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"Stereoselective Prins-Cyclizations of d,e-Unsaturated Ketones to *cis*-1,3-Chlorocyclohexanols"

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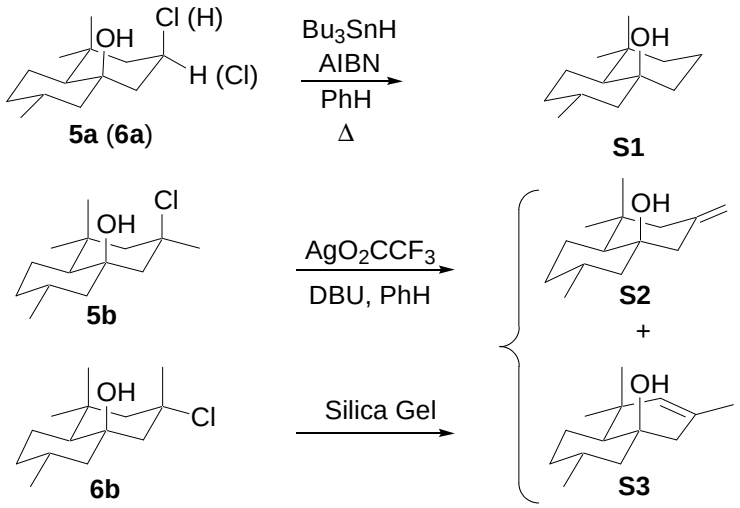
Contents: Discussion of structure elucidation for chlorohydrins (pages 2-3) and experimental procedures together with analytical and spectral data for all compounds (pages 3-40).

Structure Elucidation

The structures of the cyclization products were determined by a combination of NMR analysis, X-ray crystallography, and chemical conversions (Scheme S1). For example, the connectivity of cis chlorohydrin **5a** was deduced using a combination of HMQC and HMBC NMR spectroscopy and the relative configuration of the chloro and hydroxyl substituents was established by analysis of ^{1}H NMR spin-spin coupling (app. quint, J = 3.9 Hz, C*H*Cl) and ^{1}H NMR NOE spectra (H6α ↔ H2α, 1.6%; H6α ↔ H4α, ~3%). Reductive dechlorinations (Bu_3SnH, AIBN, PhH, reflux) of **5a** and **6a** gave the same tertiary alcohol **S1** (70% and 61%), thereby establishing that the minor chlorohydrin is the trans isomer. Chlorohydrin isomers **8a** and **9a** obtained from acyclic enone **7a** were identified in an analogous fashion. ^{1}H NMR NOE spectra of trans chlorohydrin **9b** (5βCH_3 ↔ 3βCH_3, 2.3%) revealed that the molecule adopts a solution conformation with the chloro group in an equatorial position.

Reductive dechlorination (Bu_3SnH, AIBN) of exo bicyclic chlorohydrin **11** and a 3.8:1 mixture of **12**:**11** gave the same known tertiary alcohol (50% and 60%) previously prepared by reductive cyclization of a bromo ketone precursor.[1] The structure assignment for chlorohydrin **14** is based upon ^{1}H NMR analysis, HMBC correlations, and NOE correlations in addition to conversion (DBU, 23%) to the known 3-methylneomenth-7-en-3-ol.[2] The olefinic products were identified through a combination of ^{1}H NMR analysis, HMBC correlation, and chemical correlation with the cis-chlorohydrin. For example, dehydrochlorination of cis chloro decalol **5b** with AgO_2CCF_3 and DBU gave a 1:18 mixture (^{1}H NMR integration) of olefins **S2** and **S3** (36%). The silica gel-induced elimination of **6b** provided endocylic olefin **S3** (39%). Dehydrochlorination of cis chlorohydrin **8b** with AgO_2CCF_3 and DBU gave a 20:1 mixture (^{1}H NMR integration) of endocyclic and exocyclic homoallylic cyclohexanols. Treatment of trans chlorohydrins **6b** and **9b** with DBU and AgO_2CCF_3 gave keto olefins **4b** and **7b**, respectively.

Scheme S1. Correlations of cis and trans chlorohydrins



General Experimental Procedures:

All reactions were performed under N_2 using oven dried glassware. Et_2O, THF, and benzene were distilled from sodium / benzophenone ketyl before use. CH_2Cl_2, pentane, and toluene were distilled from calcium hydride before use. Anhydrous HCl vapor was used directly from the compressed gas cyclinder. $TiCl_4$ (Aldrich) was distilled from Cu powder and stored as a 1.0 M solution in anhydrous CH_2Cl_2, pentane, or toluene.[3] Allylsilane and methallylsilane were purchased from Gelest or Aldrich Chem. Co. Keto olefins 5-hexen-2-one and 5-methyl-5-hexen-2-one were purchased from Aldrich Chem. Co. Allyl bicyclo[3.3.0]octanone (**15**) was prepared as described previously.[4] Solvents used for chromatography were distilled prior to use. All other reagents and solvents used were reagent grade.

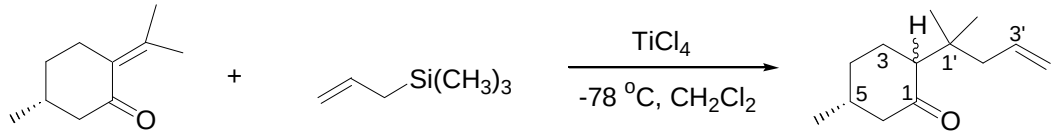
Column chromatography was performed according to Still's procedure[5] using 100-200 times excess Woelm 32-64 μm grade silica gel. TLC analysis was performed using Merck glass TLC plates (0.25 mm 60 F-254 silica gel). Visualization of the developed plates was accomplished by staining with ethanolic phosphomolybdic acid, ceric ammonium molybdate, or *p*-anisaldehyde followed by heating on a hotplate (ca. 120 °C). Gas chromatography (GC) was conducted using a Shimadzu Model 14A-GC on a

Rt_x-5 30-m fused silica capillary column (split ratio~ 100:1). The following programs were used: Method A = initial temperature of 75 °C for 2.0 min, ramp 12 °C/min to 270 °C, and hold for 20 min; Method B = initial temperature of 125 °C for 2.0 min, ramp 12 °C/min to 270 °C, and hold for 10 min. The standard operating conditions were 300 °C injector temperature and 310 °C detector temperature. A Hewlett-Packard 3395 integrator was used to integrate the FID detector signal. GC-MS was conducted with a Hewlett-Packard HP 5890A using a J&W Scientific DB-5 column using method A temperature program.

NMR spectral data were collected in the University of Illinois Varian-Oxford Instruments Center for Excellence in NMR (V.O.I.C.E.) using the Unity 400, Unity 500, and Unity-Inova 500 NB spectrometers. The following solvents and reference values (ppm) were used: $CDCl_3$ (^{1}H: 7.26, ^{13}C: 77.0), C_6D_6 (^{1}H: 7.15, ^{13}C: 128.0). The abbreviation "app." (apparent) in ^{1}H NMR assignments refers to the appearance of the multiplet observed and the coupling constants deduced in these cases were obtained by first-order coupling analysis. 2D-NMR data were reported as follows: acquisition technique (MHz, solvent): (δ of reference signal) δ ^{1}H correlations. ^{1}H NMR NOE data were reported as follows: (MHz, solvent): Irrad. δ data, obs. δ data (% NOE enhancement). The samples for NOE analysis were prepared by performing at least five freeze-pump-thaw cycles. The product ratios for crude and purified products were determined by ^{1}H NMR analysis unless noted otherwise. The crude yields for the tertiary chlorohydrins were determined by ^{1}H NMR analysis using ethylene glycol dimethyl ether as an internal standard. The purity of all products was determined to be >95% by NMR and/or GC analyses unless specified otherwise. IR spectra were collected using a Mattson Galaxy Series Model 5000 IR. Samples for IR analysis were prepared as either dilute solutions in CCl_4 or neat liquids on NaCl plates and data are reported as wave numbers (cm^{-1}). Melting points were determined in open capillary tubes and are uncorrected. Optical rotations were measured using a Jasco DIP-360 digital polarimeter with a sodium lamp using a 1.00 ± 0.03 (g/100 mL) solution of sample in $CHCl_3$ at 24 ^oC. Microanalysis and mass spectral data were collected by the University of Illinois Microanalysis and Mass Spectroscopy Laboratories, respectively. Compounds that only

appear in the supporting information have been assigned a structure number (S#) in the order in which they appear.

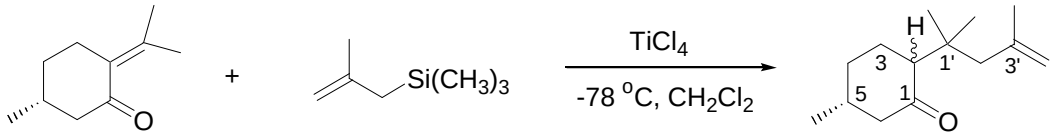
Keto olefin Preparations



4a, S4

(2S,5R)- and (2R,5R)-2-(1',1'-Dimethyl-3-butenyl)-5-methylcyclohexanones (4a and S4). The procedure for this conjugate addition was based on that described by Sakurai and Santelli,[6,7] although modified for large scale. A solution of (*R*)-pulegone (40.0 g, 0.26 mol) and CH_2Cl_2 (700 mL) was mechanically stirred and cooled at –78 °C as an aliquot of $TiCl_4$ (29 mL, 0.26 mol) was added dropwise over 5 min. After 5 min, a solution of allylsilane (39 g, 0.34 mol) in CH_2Cl_2 (160 mL) was added dropwise over 10 min. The resultant dark purple colored solution was stirred for 10 min at –78 °C and 10 min at 0 °C. A solution of Et_3N (183 mL, 1.32 mol) and MeOH (59 mL, 1.32 mol) was added dropwise over 5 min. After 5 min, the heterogeneous mixture was diluted with Et_2O (3.0 L) and the resultant mixture was divided into four equal portions (~1 L). Each portion was washed with 10% HCl (2 x 250 mL), satd. $NaHCO_3$ (250 mL) and satd. NaCl (250 mL); dried ($MgSO_4$); and evaporated under reduced pressure to afford 46.3 g of crude that was a 1.7:1 mixture of trans and cis keto olefins (GC). Column purification (2:98 Et_2O:hexane) of a 3.0 g sample afforded 0.11 g (2%) of colorless oil containing trans keto olefin that was 58% pure (GC), 1.21 g (37%) of trans keto olefin, and 0.95 g (29%) of colorless oil that was a 8:1 mixture of cis:trans keto olefin isomers (GC). Additional column purification (2:98 Et_2O:hexane) of the 8:1 isomer mixture afforded 73 mg of trans keto olefin and 0.79 g of cis keto olefin as a colorless oil. **4a**: TLC R_f = 0.62 (15:85 EtOAc:hexane); t_R = 9.83 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (s, 3H, C1'-CH_3), 0.99 (d, 3H, *J* = 6.2 Hz, C5-CH_3), 1.01 (s, 3H, C1'-CH_3), 1.31 (qdd, 1H, *J* = 12.6, 3.4, 1.3 Hz), 1.45 (qd, 1H, *J* = 12.9, 3.2 Hz), 1.80-1.91 (m, 2H), 1.99 (td, 1H, *J* = 12.2, 1.3 Hz), 2.02 (ddt, 1H, *J* = 13.3, 7.5, 1.1 Hz), 2.07-2.12 (m, 1H), 2.16 (ddd, 1H, *J* =

