J* = 7.6 Hz), 0.99 (3 H, d, *J* = 6.8 Hz), 1.16 (3 H, s), 1.01–1.18 (2 H, m), 1.19–1.38 (3 H, m), 1.47–1.61 (2 H, m), 1.88–1.93 (1 H, m), 2.03–2.09 (1 H, m), 2.69 (1 H, ddd, *J* = 12.4, 6.8, 6.4 Hz, 6ax), 5.01 (1 H, dd, *J* = 17.6, 1.6 Hz), 5.24 (1 H, dd, *J* = 10.8, 1.2 Hz), 5.84 (1 H, ddd, *J* = 17.6, 11.2, 1.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 14.9, 15.1, 22.9, 26.5, 29.9, 30.5, 35.1, 40.7, 46.9, 113.9, 142.2, 215.2.

MS (EI) *m/z*: 208 (M^+, 71%), 81 (M^+–127, 100%).

HRMS calcd for $C_{14}H_{24}O$, 208.1827; found, 208.1830.

Anal. calcd for $C_{10}H_{16}O$: C, 80.71; H, 11.62. Found: C, 80.49; H, 11.77.

The stereochemistry was determined by analogy to the 3-methyl derivatives. The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ 1.16) and the 6-axial proton (δ 2.69).

(2*S,3*S**,6*R**)-3-Butyl-2-ethenyl-2,6-dimethylcyclohexanone**
IR (neat): 3080, 1706, 1634, 1456, 995 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (3 H, t, *J* = 6.4 Hz), 1.03 (3 H, d, *J* = 6.8 Hz), 1.06–1.17 (2 H, m), 1.18–1.33 (3 H, m), 1.34 (3 H, s), 1.43–1.63 (3H, m), 1.74–1.80 (1 H, m), 1.90–1.98 (1 H, m), 2.00–2.09 (1 H, m), 2.71 (1 H, ddd, *J* = 10.8, 6.8, 6.4 Hz, 6ax), 5.05 (1 H, dd, *J* = 17.6, 1.2 Hz), 5.16 (1 H, dd, *J* = 11.2, 1.6 Hz), 6.28 (1 H, dd, *J* = 17.6, 11.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 15.9, 22.8, 23.0, 23.3, 28.8, 30.0, 30.2, 40.3, 47.0, 54.5, 114.2, 139.6, 215.6.

MS (EI) *m/z*: 208 (M^+, 78%), 81 (M^+-127, 100%).

HRMS calcd for $C_{14}H_{24}O$, 208.1827; found, 208.1831.

The stereochemistry was determined by analogy to the 3-methyl derivatives. The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ 1.34) and the 6-axial proton (δ 2.71).

(2*R,3*S**,6*R**)-3-Butyl-2-ethenyl-2,6-dimethylcyclohexanone**
IR (neat): 3080, 1708, 1628, 1456, 1260, 991, 916 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 7.7 Hz), 0.99 (3 H, d, *J* = 6.4 Hz), 1.10 (3 H, s), 1.06–1.51 (7 H, m), 1.57–1.63 (1 H, m), 1.86–1.98 (2 H, m), 2.02–2.10 (1 H, m), 2.81 (1 H, ddd, *J* = 13.2, 6.0, 6.0 Hz, 6ax), 4.91 (1 H, d, *J* = 17.6 Hz), 5.11 (1 H, d, *J* = 11.2 Hz), 6.03 (1H, dd, *J* = 17.6, 10.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 15.1, 21.1, 22.9, 23.7, 27.2, 29.9, 31.2, 41.0, 46.4, 56.3, 114.7, 144.9, 215.1.

MS (EI) *m/z*: 208 (M^+, 53%), 81 (M^+–127, 100%).

HRMS calcd for $C_{14}H_{24}O$, 208.1827; found, 208.1844.

The stereochemistry was determined by analogy to the 3-methyl derivatives. The equatorial configuration of the 2-methyl group was determined by NOE between the 2-ethenyl proton (δ 6.03) and the 6-axial proton (δ 2.81).

(2*S,3*R**,5*R**)-2-Ethenyl-3,5-diisopropyl-2-methylcyclo-hexanone**
IR (neat): 3085, 1707, 1628, 992, 915 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ= 0.86 (3 H, d, *J* = 6.4 Hz), 0.91 (6 H, d, *J* = 6.8 Hz), 0.95 (3 H, d, *J* = 6.4 Hz), 1.20 (3 H, s), 1.49 (1 H, sixtet, *J* = 7.2 Hz), 1.70–1.78 (4 H, m), 1.80–1.89 (2H, m), 2.41–2.43 (2 H, m, 6ax,eq), 5.02 (1 H, d, *J* = 17.6 Hz), 5.17 (1 H, d, *J* = 11.2 Hz), 5.86 (1 H, dd, *J* = 17.6, 10.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2, 19.6, 20.0, 20.2, 24.1, 24.4, 27.6, 31.4, 41.4, 41.5, 47.5, 56.1, 114.6, 143.5, 214.6.

MS (EI) *m/z*: 222 (M^+, 20%), 95 (M^+–127, 100%).

HRMS calcd for $C_{15}H_{26}O$, 222.1984; found, 222.1982.