12.6, 4.7, 1.1 Hz), 2.24 (ddd, 1H, *J* = 12.2, 3.9, 1.9 Hz), 2.31 (dd, 1H, *J* = 13.5, 7.7 Hz), 4.97 (dm, 1H, *J* = 16.9 Hz, $=CH_2$), 5.00 (dm, 1H, *J* = 10.1 Hz, $=CH_2$), 5.76 (dddd, 1H, *J* = 17.6, 10.0, 7.7, 7.3 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.33, 24.23, 25.16, 28.16, 34.55, 34.71, 36.44, 44.85, 52.42, 56.75, 117.01, 135.44, 212.28 (C=O); IR (neat) 2953, 2872, 1711 (C=O), 1454, 1363, 914;); $[\alpha]_D$ -18.6. **S4**: TLC R_f = 0.56 (15:85 EtOAc:hexane); t_R = 10.05 min (Method A); ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (d, 3H, *J* = 7.1 Hz, C5-CH_3), 0.95 (s, 3H, C1'-CH_3), 1.01 (s, 3H, Cl'-CH_3), 1.60 (m, 1H), 1.71-1.86 (m, 2H), 1.92 (m, 1H), 2.01-2.06 (m, 2H), 2.19 (ddd, 1H, *J* = 11.1, 5.6, 0.9 Hz), 2.26 (dd, 1H, *J* = 13.5, 7.5 Hz), 2.32 (m, 1H), 2.48 (dd, 1H, *J* = 12.6, 5.8 Hz), 4.99 (dm, 1H, *J* = 16.9 Hz, $=CH_2$), 5.00 (dm, 1H, *J* = 10.3 Hz, $=CH_2$), 5.77 (ddt, 1H, *J* = 17.8, 10.3, 7.5 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.13, 24.02, 24.53, 25.25, 31.38, 32.32, 34.94, 44.99, 50.37, 56.98, 117.13, 135.35, 213.02 (C=O); IR (neat) 2956, 1711 (C=O), 1456, 1383, 914; $[\alpha]_D$ +36.5. The physical data were similar to those reported in the literature (^1H NMR, 200 MHz, CCl_4).[8]

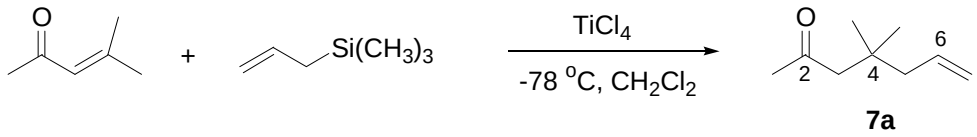


4b, S5

(2S,5R)- and (2R,5R)-2-(1',1',3'-Trimethyl-3-butenyl)-5-methylcyclohexanones (4b and S5). The procedure for this conjugate addition is based on that described above for the preparation of **4a**. A 1.0 M solution of $TiCl_4$ in CH_2Cl_2 (19.7 ml, 19.7 mmol) was added dropwise over 5 min to a solution of (*R*)-pulegone (3.0 g, 19.7 mmol) in CH_2Cl_2 (35 mL) at –78 °C. After 5 min, a solution of methallylsilane (3.29 g, 25.6 mmol) in CH_2Cl_2 (12 mL) was added dropwise over 5 min. After stirring 5 min at –78 °C and 10 min at 0 °C, a solution of Et_3N (13.8 mL, 99 mmol) and MeOH (4.4 mL, 99 mmol) was added dropwise over 5 min. The resultant heterogeneous mixture was stirred 10 min then diluted with Et_2O (200 mL) and 10% HCl (75 mL). The aqueous layer was extracted with Et_2O (100 mL). The organic layers were combined and washed with satd. $NaHCO_3$

(75 mL), and satd. NaCl (75 mL); dried ($MgSO_4$); and evaporated to give 4.46 g of crude oil that was a 1.4:1 (GC) mixture of trans and cis keto olefins. Column purification (2:98, Et_2O:hexane) afforded 1.12 g of trans keto olefin (23%) as a colorless oil and 1.19 g of colorless oil that was a mixture of cis and trans isomers. Addition column purification (2:98 Et_2O:hexane) of the isomer mixture afforded 70 mg (2%) of trans keto olefin, 42 mg (1%) that was a 3:1 mixture (GC) of cis:trans isomers, and 1.0 g (24%) of cis keto olefin. **4b**: TLC R_f = 0.74 (15:85 EtOAc:hexane); t_R = 6.92 min (Method B); ^{1}H NMR 500 MHz, C_6D_6) δ 0.67 (d, 3H, *J* = 6.2 Hz), 0.88 (qd, 1H, *J* = 12.9, 3.6 Hz), 1.00 (s, 3H), 1.16 (s, 3H), 1.18 (qd, 1H, *J* = 13.1, 3.2 Hz), 1.42-1.54 (m, 2H), 1.62 (td, 1H, *J* = 12.3, 1.1 Hz), 1.74 (m, 3H), 1.76-1.80 (m, 1H), 1.98 (ddd, 1H, *J* = 13.2, 4.6, 1.0 Hz), 2.05 (d, 1H, *J* = 12.9 Hz), 2.19 (ddd, 1H, *J* = 11.8, 3.8, 2.4 Hz), 2.57 (d, 1H, *J* = 12.9 Hz), 4.77 (m, 1H, $=CH_2$), 4.93 (m, 1H, $=CH_2$); ^{13}C NMR (126 MHz, C_6D_6) δ 22.23, 24.95, 25.66, 26.46, 28.39, 34.70, 35.33, 36.25, 47.63, 52.35, 57.22, 114.78 ($=CH_2$), 143.85 (=C), 210.21 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (s, 3H, Cl′-CH_3), 0.99 (d, 3H, *J* = 6.2 Hz, C5-CH_3), 1.03 (s, 3H, Cl′-CH_3), 1.32 (qdd, 1H, *J* = 13.1, 3.4, 1.3 Hz), 1.46 (qd, 1H, *J* = 13.0, 3.1 Hz), 1.75 (s, 3H, C3′-CH_3), 1.82-1.92 (m, 2H), 1.998 (d, 1H, *J* = 13.1 Hz), 2.003 (td, 1H, *J* = 12.3, 1.3 Hz), 2.13 (m, 1H), 2.20-2.27 (m, 2H), 2.37 (d, 1H, *J* = 12.9 Hz), 4.59 (dd, 1H, *J* = 1.7, 0.9 Hz, $=CH_2$), 4.82 (app. sext., 1H, *J* = 1.4 Hz, $=CH_2$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.32, 24.78, 25.50, 26.34, 28.44, 34.75, 35.14, 36.56, 47.44, 52.60, 57.29, 114.36 ($=CH_2$), 143.75 (=C), 212.49 (C=O); IR (neat) 3074, 2955, 2872, 1711 (C=O), 1640, 1455, 1374, 1364, 1206, 892; MS (EI, 70 eV) *m/z* (rel intensity %) 208 (34), 193 (60), 175 (16), 153 (63), 135 (13), 119 (7), 109 (65), 97 (86), 81 (46), 69 (100); $[\alpha]_D$ -17.2. Kugelrohr distillation at 85-90 ^{o}C (1.0 torr) gave a sample an analytical sample: Anal. Calcd for $C_{14}H_{24}O$ (208.33): C, 80.71; H, 11.61. Found: C, 80.77; H, 11.60. **S5**: TLC R_f = 0.71 (15:85 EtOAc:hexane); t_R = 7.12 min (Method B); ^{1}H NMR (500 MHz, C_6D_6) δ 0.74 (d, 3H, *J* = 6.9 Hz, C5-CH_3), 0.98 (s, 3H, Cl′-CH_3), 1.13 (s, 3H, Cl′-CH_3), 1.20-1.25 (m, 1H), 1.39-1.53 (m, 2H), 1.60-1.65 (m, 1H), 1.73 (m, 3H), 1.89-1.96 (m, 2H), 2.02-2.06 (4-line m, 2H), 2.14 (app. dd, 1H, *J* = 12.7, 5.8 Hz), 2.51 (d, 1H, *J* = 13.1 Hz), 4.76 (m, 1H, $=CH_2$), 4.93 (m, 1H, $=CH_2$); ^{13}C NMR (126 MHz, C_6D_6) δ 18.72, 24.22, 25.03, 25.63, 26.37, 31.52, 32.40, 35.56, 47.64, 50.32, 57.66, 114.83

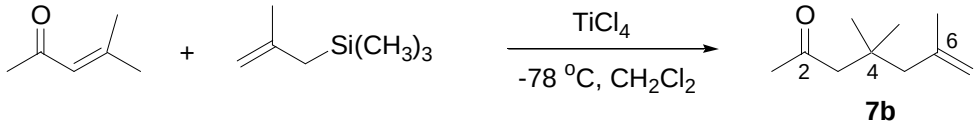
(=CH_2), 143.77 (=C), 210.71 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (d, 3H, *J* = 7.1 Hz, C5-CH_3), 0.98 (s, 3H, Cl′-CH_3), 1.03 (s, 3H, Cl′-CH_3), 1.61 (m, 1H), 1.72-1.88 (m, 2H), 1.76 (m, 3H, C3′-CH_3), 1.96 (dqm, 1H, *J* = 12.6, 4.8 Hz), 2.01 (d, 1H, *J* = 12.6 Hz), 2.03 (ddd, 1H, *J* = 12.6, 4.5, 1.5 Hz), 2.26 (dd, 1H, *J* = 11.3, 5.5 Hz), 2.32 (d, 1H, *J* = 13.1 Hz), 2.34 (m, 1H), 2.49 (dd, 1H, *J* = 12.6, 5.8 Hz), 4.60 (m, 1H, =CH_2), 4.83 (app. sept., 1H, *J* = 1.3 Hz, =CH_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.09, 24.30, 24.99, 25.51, 26.32, 31.46, 32.44, 35.51, 47.55, 50.53, 57.59, 114.49 (=CH_2), 143.61 (=C), 213.13 (C=O); IR (neat) 3074, 2958, 2920, 2875, 1711 (C=O), 1640, 1455, 1383, 891; MS (EI, 70 eV) *m/z* (rel intensity %) 208 (24), 193 (38), 175 (14), 153 (63), 135 (13), 119 (9), 109 (62), 97 (89), 81 (56) 69 (100); $[\alpha]_D$ +33.0. Kugelrohr distillation at 75-80 ^{o}C (0.40 torr) gave an analytical sample: Anal. Calcd for $C_{14}H_{24}O$ (208.33): C, 80.71; H, 11.61. Found: C, 80.47; H, 11.71.



7a

4,4-Dimethyl-hept-6-en-2-one (7a). The procedure for this conjugate addition was based on that described by Sakurai, except the reaction time was increased.[6] A 1.0 M solution of $TiCl_4$ in CH_2Cl_2 (41 ml, 41 mmol) was added dropwise over 5 min to a solution of mesityl oxide (4.0 g, 41 mmol) in CH_2Cl_2 (40 mL) at –78 ^{o}C. After 5 min, a solution of allylsilane (6.1 g, 53 mmol) in CH_2Cl_2 (40 mL) was added dropwise over 5 min. The resultant rusty-brown colored solution was placed in a rt H_2O bath and stirred 15 min. The dark purple solution was cooled to 0 ^{o}C (5 min, 0 ^{o}C bath) and H_2O (40 mL) was added to hydrolyze the $TiCl_4$. After 5 min, the mixture was diluted with Et_2O (120 mL) and the organic layer was washed with 10% HCl (60 mL), satd. $NaHCO_3$ (60 mL), and satd. NaCl (60 mL); dried ($MgSO_4$); and evaporated. The crude oil was fractionally distilled using a 5 cm vigereaux column (14/20) at 80 ^{o}C and 47 mmHg to afford 4.25 g (74%) of colorless oil: TLC R_f = 0.58 (15:85 EtOAc:hexane); t_R = 4.62 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (s, 6H, $C(CH_3)_2$), 2.08 (d, 2H, *J* = 7.7

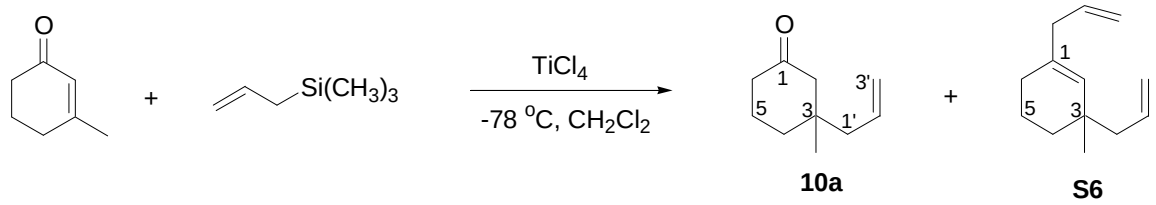
Hz, H5), 2.11 (s, 3H, $COCH_3$), 2.32 (s, 2H, H3), 5.01 (dm, 1H, J = 16.9 Hz, $=CH_2$), 5.05 (dm, 1H, J = 10.1 Hz, $=CH_2$), 5.79 (ddt, 1H, J = 17.0, 10.3, 7.5 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.15 (CH_3), 32.41 (CH_3), 33.56 (C3), 46.41 (CH_2), 53.35 (CH_2), 117.56 ($=CH_2$), 135.00 (=CH), 208.86 (C=O); IR (neat) 3077, 2959, 1714 (C=O), 1361, 916. The physical data were similar to those reported in the literature (^1H NMR, 60 MHz, CCl_4).[9]



7b

4,4,6-Trimethyl-hept-6-en-2-one (7b). The procedure for this conjugate addition is based on that described for the preparation of **7a**. A solution of mesityl oxide (7.9 g, 80 mmol) in CH_2Cl_2 (150 mL) was stirred and cooled at –78 °C as an aliquot of $TiCl_4$ (8.8 mL, 80 mmol) was added dropwise over 5 min. After 5 min, a solution of methallylsilane (13.3 g, 104 mmol) in CH_2Cl_2 (80 mL) was added dropwise over 10 min. The resultant opaque purple solution was stirred 10 min at –78 °C and 5 min at 0 °C. A solution of Et_3N (56 mL, 400 mmol) and MeOH (18 mL, 400 mmol) was added dropwise over 5 min. The heterogeneous mixture was stirred 5 min at 0 °C and diluted with Et_2O (600 mL). The organic layer was washed with 10% HCl (2 x 250 mL), satd. $NaHCO_3$ (250 mL), and satd. NaCl (250 mL); dried ($MgSO_4$); and evaporated to give 12.8 g of crude oil. Column purification of a 3.0 g sample (7:93 EtOAc:hexane) afforded 1.64 g (57%) of keto olefin as a colorless oil: TLC R_f = 0.59 (15:85 EtOAc:hexane); t_R = 6.07 min (Method A); ^1H NMR (500 MHz, $CDCl_3$) δ 1.03 (s, 6H, C4-CH_3), 1.76 (m, 3H C6-CH_3), 2.08 (s, 2H), 2.11 (s, 3H, $COCH_3$), 2.36 (s, 2H), 4.63 (m, 1H, $=CH_2$), 4.86 (app. sext., 1H, J = 1.4 Hz, $=CH_2$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.30, 27.81, 32.41, 34.07, 49.49, 53.91, 114.69 ($=CH_2$), 143.13 (=C), 208.92 (C=O); IR (neat) 3074, 2958, 1714 (C=O), 1641, 1471, 1362, 1155, 893; MS (EI, 70 eV) *m/z* (rel intensity %) 209 (18), 171 (9), 155 (7), 154 (4), 139 (29), 121 (31), 96 (100), 81 (58). Kugelrohr distillation at 30-35 °C (0.40 torr) gave a sample for elemental analysis: Anal. Calcd for $C_{10}H_{18}O$ (154.24): C, 77.87; H, 11.76. Found: C, 78.09; H, 11.99. HRMS (EI, 70 eV) Calcd for

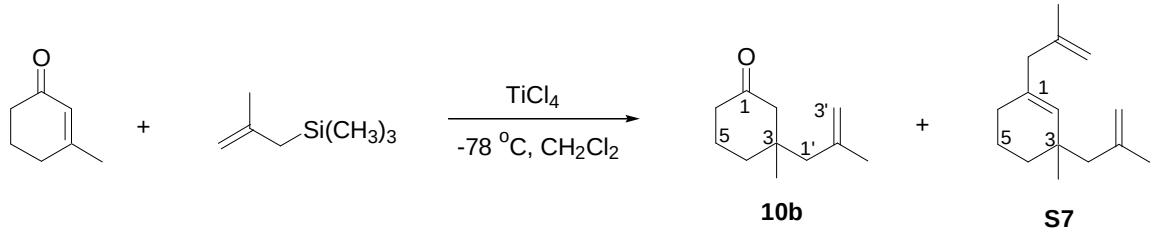
$C_{10}H_{18}O$: 154.1358. Found: 154.1357 (Δ=0.5). No physical data were reported for this known compound.[10]



10a **S6**

3-Methyl-3-(prop-2-enyl)cyclohexanone (10a). The procedure for this conjugate addition is based on that described by Cunningham.[11] A 1.0 M solution of $TiCl_4$ in CH_2Cl_2 (20 ml, 20 mmol) was added dropwise over 5 min to a solution of 3-methyl-2-cyclohexen-1-one (2.20 g, 20 mmol) in CH_2Cl_2 (20 mL) at –20 °C. After 2 min, allylsilane (4.5 mL, 28 mmol) was added dropwise over 1 min. After stirring 7 h at –20 °C, a solution of Et_3N (13.9 mL, 100 mmol) and MeOH (4.5 mL, 100 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 5 min. The resultant orange heterogeneous mixture was stirred 5 min then diluted with Et_2O (250 mL). The organic layer was washed with 10% HCl (2 x 75 mL), satd. $NaHCO_3$ (75 mL), and satd. NaCl (75 mL); dried ($MgSO_4$); and evaporated to give 2.97 g of crude oil that was a 5.4:1 mixture of keto olefin and triene. Column purification (8:92 EtOAc:hexane) afforded 1.47 g (48%) of keto olefin and 0.53 g (15%, 11% Corr. for purity) of triene as a colorless oil that was 74% pure by GC. **10a**: TLC R_f = 0.70 (30:70 EtOAc:hexane); t_R = 8.32 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (s, 3H, C3-CH_3), 1.53 (dtm, 1H, *J* = 14.2, 5.4 Hz), 1.64 (ddd, 1H, *J* = 13.7, 9.0, 4.7 Hz), 1.80-1.93 (m, 2H), 2.02 (app. d, 2H, *J* = 7.5 Hz), 2.08 and 2.21 (ABq, 2H, *J* = 13.5 Hz), 2.24-2.30 (m, 2H), 5.03 (dm, 1H, *J* = 17.0 Hz, =CH_2), 5.08 (dm, 1H, *J* = 10.1 Hz, =CH_2), 5.77 (ddt, 1H, *J* = 17.3, 10.0, 7.4 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.94 (CH_2), 24.98 (CH_3), 35.54 (CH_2), 38.75 (C), 40.93 (CH_2), 45.99 (CH_2), 53.23 (CH_2), 118.17 (=CH_2), 133.70 (=CH), 212.22 (C=O); IR (neat) 3076, 2958, 1711 (C=O), 1639, 1456, 1227, 916. The physical data agreed with those reported in the literature.[11] **3-Methyl-1,3-bis-(prop-2-en-1-yl)cyclohexene (S6)**: TLC R_f = 0.60 (hexane); t_R = 8.44 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (s, 3H, C3-

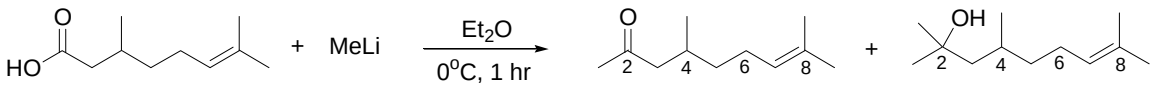
CH_3), 1.27-1.66 (m, 4H, integrates to 7H), 1.85 (app. t, 2H, *J* = 5.7 Hz), 2.02 (m, 2H), 2.66 (d, 2H, *J* = 6.2 Hz), 4.97-5.04 (m, 4H), 5.16 (s, 1H, =CH), 5.74-5.83 (m, 2H, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.48, 27.26, 28.34, 34.49, 42.31, 44.33, 47.29, 115.40, 116.68, 116.83, 131.39, 135.67, 137.04; IR (neat) 3076, 2929, 1637, 1454, 995, 912. The physical data agreed with those reported in the literature.[11]



10b **S7**

3-Methyl-3-(2'-methyl-2'-propenyl)-cyclohexanone (10b). The procedure for this conjugate addition is based on that described for the preparation of **10a**. A 1.0 M solution of $TiCl_4$ in CH_2Cl_2 (30 ml, 30 mmol) was added dropwise over 5 min to a solution of 3-methyl-2-cyclohexen-1-one (3.30 g, 30 mmol) in CH_2Cl_2 (30 mL) at –78 °C. After 2 min, methallylsilane (5.77 g, 45 mmol) was added dropwise over 1 min. After stirring 1 h at –78 °C, a solution of Et_3N (21 mL, 150 mmol) and MeOH (6.7 mL, 150 mmol) in CH_2Cl_2 (30 mL) was added dropwise over 5 min. The resultant heterogeneous mixture was stirred 5 min at –78 °C, warmed to rt (rt H_2O bath, 2 min), and diluted with Et_2O (375 mL). The organic layer was washed with 10% HCl (2 x 110 mL), satd. $NaHCO_3$ (110 mL), and satd. NaCl (110 mL); dried ($MgSO_4$); and evaporated to give 5.09 g of crude oil that was a 6.7:2.6:1 mixture of keto olefin, triene, and starting enone. Column purification of a 3.5 g sample (10:90 EtOAc:hexane (2.1 L), EtOAc (1 L)) afforded 0.99 g of triene (23%) as a colorless oil, 1.78 g (52%) of keto olefin **10b** as a colorless oil, and 160 mg of starting enone that was 90% pure (GC). **10b**: TLC R_f = 0.66 (30:70 EtOAc:hexane); t_R = 9.86 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (s, 3H, C3-CH_3), 1.57 (dtm, 1H, *J* = 13.5, 5.3 Hz), 1.68 (ddd, 1H, *J* = 13.7, 9.6, 4.3 Hz), 1.78 (m, 3H, C2′-Me), 1.80-1.97 (m, 2H), 2.01 (s, 2H), 2.09 (dt, 1H, *J* = 13.3, 1.7 Hz), 2.22-2.32 (m, 3H), 4.66 (m, 1H, =CH_2), 4.90 (m, 1H, =CH_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.10 (CH_2), 25.22 (CH_3), 25.48 (CH_3), 36.24 (CH_2), 39.43 (C), 40.90 (CH_2), 49.74