Anal. calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.01; H, 11.88.

The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ 1.20) and the 6-axial proton (δ 2.41−2.43).

Synthesis of (1*S,2*S**,3*R**,5*R**)-2-Ethenyl-2-methyl-3,5-diisopropyl-1-cyclohexanol, (1*R**,2*S**,3*R**,5*R**)-2-Ethenyl-2-methyl-3,5-diisopropyl-1-cyclohexanol**
Under an Ar atmosphere, to a suspension $LiAlH_4$ (0.15 mmol, 5.6 mg) in Et_2O (1.0 mL) was added (2*S**,3*R**,5*R**)-2-ethenyl-3,5-diisopropyl-2-methylcyclohexanone (64.4 mg, 0.39 mmol) in Et_2O (2.0 mL) at 0 °C. The resulting mixture was stirred vigorously for 10 min at 0 °C, and hydrolyzed with H_2O and MeOH. The organic materials were extracted twice with Et_2O. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography (hexene: Et_2O, 30:1) to give (1*S**,2*S**,3*R**,5*R**)-2-ethenyl-2-methyl-3,5-diisopropylcyclohexanone (31.4 mg, 48%) and (1*R**,2*S**,3*R**,5*R**)-2-ethenyl-2-methyl-3,5-isopropylcyclohexanol (26.9 mg, 41%).

(1*R,2*S**,3*R**,5*R**)-2-ethenyl-2-methyl-3,5-diisopropylcyclohexanol**
^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, d, *J* = 7.2 Hz), 0.89 (3 H, d, *J* = 6.8 Hz), 0.90 (3 H, d, *J* = 6.4 Hz), 0.96 (3 H, d, *J* = 6.8 Hz), 1.14 (3 H, s), 1.36–1.43 (3 H, m), 1.51–1.55 (1 H, m), 1.60 (1 H, q, *J* = 4.4 Hz), 1.61–1.67 (1 H, m), 1.71 (1 H, dt, *J* = 12.4, 3.6 Hz), 1.87–1.91 (1 H, m), 3.51 (1 H, br. s), 5.12 (1H, dd, *J* = 17.6, 1.6 Hz), 5.19 (1 H, dd, *J* = 11.2, 1.2 Hz), 6.07 (1 H, dd, *J* = 17.6, 11.2 Hz).

(1*S,2*S**,3*R**,5*R**)-2-Ethenyl-2-methyl-3,5-diisopropylcyclohexanol**
^1H NMR (400 MHz, $CDCl_3$): δ = 0.79 (3 H, d, *J* = 6.4 Hz), 0.87 (3 H, d, *J* = 7.2 Hz), 0.89 (3 H, d, *J* = 6.4 Hz), 0.95 (3 H, d, *J* = 6.4 Hz), 0.97 (3 H, s), 1.24 (1H, dt, *J* = 13.2, 1.6 Hz, 3ax), 1.36 (1 H, td, *J* = 13.2, 5.2 Hz, 4ax), 1.39–1.42 (1 H, m, 5eq), 1.46 (1 H, td, *J* = 13.2, 5.2 Hz, 6ax), 1.58 (1 H, ddd, *J* = 12.4, 3.8, 3.0 Hz, 4eq), 1.68–1.78 (2 H, m), 1.90 (1 H, dquintet, *J* = 13.2, 3.6 Hz, 6eq), 3.38 (1 H, dd, *J* = 12.8, 4.4 Hz, 1ax), 5.12 (1 H, dd, *J* = 17.6, 1.2 Hz), 5.24 (1 H, dd, *J* = 11.2, 1.2 Hz), 5.63 (1 H, dd, *J* = 17.6, 11.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.1, 19.0, 21.5, 21.8, 22.8, 25.0, 27.0, 27.3, 30.2, 40.0, 43.9, 48.4, 70.8, 115.3, 147.5.

IR (neat): 3455, 2955, 2870, 1461, 1386, 1367, 1050, 910 cm^{-1}.

MS (EI) *m/z*: 224 (M^+, 1%), 95 (M^+–129, 100%).

HRMS calcd for $C_{15}H_{28}O$, 224.2140; found, 224.2152.

The equatorial configuration of the 2-ethenyl group was determined by NOE between the 2-methyl protons (δ 0.97) and the 6-axial proton (δ 1.46). The coupling constant between the 5-proton and the 6-axial proton (*J* = 4.4 Hz) showed the axial configuration of the 5-isopropyl group. The coupling constant between the 4-equatorial proton and the 3-axial proton (*J* = 3.8 Hz) showed the equatorial configuration of the 3-isopropyl group.

Gallium Enolate of 3-Butylcyclohexanone
Under an Ar atmosphere, to a cyclohexane-d_{12} (0.3 mL) solution of 3-butyl-1-trimethylsilyloxycyclohexene (0.5 mmol, 113 mg) was added a cyclohexane-d_{12} (0.5 mL) solution of $GaCl_3$ (0.5 mmol, 87.5 mg) at r.t. and the NMR spectrum was taken immediately.

^{13}C NMR (100 MHz, C_6D_{12}): δ = 2.3, 15.0, 22.5, 24.2, 28.8, 30.6, 31.6, 36.7, 125.0, 150.6.

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