(CH_2), 53.66 (CH_2), 115.28 (=CH_2), 142.02 (=C), 212.38 (C=O); IR (neat) 3074, 2958, 1711 (C=O), 1643, 1456, 1228, 893; MS (EI, 70 eV) *m/z* (rel intensity %) 167 (1), 166 (0.4), 149 (4), 123 (3), 111 (100), 93 (4), 83 (19), 69 (10). Kugelrohr distillation at 60-65 ^{o}C (0.45 torr) gave a sample for elemental analysis: Anal. Calcd for $C_{11}H_{18}O$ (166.25): C, 79.46; H, 10.91. Found: C, 79.36; H, 11.05. No physical data were reported for this known compound.[12] **3-Methyl-1,3-bis-(2-methyl-2-propenyl)cyclohexene (S7)**: TLC R_f = 0.69 (hexane); t_R = 11.35 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (s, 3H, C3-CH_3), 1.30 (ddd, 1H, *J* = 12.4, 7.3, 3.2 Hz), 1.51-1.66 (m, 3H), 1.64 (s, 3H, =CCH_3), 1.75 (q, 3H, *J* = 0.8 Hz, =CCH_3), 1.79 (d, 2H, *J* = 7.1 Hz), 2.03 (s, 2H), 2.62 (s, 2H), 4.65 (m, 1H, =CH_2), 4.69 (m, 1H, =CH_2), 4.74 (m, 1H, =CH_2), 4.82 (app. sext., 1H, *J* = 1.4 Hz, =CH_2), 5.23 (s, 1H, =CH); ^{13}C NMR (126 MHz, $CDCl_3$), δ 19.61, 21.86, 25.10, 27.64, 28.43, 34.88, 35.22, 47.06, 50.75, 111.36, 113.95, 133.23, 133.38, 143.78, 144.25; IR (neat) 3074, 2929, 1645, 1454, 1373, 889; MS (EI, 70 eV) *m/z* (rel intensity %) 205 (2), 203 (3), 149 (100), 121 (3), 107 (8), 81 (7). Kugelrohr distillation at 65-70 ^{o}C (0.45 torr) gave a sample for elemental analysis: Anal. Calcd for $C_{15}H_{24}$ (204.34): C, 88.16; H, 11.84. Found: C, 87.96; H, 12.02.

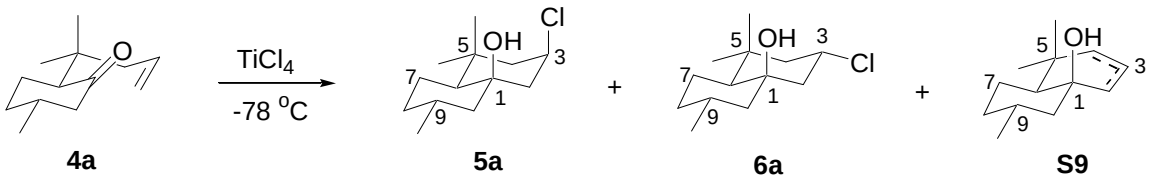


13 **S8**

4,8-Dimethyl-non-7-en-2-one (13). This methylation was peformed as described by Mori[13] to give 4.8 g of crude that upon column purification (3:97 EtOAc:hexane, wash: EtOAc) afforded 3.0 g (61%) of keto olefin and 1.6 g (30%) of tertiary alcohol. **13**: TLC R_f = 0.48 (15:85 EtOAc:hexane); t_R = 7.86 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (d, 3H, *J* = 6.6 Hz, C4-CH_3), 1.19 (m, 1H), 1.30 (m, 1H), 1.59 (s, 3H, =CCH_3), 1.67 (s, 3H, =CCH_3), 1.90-2.04 (m, 3H), 2.12 (s, 3H, $COCH_3$), 2.22 and 2.41 (ABX, 2H, J_{AB} = 15.9 Hz, J_{AX} = 5.5 Hz, J_{BX} = 8.4 Hz, H3), 5.08 (tm, 1H, *J* = 7.1 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.60, 19.65, 25.39, 25.66, 28.91, 30.37, 36.90, 51.17, 124.26, 131.53, 209.16 (C=O); IR (neat) 2964, 2918, 1716 (C=O), 1454, 1365. The

physical data were similar to those reported in the literature (^{1}H NMR, 60 MHz, CCl_4).[13] **2,4,8-Trimethyl-non-7-en-2-ol (S8)**: TLC R_f = 0.26 (15:85 EtOAc:hexane); t_R = 8.34 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (d, 3H, *J* = 6.6 Hz, C4-CH_3), 1.19 (m, 1H), 1.22 (s, 6H, C(OH)(C*H*$_3$)$_2$), 1.31 (dd, 1H, *J* = 14.1, 7.1 Hz), 1.31-1.40 (m, 1H), 1.50 (dd, 1H, *J* = 14.2, 4.1 Hz), 1.58 (m, 1H), 1.60 (s, 3H, =CCH_3), 1.68 (s, 3H, =CCH_3), 1.90-2.03 (m, 2H), 5.09 (tm, 1H, *J* = 7.2 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.62, 21.83, 25.52, 25.68, 28.86, 29.62, 30.16, 38.90, 50.59, 71.62 (COH), 124.74, 131.26; IR (neat) 3410 (OH), 2970, 2914, 1454, 1377, 1173, 903. The physical data were similar to those reported in the literature (^{1}H NMR, 60 MHz, CCl_4).[14]

Prins Cyclizations



4a **5a** **6a** **S9**

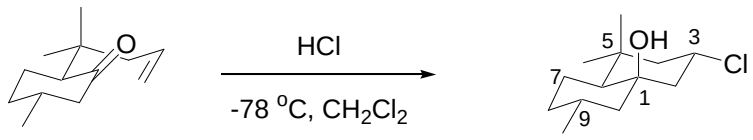
(1R,3R,6S,9R)- 3-Chloro-5,5,9-trimethylbicyclo[4.4.0]decan-1-ol (5a). **Method A.** (Solvent: CH_2Cl_2**)** See manuscript for procedure. Physical data for **5a**: TLC R_f = 0.66 (15:85, EtOAc:Hexane); t_R = 8.76 min (Method B); ^{1}H NMR (500 MHz, $CDCl_3$) 0.81 (t, 1H, *J* = 12.5 Hz, H10α), 0.85 (d, 3H, *J* = 6.4 Hz, C9-CH_3), 0.88 (m, 1H, H8), 0.91 (s, 3H, C5-CH_3), 0.96 (dd, 1H, *J* = 10.1, 5.6 Hz, H6), 1.19 (s, 3H, C5-CH_3), 1.57–1.62 (m, 2H, H7α+H7β), 1.66 (ddd, 1H, *J* = 13.1, 3.6, 2.4 Hz, H10β), 1.76 (dd, 1H, *J* = 15.0, 4.10 Hz, H4α), 1.78–1.87 (m, 2H, H8+H9), 1.87 (dd, 1H, *J* = 15.3, 4.8 Hz, H2α), 2.06 (ddd, 1H, *J* = 14.8, 3.6, 2.3 Hz, H4β), 2.15 (ddd, 1H, *J* = 15.2, 3.0, 2.4 Hz, H2β), 2.41 (br s, 1H, exch. D_2O, O*H*), 4.53 (app. quint, 1H, *J* = 3.9 Hz, C*H*Cl); ^{13}C NMR (126 MHz, $CDCl_3$) 22.02 (C7), 22.49 (C9-CH_3), 24.38 (C5-CH_3), 27.41 (C9), 32.92 (C5), 33.27 (C5-CH_3), 35.95 (C8), 46.15 (C2), 47.42 (C4), 50.82 (C6), 50.89 (C10), 57.29 (CHCl), 71.97 (COH); IR (neat film) 3592 (OH), 3479 (OH, H-Bonded), 2947, 2867, 1455, 1370, 1265, 1167, 1009 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity %) 230 (13), 215 (88), 195 (30), 177 (25), 161 (27), 153 (100), 145 (20), 112 (62), 95 (21), 83 (45). Recrystallization from

hexane gave an analytical sample: mp 63-65 °C; Anal. Calcd for $C_{13}H_{23}ClO$ (230.78): C, 67.66; H, 10.05; Cl, 15.36 Found: C, 67.74; H, 10.35; Cl, 15.67; $[\alpha]_D$ = +2.7. COSY (500 MHz, $CDCl_3$): (0.81) δ 1.66, 1.78-1.87; (0.85) δ 1.78-1.87; (0.88) δ 1.57-1.62, 1.78-1.87; (0.96) δ 1.57-1.62; (1.57-1.62) δ 0.88, 0.96, 1.57-1.62, 1.57-1.62, 1.78-1.87; (1.66) δ 0.81, 1.78-1.87; (1.76) δ 2.06; (1.78-1.87) δ 0.81, 0.88, 1.57-1.62, 1.66, 1.78-1.87; (1.87) δ 2.15; (2.06) δ 1.76, 2.15; (2.15) δ 1.87, 2.06; (4.53) δ 1.76, 1.87, 2.06, 2.15. HMQC (500 MHz, $CDCl_3$): (22.02) δ 1.57-1.62; (22.49) δ 0.85; (24.38) δ 1.19; (27.41) δ 1.78-1.87; (33.27) δ 0.91; (35.95) δ 0.88, 1.78-1.87; (46.15) δ 1.87, 2.15; (47.42) δ 1.76, 2.06; (50.82) δ 0.96; (50.89) δ 0.81, 1.66; (57.29) δ 4.53. HMBC (500 MHz, $CDCl_3$): (22.02) δ 0.96; (22.49) δ 0.81; (24.38) δ 0.91, 0.96, 1.76, 2.06; (27.41) δ 0.81, 0.85, 0.88, 1.57-1.62, 1.66, 1.78-1.87; (32.92) δ 0.91, 0.96, 1.19, 1.57-1.62, 1.76, 2.06, 4.53; (33.27) δ 0.96, 1.19, 1.76; (35.95) δ 0.81, 0.85, 0.96, 1.57-1.62, 1.66; (46.15) δ 0.81, 1.66, 1.76, 2.06, 4.53; (47.42) δ 0.91, 1.19, 1.87, 2.15; (57.29) δ 1.76, 1.87, 2.06, 2.15; (71.97) δ 0.81, 0.96, 1.57-1.62, 1.66, 1.87, 2.15, 4.53. ^{1}H NMR NOE (500 MHz, $CDCl_3$): Irrad. δ 0.96, obs. δ 0.81 (3.2%), 1.57-1.62 (3.4%), 1.76 (~3%), 1.87 (1.6%), 4.53 (1.1%); Irrad. δ 1.76, obs. δ 0.91 (4.3%), 0.96 (5.7%), 4.53 (8.7%); Irrad. δ 1.87, obs. δ 0.96 (2.5%), 4.53 (8.1%). **(1R,6S,9R)-5,5,9-Trimethylbicyclo[4.4.0]dec-2-en-1-ol (S9)**. Physical data for olefin was taken from the chlorohydrin/olefin mixture: TLC R_f = 0.63 (15:85 EtOAc:Hexane); t_R = 11.05 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (m, 1H), 2.08 (app. dt, 1H, *J* = 17.6, 1.8 Hz), 5.45-5.52 (m, 2H, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.31 (CH_3), 22.69 (CH_2), 24.48 (CH_3), 27.95 (CH), 30.64 (CH_3), 35.41 (CH_2), 40.42 (CH_2), 48.15 (CH), 48.92 (CH_2), 70.44 (COH), 119.74 (=CH), 139.55 (=CH). The signal for *C*$(Me)_2$ was too weak to be observed. GC-MS (EI, 70 eV) *m/z* (rel intensity %) 194 (8), 176 (4), 161 (4), 112 (100), 97 (12), 82 (34); GC-HRMS (EI, 70 eV) Calcd for $C_{13}H_{22}O$: 194.1671. Found 194.1667 (Δ = 1.9 ppm). The physical data for **6a** matched that obtained below.

Method B. (Solvent: CH_2Cl_2) A solution of keto olefin **4a** (389 mg, 2.0 mmol) in CH_2Cl_2 (15 mL) was stirred and cooled at –78 °C as an aliquot of 1.0 M $TiCl_4$ in CH_2Cl_2 (2.0 mL, 2.0 mmol) was added dropwise over 1 min. After 30 s, a solution of Et_3N (1.4 mL, 10 mmol) and MeOH (0.45 mL, 10 mmol) was added dropwise over 30 s. The

heterogeneous mixture was stirred 5 min at –78 °C, warmed to rt (rt H_2O bath, 2 min), and diluted with Et_2O (50 mL). The organic layer was washed with 10% HCl (2 x 15 mL), satd. $NaHCO_3$ (15 mL), and satd. NaCl (15 mL); dried ($MgSO_4$); and evaporated to give 419 mg of colorless oil that was a 7:1 mixture of cis and trans chlorohydrins. Column purification (2:98 Et_2O:hexane (700 mL), 5:95 Et_2O:hexane (270 mL)) afforded 259 mg (56%) of cis chlorohydrin as a white crystalline solid and 33 mg of colorless oil that was an 5:1 mixture of trans chlorohydrin (6%) and olefin (1%). The physical data matched those obtained previously.

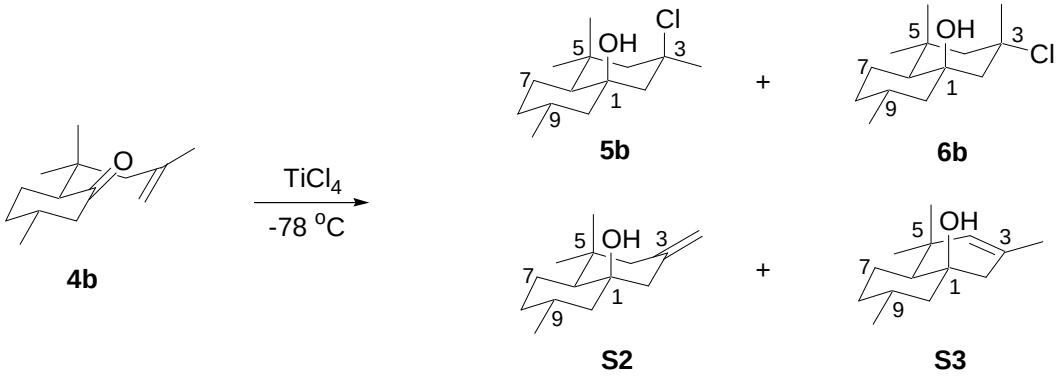
Method C. (Solvent: pentane) A solution of keto olefin **4a** (136 mg, 0.70 mmol) in pentane (8 mL) was stirred and cooled at –78 °C as an aliquot of 1.0 M $TiCl_4$ in pentane (0.70 mL, 0.70 mmol) was added dropwise over 20 s. After 2 min, a solution of Et_3N (0.49 mL, 3.5 mmol) and MeOH (0.16 mL, 3.5 mmol) in pentane (1 mL) was added dropwise over 20 s. The heterogeneous mixture was stirred 5 min at –78 °C, warmed to rt (rt H_2O bath, 2 min), and diluted with Et_2O (15 mL). The organic layer was washed with 10% HCl (2 x 5 mL), satd. $NaHCO_3$ (5 mL), and satd. NaCl (5 mL); dried ($MgSO_4$); and evaporated to give 128 mg of colorless oil that was a 1.4:1 mixture of cis:trans chlorohydrins in addition to a trace amount of keto olefin starting material. Column purification (2:98 Et_2O:hexane) afforded 7 mg (3% Corr. for purity) of keto olefin that was approximately 50% pure (^{1}H NMR), 52 mg (32%) of cis chlorohydrin as a colorless oil, and 31 mg (19%) of trans chlorohydrin as a colorless oil. The physical data were identical to those obtained above.



4a **6a**

(1R,3S,6S,9R)-3-Chloro-5,5,9-trimethyl-bicyclo[4.4.0]decan-1-ol (6a). A solution of keto olefin **4a** (300 mg, 1.54 mmol) in CH_2Cl_2 (20 mL) was stirred and cooled at –78 °C as a slow stream of anhydrous HCl (g) was bubbled through the reaction solution via a glass frit dispersion tube for 2 min. After 3 min at –78 °C, the reaction solution was

warmed to rt (rt water bath) over 90 s. (Caution: rapid evolution of HCl(g)) and immediately neutralized by the addition of satd. $NaHCO_3$ (10 mL). The organic layer was washed with satd. $NaHCO_3$ (10 mL) and satd. NaCl (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give 281 mg of crude. Column purification (4:96 Et_2O:hexane) afforded 229 mg (64%) of clear, colorless oil: TLC R_f = 0.57 (15:85 EtOAc:hexane); t_R = 8.77 min (Method B); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (d, 3H, *J* = 6.6, C9-CH_3), 0.91 (s, 3H, C5-CH_3), 0.95 (dd, 1H, *J* = 12.6, 3.2 Hz), 0.98 (s, 3H, C5-CH_3), 1.03 (t, 1H, *J* = 13.1 Hz), 1.12 (s, 1H, exch. D_2O, OH), 1.31 (qd, 1H, *J* = 13.0, 3.5 Hz), 1.52 (ddd, 1H, *J* = 13.5, 3.9, 2.4 Hz), 1.52 (t, 1H, *J* = 12.4 Hz), 1.57 (t, 1H, *J* = 12.4 Hz), 1.62 (dq, 1H, *J* = 13.5, 3.4 Hz), 1.65-1.74 (m, 1H), 1.79 (app. d. quint., 1H, *J* = 12.9, 3.3 Hz), 1.99 (ddd, 1H, *J* = 12.8, 3.9, 2.5 Hz), 2.12 (ddd, 1H, *J* = 12.9, 4.0, 2.5 Hz), 4.38 (tt, 1H, *J* = 12.1, 4.0, CHCl); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.39, 21.98, 22.06, 27.62, 31.72, 35.28, 35.70, 49.98, 50.45, 51.00, 52.43, 54.57, 73.81 (COH); IR (neat) 3567 (OH), 3483 (OH), 2948, 2869, 1456, 1368, 1240, 1028, 775; MS (EI, 70 eV) *m/z* (rel intensity %) 230 (24), 215 (100), 195 (16), 177 (13), 161 (27), 153 (36), 137 (26), 112 (34), 81 (48); $[\alpha]_D$ +5.2. Recrystallization from hexane gave an analytical sample: mp 61-62 °C; Anal. Calcd for $C_{13}H_{23}ClO$ (230.78): C, 67.66; H, 10.05; Cl, 15.36. Found: C, 67.60; H, 10.39; Cl, 15.02.



(1R,3R,6S,9R)-and (1R,3S,6S,9R)-3-Chloro-3,5,5,9-tetramethylbicyclo[4.4.0]decan-1-ols (5b and 6b).

Method A. (Solvent: CH_2Cl_2) A solution of keto olefin **4b** (625 mg, 3.0 mmol) in CH_2Cl_2 (20 mL) was stirred and cooled at –78 °C as an aliquot of 1.0 M $TiCl_4$ in CH_2Cl_2

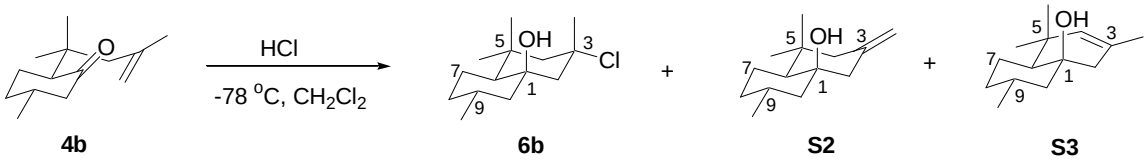
(3.0 mL, 3.0 mmol) was added dropwise over 1 min. After 15 s, a solution of Et_3N (2.1 mL, 15 mmol) and MeOH (0.67 mL, 15 mmol) was added dropwise over 30 s. The heterogeneous mixture was stirred 5 min at –78 ^oC, warmed to rt (rt H_2O bath, 2 min), and diluted with Et_2O (75 mL). The organic layer was washed with 10% HCl (2 x 20 mL), satd. $NaHCO_3$ (20 mL), and satd. NaCl (20 mL); dried ($MgSO_4$); and evaporated to give 590 mg of colorless oil that was a 12.8:3:1 mixture of cis chlorohydrin (51%), endocyclic olefin (12%), and trans chlorohydrin (4%). Column purification (1:2:97 Et_3N:Et_2O:hexane) afforded 174 mg (24%) of cis chlorohydrin as a white crystalline solid; 62 mg of colorless oil that was a 1.4:1.2:1 mixture of cis chlorohydrin (4%), endocyclic olefin (3%), and exocyclic olefins (3%); 76 mg (12%) of endocyclic olefin; and 40 mg (6%, 4% Corr. for purity) of endocyclic olefin (70% pure, GC). **5b**: TLC R_f = 0.83 (15:85 EtOAc:hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 0.76 (t, 1H, *J* = 12.5 Hz), 0.84 (d, 3H, *J* = 6.6 Hz, C9-CH_3), 0.85-0.89 (m, 2H), 0.89 (s, 3H, C5-CH_3), 1.18 (s, 3H, C5-CH_3), 1.50 (d, 1H, *J* = 15.2 Hz), 1.55-1.62 (m, 3H), 1.58 (s, 3H, C3-CH_3), 1.64 (ddd, 1H, *J* = 12.9, 3.6, 2.3 Hz), 1.80 (app. d. quint., 1H, *J* = 12.9, 3.2 Hz), 1.88 (m, 1H), 2.04 (dd, 1H, *J* = 15.2, 2.8 Hz), 2.16 (dd, 1H, *J* = 15.3, 2.9 Hz), 2.98 (br s, 1H, exch. D_2O, OH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.54, 22.27, 22.91, 27.04, 33.33, 33.67, 35.83, 36.80, 50.59, 50.72, 52.12, 54.68, 70.12, 71.68; IR (CCl_4 soln) 3585 (OH), 2949, 1454, 1371, 1182, 1061; MS (FI, 70 eV) *m/z* (rel intensity %) 244 (100), 208 (5); $[\alpha]_D$ -6.7. Recrystallization from hexane gave an analytical sample and crystals suitable for X-ray analysis: mp 57-58 ^oC; Anal. Calcd for $C_{14}H_{25}ClO$ (244.79): C, 68.69; H, 10.29; Cl, 14.48. Found: C, 68.65; H, 10.58; Cl, 14.42. **(1R,6S,9R)-3,5,5,9-tetramethylbicyclo[4.4.0]dec-3-en-1-ol (S3):** TLC R_f = 0.61 (15:85 EtOAc:hexane); t_R = 11.77 min (Method A); ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (d, 3H, *J* = 6.2 Hz, C9-CH_3), ~0.91 (m, 1H, H8), 0.95 (s, 6H, C5-$(CH_3)_2$), ~0.97 (m, 1H, H10), 1.17 (dd, 1H, *J* = 12.4, 3.9 Hz, H6), 1.46 (br. s, 1H, OH, exch. D_2O), 1.51 (qd, 1H, *J* = 12.9, 3.4, H7β), 1.58-1.63 (m, 1H, H7α), 1.66 (br. s, 3H, =CCH_3), ~1.72 (m, 1H), ~1.77 (m, 1H), ~1.80 (m, 1H, H8), 1.85 (d, 1H, *J* = 17.2 Hz, H2), 2.05 (app. dq, 1H, *J* = 16.1, 1.3 Hz, H2), 5.20 (s, 1H, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.33 (C9-CH_3), 22.61 (C7), 23.86 (C3-CH_3), 24.81 (C5-CH_3), 27.93 (C9), 31.07 (C5-CH_3), 34.40 (C5), 35.48 (C8), 45.38 (C2), 47.71 (C6), 48.80 (C10), 71.20 (COH), 127.00 (=C), 133.28 (=CH); IR (neat) 3585

(OH), 3487 (OH), 2926, 1452, 1377, 889, 735; MS (EI, 70 eV) *m/z* (rel intensity %) 208 (38), 191 (100), 175 (66), 165 (4), 150 (7), 134 (17), 119 (30), 97 (52), 81 (27); HRMS (EI, 70 eV) Calcd for $C_{14}H_{24}O$: 208.1827. Found: 208.1830 (Δ = -1.4); $[\alpha]_D$ +35.8. HMQC (500 MHz, $CDCl_3$): (22.33) δ 0.88; (22.61) δ 1.51, 1.58-1.63; (23.86) δ 1.66; (24.81) δ 0.95; (31.07) δ 0.95; (35.48) δ ~0.91, ~1.80; (45.38) δ 1.85, 2.05; (47.71) δ 1.17; (48.80) δ ~0.97. HMBC (500 MHz, $CDCl_3$): (22.61) δ 1.17, ~1.80; (23.86) δ 1.85, 5.20; (24.81) δ 0.95, 1.17, 1.66; (27.93) δ 0.88, ~0.91, ~0.97, 1.51. 1.58-1.63; (31.07) δ 0.95, 1.17, 1.66, 5.20; (34.40) δ 0.95, 1.17, 1.85, 5.20; (35.48) δ 0.88, 1.17, 1.51, 1.58-1.63, ~1.72, ~1.77;
(45.38) δ 1.17, 1.66, 5.20; (47.71) δ 0.95, 1.51, 1.58-1.63, 1.85, 5.20; (48.80) δ 0.88, 2.05, 1.17, ~1.80; (71.20) δ 1.17, 1.51, 1.58-1.63, 1.85, 2.05, ~1.77; (127.00) δ 1.66, 1.85, 2.05; (133.28) δ 0.95, 1.66, 1.85, 2.05. The physical data for the exocyclic olefin **S2** matched those obtained below.

Method B. (Solvent: pentane) The procedure for the cyclization of **4b** (146 mg, 0.70 mmol) using 1.0 M $TiCl_4$ in pentane (0.70 mL, 0.70 mmol) in pentane (8 mL) was carried out as described for the preparation of **5a** (Method C), except the reaction was stirred for only 30 s after $TiCl_4$ was added to afford 118 mg of crude that was a 7.2:3.4:1.6:1 mixture of cis chlorohydrin (36%), endocyclic olefin (17%), exocyclic olefin (8%), and trans chlorohydrin (5%) in addition to a trace amount of starting material (~1%). Column purification (1:2:97 Et_3N:Et_2O:hexane) gave 32 mg of colorless oil that was a 10:1 mixture of cis chlorohydrin (17%) and keto olefin (2%), 11 mg (8%) of exocyclic olefin as a colorless oil, 24 mg (16%) of endocyclic olefin as a colorless oil, and 16 mg (8% Corr for purity) of colorless oil that contained endocyclic olefin (GC: 70% Pure). The physical data matched those obtained previously.

Method C. (Solvent: PhMe) A solution of keto olefin **4b** (146 mg, 0.70 mmol) in PhMe (5 mL) was stirred and cooled at –78 ^oC as an aliquot of 1.0 M $TiCl_4$ in PhMe (0.70 mL, 0.70 mmol) was added dropwise over 20 s. After 30 s, a solution of Et_3N (0.49 mL, 3.5 mmol) and MeOH (0.16 mL, 3.5 mmol) was added dropwise over 30 s. The heterogeneous mixture was stirred 5 min at –78 ^oC, warmed to rt (rt H_2O bath, 2 min), and diluted with Et_2O (15 mL). The organic layer was washed with 10% HCl (2 x 5 mL),

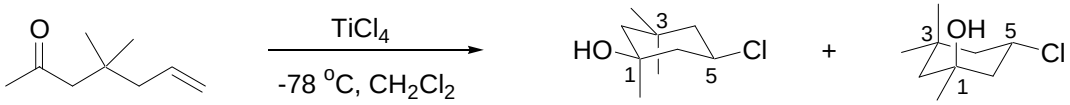
satd. $NaHCO_3$ (5 mL), and satd. NaCl (5 mL); dried ($MgSO_4$); and evaporated to give 141 mg of colorless oil that was a 6.6:2.5:1.5:1 mixture of cis chlorohydrin (53%), endocyclic olefin (20%), trans chlorohydrin (12%), and exocyclic olefin (8%). Column purification (1:2:97 Et_3N:Et_2O:hexane) afforded 33 mg (19%) of cis chlorohydrin as a colorless oil, 4 mg of colorless oil that was a 5:1 mixture of cis chlorohydrin (2%) and exocyclic olefin (0.4%), 7 mg (5%) of exocyclic olefin as a colorless oil, 4 mg (3%, 2% Corr. for purity) of exocyclic olefin (GC Purity: 69%), 28 mg (19%, 17% Corr. for purity) of endocyclic olefin (GC Purity: 91%), and 10 mg (7%, 4% Corr. for purity) of endocyclic olefin (GC Purity: 58%). The physical data matched those previously obtained.



4b **6b** **S2** **S3**

(1R,3S,6S,9R)-3-Chloro-3,5,5,9-tetramethylbicyclo[4.4.0]decan-1-ol (6b).
A solution of keto olefin **4b** (521 mg, 2.50 mmol) in CH_2Cl_2 (20 mL) was stirred and cooled at –78 °C as an aliquot of 1.0 M HCl in Et_2O (2.25 mL, 2.25 mmol) was added dropwise over 1 min. After 30 s, remaining HCl was neutralized by the addition of Et_3N (174 μL, 1.25 mmol) dropwise over 10 s. The mixture was stirred 2 min at –78 °C, warmed to rt (rt H_2O bath, 2 min), and diluted with Et_2O (30 mL). The organic layer was washed with 10% HCl (15 mL), satd. $NaHCO_3$ (15 mL), and satd. NaCl (15 mL); dried ($MgSO_4$); and evaporated to give 524 mg of colorless oil that was a 7:5:1 mixture of chlorohydrin (50%), exocyclic olefin (34%), and endocyclic olefin (7%). Physical data were taken from the mixture of chlorhydrin and olefins: **6b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (d, 3H, *J* = 6.6 Hz, C9-CH_3), 0.92 (s, 3H, C5-CH_3), 1.00 (d, 1H, *J* = 12.4 Hz), 1.04 (s, 3H, C5-CH_3), 1.33 (qd, 1H, *J* = 13.1, 3.6 Hz), 1.51-1.72 (m, ~5H), ~1.80 (m, 1H), 1.93 (s, 3H, C3-CH_3), 2.03 (app. d, 2H, *J* = 12.8 Hz), 2.07 (app. dd, 1H, *J* = 13.6, 2.3 Hz), 2.18 (app. dd, 1H, *J* = 13.8, 2.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.42 (CH_2), 22.07 (CH_3), 22.82 (CH_3), 27.53 (CH), 33.01 (CH_3), 33.36 (CH_3), 35.36 (CH_2), 35.62 (C), 50.38 (CH), 50.80 (CH_2), 55.23 (CH_2), 57.55 (CH_2), 73.31 (C), 73.98 (C); IR

(neat) 3558 (OH), 3479 (OH), 2947, 1456, 1379, 1190, 874; MS (FI, 70 eV) *m/z* (rel intensity %) 247 (5), 246 (31), 245 (16), 244 (100), 208 (25). Anal. Calcd for $C_{14}H_{25}ClO$ (244.79): C, 68.69; H, 10.29; Cl, 14.48. Found: C, 73.41; H, 10.99; Cl, 8.37. Column chromatography (Et_3N:Et_2O:hexane, 1:3:96) of a 462 mg sample that was a 6.4:4.4:1 mixture of trans chlorohydrin (1.27 mmol), exocyclic olefin (0.86 mmol), and endocyclic olefin (0.21 mmol) obtained from and identical run afforded 152 mg of exocyclic olefin, 46 mg that was 1.6:1 mixture of endocyclic olefin and exocyclic olefins, and 119 mg of endocyclic olefin. This solvolysis/column chromatography afforded endocyclic olefin in 39% yield from the crude trans chlorohydrin.



7a **8a** **9a**

(1S*,5R*)-and (1S*,5S*)-3-Chloro-1,3,3-trimethyl-cyclohexanols (8a and 9a). **Method A**. (Solvent: CH_2Cl_2**)** A solution of keto olefin **7a** (0.80 g, 5.7 mmol) in CH_2Cl_2 (40 mL) was stirred and cooled at –78 °C as an aliquot of 1.0 M $TiCl_4$ in CH_2Cl_2 (5.7 mL, 5.7 mmol) was added dropwise over 5 min. After 15 min, the reaction was neutralized by the addition of a solution of Et_3N (4.0 mL, 29 mmol) and MeOH (1.3 mL, 29 mmol) dropwise over 2 min. The resultant mixture was stirred 5 min at –78 °C, warmed to rt (5 min), and diluted with Et_2O (120 mL) and 10% HCl (40 mL). The organic layer was washed with 10% HCl (40 mL), satd. $NaHCO_3$ (40 mL), satd. NaCl (40 mL); dried ($MgSO_4$); and evaporated under reduced pressure to give 0.97 g of crude that was a 5.1:1 mixture of cis and trans chlorohydrins. Column purification (13:87 EtOAc:hexane,) afforded 99 mg (10 %) of trans chlorohydrin as a white crystalline solid, 534 mg (53%) of cis chlorohydrin as a clear colorless oil, and 52 mg (5%, 2% Corr. for purity) of cis chlorohydrin that was 41% pure by GC analysis, and 103 mg (10%, 1% Corr. for purity) of cis chlorohydrin as a colorless oil that was 14% pure by GC analysis. **8a**: TLC R_f = 0.44 (30:70 EtOAc:hexane); t_R = 8.79 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (s, 3H, C3-βMe), 1.02 (s, 3H, C3-αMe), 1.33 (s, 3H, Cl-Me), 1.39 (d, 1H, *J* = 13.5

Hz, H2α), 1.48 (t, 1H, *J* = 14.5 Hz, H4α), 1.56 (dt, 1H, *J* = 13.5, 1.9 Hz, H2β), 1.67 (t, 1H, *J* = 12.2 Hz, H6α), 1.93 (ddt, 1H, *J* = 13.1, 3.9, 1.9 Hz, H4β), 2.24 (ddt, 1H, *J* = 12.2, 3.9, 1.9 Hz, H6β), 4.00 (tt, 1H, *J* = 12.0, 4.0 Hz, CHCl); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.01 (C3-βMe), 28.91 (C3-αMe), 32.65 (C3), 34.08 (Cl-Me), 49.14 (C4), 50.70 (C6), 52.10 (C2), 54.84 (C5), 71.45 (COH); IR (neat) 3371 (OH), 2960, 2932, 1465, 1378, 1331, 1240, 1127, 916, 904, 806, 733; MS (EI, 70 eV) *m/z* (rel intensity %) 176 (1), 161 (100), 141 (96), 125 (53), 107 (36), 99 (60), 83 (54), 71 (26), 57 (63). Kugelrohr distillation at 80-85 ^{o}C (0.40 torr) gave a sample for elemental analysis: Anal. Calcd for $C_9H_{17}ClO$ (176.68): C, 61.18; H, 9.70; Cl, 20.07. Found: C, 60.78; H, 9.82; Cl, 20.44. HMQC (500 MHz, $CDCl_3$): (27.01) δ 0.98; (28.91) δ 1.33; (34.08) δ 1.02; (49.14) δ 1.48, 1.93; (50.70) δ 1.67, 2.24; (52.10) δ 1.39, 1.56; (54.84) δ 4.00. HMBC (500 MHz, $CDCl_3$): (27.01) δ 1.02, 1.39, 1.48, 1.56, 1.93; (28.91) δ 1.39, 1.56, 1.67, 2.24; (32.65) δ 0.98, 1.02, 1.39, 1.48, 1.56, 1.93; (34.08) δ 0.98, 1.39, 1.48; (49.14) δ 0.98, 1.02, 1.56, 1.67, 2.24, 4.00; (50.70) δ 1.33, 1.48, 1.56, 1.93, 4.00; (52.10) δ 0.98, 1.02, 1.33, 1.93, 2.24, 1.67; (54.84) δ 1.48, 1.67, 1.93, 2.24; (71.45) δ 1.33, 1.39, 1.56, 1.67, 2.24. ^{1}H NMR NOE (500 MHz, $CDCl_3$): Irrad. δ 1.33, obs. δ 0.98 (1.6%), 2.24 (1.9%), 4.00 (3.4%); Irrad. δ 4.00, obs. δ 0.98 (3.8%), 1.33 (3.5%), 1.93 (3.1%), 2.24 (4.1%). **9a**: TLC R_f = 0.61 (30:70 EtOAc:hexane); t_R = 8.34 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (s, 3H, C3-αMe), 1.13 (s, 3H, C3-βMe), 1.24 (s, 3H, Cl-Me), 1.25 (d, 1H, *J* = 14.6 Hz, H2α), 1.41 (t, 1H, *J* = 12.6 Hz, H4α), 1.44 (dt, 1H, *J* = 14.6, 2.3 Hz, H2β), 1.55 (dd, 1H, *J* = 13.1, 12.2 Hz, H6α), 1.98 (ddt, 1H, *J* = 12.6, 3.9, 2.0 Hz, H4β), 2.19 (ddt, 1H, *J* = 13.2, 4.0, 2.3 Hz, H6β), 4.36 (tt, 1H, *J* = 12.1, 4.0 Hz, CHCl); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.82 (C3-βMe), 32.81 (Cl-Me), 33.26 (C3), 33.88 (C3-αMe), 49.34, 49.42, 49.61, 54.91 (CHCl), 72.72 (COH); IR (CCl_4 soln) 3614 (OH), 2957, 2927, 1458, 1368, 1233, 1173, 1090, 1051, 903; MS (FI, 70 eV) *m/z* (rel intensity %) 176 (100), 161 (75), 154 (2), 140 (14), 113 (3). Recrystallization from hexane gave an analytical sample: mp 63-64 ^{o}C; Anal. Calcd for $C_9H_{17}ClO$ (176.68): C, 61.18; H, 9.70; Cl, 20.07. Found: C, 61.42; H, 9.62; Cl, 20.18. HMQC (500 MHz, $CDCl_3$): (26.82) δ 1.13; (32.81) δ 1.24; (33.88) δ 0.95; (54.91) δ 4.36. HMBC (500 MHz, $CDCl_3$): (26.82) δ 0.95, 1.25, 1.41, 1.44; (32.81) δ 1.55; (33.26) δ 0.95, 1.13, 1.98; (33.88) δ

1.13, 1.25, 1.41, 1.44; (54.91) δ 1.41, 1.55, 1.98, 2.19; (72.72) δ 1.24, 1.25, 1.44, 1.55, 2.19. ^{1}H NMR NOE (500 MHz, $CDCl_3$): Irrad. δ 1.13, obs. δ 1.45 (1.1%), 1.98 (1.8%), 4.36 (5.9%); Irrad. δ 4.36, obs. δ 1.12 (4.8%), 1.98 (4.5%), 2.19 (4.9%).

Method B. (Solvent: CH_2Cl_2) The procedure for this cyclization was carried out as described for the preparation of **5a** (Method B), except the reaction was stirred for 5 min after the $TiCl_4$ was added. A solution of keto olefin **7a** (280 mg, 2.0 mmol) in CH_2Cl_2 (15 mL) and 1.0 M $TiCl_4$ in CH_2Cl_2 (2.0 mL, 2.0 mmol) was stirred for 5 min at –78 ^{o}C that upon workup gave 324 mg of colorless oil that was a 6:1 mixture of cis and trans chlorohydrins. Column purification (18:82, EtOAc:hexane) afforded 32 mg (9%) of trans chlorohydrin as a white crystalline solid and 176 mg (50%) of cis chlorohydrin as a colorless oil. The physical data matched those obtained previously.

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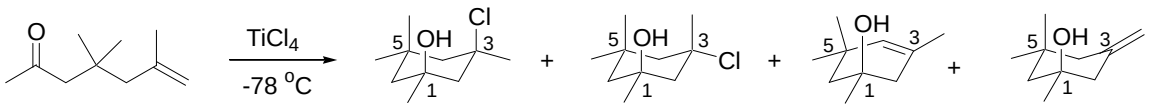


(1S*,3R*)-and (1S*,3S*)-3-Chloro-1,3,5,5-tetramethyl-cyclohexanols (8b and 9b).

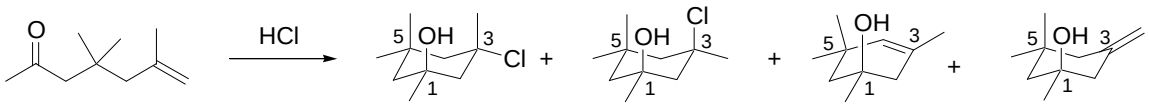
Method A. (Solvent: CH_2Cl_2) The procedure for the cyclization of keto olefin **7b** (309 mg, 2.0 mmol) in CH_2Cl_2 (15 mL) was carried out as described for the preparation of **5a** (Method B) using 1.0 M $TiCl_4$ in CH_2Cl_2 (2.0 mL, 2.0 mmol) to afford 311 mg of white solid that was a 12:1 mixture of cis chlorohydrin (86%) and trans chlorohydrin (7%). Column purification (1:14:85 Et_3N:Et_2O:hexane (280 mL), 1:20:79 Et_3N:Et_2O:hexane (180 mL)) afforded 230 mg (60%) of cis chlorohydrin as a white crystalline solid and 14 mg of colorless oil that was an 8.2:4.8:1 mixture of trans chlorohydrin (2%), endocyclic olefin (1%), and exocyclic olefin (<1%). **8b**: TLC R_f = 0.42 (15:85 EtOAc:hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (s, 3H, C5-αCH_3), 1.16 (d, 1H, *J* = 14.4 Hz, H6α), 1.19 (s, 3H, C1-CH_3), 1.34 (s, 3H, C5-βCH_3), 1.40 (d, 1H, *J* = 15.2 Hz, H4α), 1.58 (d, 1H, *J* = 15.4 Hz, H2α), 1.61 (s, 3H, C3-CH_3), 1.72 (dt, 1H, *J* = 14.4, 2.4 Hz, H6β), 2.04 (dt, 1H, *J* = 15.0, 2.3 Hz, H4β), 2.22 (dt, 1H, *J* = 15.4, 2.5 Hz, H2β), 3.09 (br s,1H, exch. D_2O, OH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.82 (C5-βCH_3), 31.15 (C5), 32.27 (C1-CH_3),

35.95 (C5-αCH$_3$), 36.77 (C3-CH$_3$), 49.34 (C6), 50.78 (C2), 51.89 (C4), 70.38 (COH), 70.90 (CCl); IR (CCl_4 soln) 3591 (OH), 2927, 1452, 1371, 1198, 1063; MS (FI, 70 eV) *m/z* (rel intensity) 193 (4), 192 (33), 191 (10), 190 (100), 175 (8), 154 (7). Recrystallization from hexane gave an analytical sample and crystals suitable for X-ray analysis: mp 90-91 ^{o}C; Anal. Calcd for $C_{10}H_{19}ClO$ (190.71): C, 62.98; H, 10.04; Cl, 18.59. Found: C, 62.86; H, 10.26; Cl, 18.57. HMQC (500 MHz, $CDCl_3$): (27.82) δ 1.34; (32.27) δ 1.19; (35.95) δ 0.92; (36.77) δ 1.61; (49.34) δ 1.16, 1.72; (50.78) δ 1.58, 2.22; (51.89) δ 1.40, 2.04. HMBC (500 MHz, $CDCl_3$): (27.82) δ 0.92, 1.16, 1.40, 1.72, 2.04; (31.15) δ 0.92, 1.16, 1.34, 1.40, 1.72, 2.04; (32.27) δ 1.16, 1.58; (35.95) δ 1.16, 1.34, 1.40; (36.77) δ 1.40, 1.58; (49.34) δ 0.92, 1.19, 1.34, 2.04, 2.22; (50.78) δ 1.19, 1.61, 1.72, 2.04; (51.89) δ 0.92, 1.34, 1.61, 1.72, 2.22; (70.38) δ 1.40, 1.61, 2.04, 2.22; (70.90) δ 1.16, 1.19, 1.58, 1.72, 2.22. The physical data for the trans chlorohydrin, endocyclic olefin, and exocyclic olefin matched those obtained below.

Method B. (Solvent: pentane) The procedure for this cyclization was carried out as described for for the preparation of **5a** (Method B), except pentane was used for the solvent and the Et_3N/MeOH mixture was added as a solution in pentane. A solution of keto olefin **7b** (309 mg, 2.0 mmol) in pentane (25 mL) and 1.0 M $TiCl_4$ in pentane (2.0 mL, 2.0 mmol) was stirred and cooled at –78 ^{o}C for 30 s then neutralized by the addition of a solution of Et_3N (1.4 mL, 10 mmol) and MeOH (0.45 mL, 10 mmol) in pentane (3 mL) that upon work up gave 347 mg of solid that was a 12.8:8.0:1.8:1 mixture of cis chlorohydrin (51%, 74% Corr. for rec. SM), starting material (32%), endocyclic olefin (7%, 10% Corr. for rec. SM), and exocyclic olefin (4%, 5% Corr. for rec. SM) Column purification (1:12:87 Et_3N:Et_2O:hexane) afforded 54 mg (17%) of keto olefin starting material, 123 mg (32%, 39% Corr. for rec. SM) of cis chlorohydrin, and 10 mg (3%, 4% Corr. for rec. SM) of colorless oil that was a 4:1 mixture of endo:exocyclic olefins. The physical data matched those obtained previously.

Method C. (Solvent: PhMe) The procedure for the cyclization of keto olefin **7b** (108 mg, 0.70 mmol) in PhMe (5 mL) was carried out as described for the preparation of **5b** (Method C) using 1.0 M $TiCl_4$ in PhMe (0.70 mL, 0.70 mmol) to give 107 mg of white crystalline solid that was a 17.2:1.7:1 mixture of cis chlorohydrin (86%), trans

chlorohydrin (5%), and endocyclic olefin (3%). Column purification (1:14:85 Et_3N:Et_2O:hexane) afforded 81 mg (61%) of cis chlorohydrin as a white solid and 3 mg of colorless oil that was a 6.0:5.8:3.7:1 mixture of cis chlorohydrin, endocyclic olefin, trans chlorohydrin, and exocyclic olefin. The physical data matched those obtained previously.

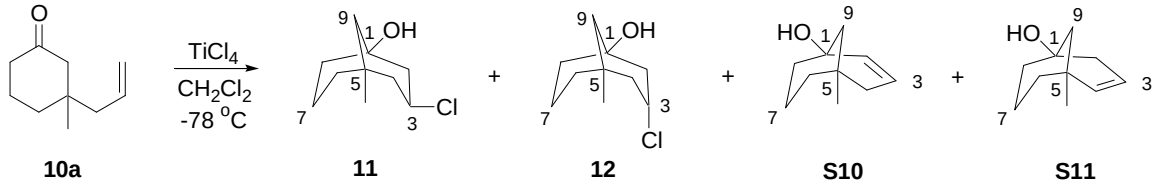


7b **9b** **8b** **S17** **S14**

(1S*,3R*)-and (1S*,3S*)-3-Chloro-1,3,5,5-tetramethyl-cyclohexanols (8b and 9b). Method A. (Solvent: CH_2Cl_2) A solution of keto olefin **7b** (386 mg, 2.5 mmol) in CH_2Cl_2 (10 mL) was stirred and cooled at 0 ^oC as an aliquot of 1.0 M HCl in Et_2O (2.5 mL, 2.5 mmol) was added dropwise over 1 min. The reaction progress was monitored as follows: A reaction aliquot (~6 uL) was diluted with a 1:1 mixture of satd. $NaHCO_3$ and hexane (0.5 mL) and after mixing an aliquot of the hexane layer was removed for TLC analysis. After 45 min at 0 ^oC, remaining HCl was neutralized upon the addition of satd. $NaHCO_3$ (5 mL) and the reaction mixture was diluted with Et_2O (30 mL). The organic layer was washed with satd. NaCl (10 mL), dried ($MgSO_4$), and evaporated to give 359 mg of colorless oil that was a 2.9:1.4:1.2:1 mixture of trans chlorohydrin (38%), exocyclic olefin (18%), endocyclic olefin (15%), and cis chlorohydrin (13%). Column purification (1:17:82 Et_3N:Et_2O:pentane) afforded 46 mg (10%) of cis chlorohydrin and 234 mg of a colorless oil that was a 2.0:1.2:1 mixture of trans chlorohydrin (26%), exocyclic olefin (16%), and endocyclic olefin (13%). Physical data for **9b**: TLC R_f = 0.58 (30:70 EtOAc:hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 0.99 (s, 3H, C5-αCH_3), 1.16 (s, 3H, C5-βCH_3), 1.30 (s, 3H, C1-CH_3), 1.36 (app. d, 1H, J = 14.4 Hz, H6α), 1.49 (app. dt, 1H, J = 14.4, 1.8 Hz, H6β), 1.89 (s, 3H, C3-CH_3), 1.92 (ν_B of ABq, 1H, J = 13.7 Hz, H4α), 1.97 (ABqt, 1H, J = 13.7 1.7 Hz, H4β), 2.03 (d, 1H, J = 13.9 Hz, H2α), 2.14 (app. dt, 1H, J = 14.2, 1.9 Hz, H2β); ^{13}C NMR (126 MHz, $CDCl_3$) δ 28.80 (CH_3), 32.97 (C5), 33.26 (CH_3), 33.53 (CH_3), 34.44 (CH_3), 49.74 (CH_2), 53.22 (CH_2), 54.25 (CH_2), 72.71

(C), 72.94 (C); IR (neat) 3427 (OH), 2954, 2926, 1460, 1377, 1205, 904; MS (FI, 70 eV) *m/z* (rel intensity %) 192 (3), 190 (6), 177 (15), 175 (47), 154 (100). An aliquot of the mixture was used for the analytical sample: Anal. Calcd for $C_{10}H_{19}ClO$ (190.71): C, 62.98; H, 10.04; Cl, 18.59. Found: C, 69.43; H, 11.19; Cl, 9.19. ^{1}H NMR NOE (500 MHz, $CDCl_3$): Irrad. δ 0.99, obs. δ 1.16 (1.0%), 1.36 (0.8%); Irrad. δ 1.16, obs. δ 0.99 (0.3%), 1.89 (2.3%), 1.97 (1.4%); Irrad. δ 1.30, obs. δ, 2.03 (1.8%), 2.04 (1.0%); Irrad. δ 1.89, obs 1.16 (2.2%).

Method B. (Solvent: Et_2O) A solution of keto olefin **7b** (309 mg, 2.0 mmol) in Et_2O (2 mL) was stirred at rt as an aliquot of 1.0 M HCl in Et_2O (2.0 mL, 2.0 mmol) was added dropwise over 1 min. After 1 h., the reaction was neutralized upon the addition of satd. $NaHCO_3$ (2 mL) and then diluted with Et_2O (20 mL). The organic layer was washed with satd. NaCl (7 mL), dried (MgSO4), and evaporated to give 290 mg of colorless oil that was a 3.9:1.3:1:1 mixture of trans chlorohydrin (54%), endocyclic olefin (18%), exocyclic olefin (14%), and cis chlorohydrin (14%). Column purification (1:20:79 Et_3N:Et_2O:hexane) afforded 26 mg (7%) of cis chlorohydrin and 175 mg of a colorless oil that was a 3.5:1.3:1 mixture of trans chlorohydrin (30%), endocyclic olefin (11%), and exocyclic olefin (9%).



(1R*,3S*,5R*)-and (1R*,3R*,5R*)-3-Chloro-5-Methylbicyclo[3.3.1]nonan-1-ols (11 and 12).

Method A. (Solvent: CH_2Cl_2) The procedure for this cyclization is based on that described for the preparation of **5a** (Method A). A solution of keto olefin (0.61 g, 4.0 mmol) in CH_2Cl_2 (30 mL) was stirred and cooled at –78 °C as an aliquot of 1.0 M $TiCl_4$ in CH_2Cl_2 (4.0 mL, 4.0 mmol) was added dropwise over 1 min. After 45 min, a solution of Et_3N (2.8 mL, 20 mmol) and MeOH (0.89 mL, 20 mmol) was added dropwise over 30 s. The hetereogeneous mixture was stirred 5 min at –78 °C, warmed to rt (rt H_2O bath, 2

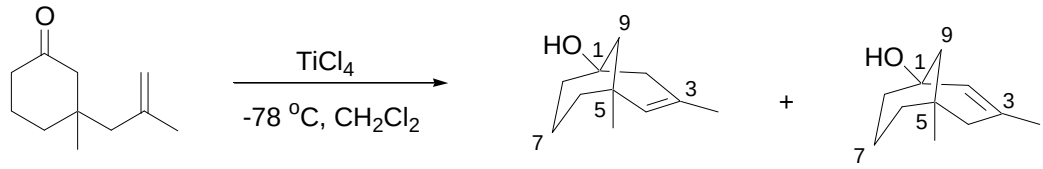
min), and diluted with Et_2O (100 mL). The organic layer was washed with 10% HCl (2 x 25 mL), satd. $NaHCO_3$ (25 mL), and satd. NaCl (25 mL); dried ($MgSO_4$); and evaporated to give 0.68 g of pale yellow oil that was a 6.3:4.8:1.2:1 mixture of β-chlorohydrin, α-chlorohydrin, starting material, and allylic alcohol. Column purification (13:87 EtOAc:hexane) afforded 27 mg (4%) of keto olefin starting material; 16 mg (2%) of allylic alcohol as a colorless oil; 7 mg (1%) of colorless oil that was a 3.7:3.1:1 mixture of allylic alcohol, β-chlorohydrin, and homoallylic alcohol; 236 mg (31%, 33% Corr. for rec. SM) of β-chlorohydrin as a white crystalline solid; 81 mg (11%) of white solid that was a 3.8:1 mixture of α:β-chlorohydrins; and 135 mg (18%, 19% Corr. for rec. SM) of white solid that was a 8:1 mixture of α:β-chlorohydrins. **11**: TLC R_f = 0.73 (65:35 EtOAc:hexane); t_R = 10.59 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (s, 3H, C5-CH_3), 1.21 (m, 1H), 1.36 (app. dt, 1H, *J* = 11.8, 2.4 Hz), 1.42-1.57 (m, 4H), 1.53 (br s, 1H, exch. D_2O, OH), 1.66-1.73 (m, 2H), 1.79 (td, 1H, *J* = 12.3, 2.8 Hz), 1.80 (m, 1H), 2.06 (ddt, 1H, *J* = 13.4, 6.1, 1.5 Hz), 2.36 (dddd, 1H, *J* = 12.6, 6.2, 2.4, 1.3 Hz), 4.64 (tt, 1H, *J* = 12.0, 6.1 Hz, CHCl); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.33 (CH_2), 31.61 (C5-CH_3), 36.31 (CH_2), 36.61 (C5), 37.93 (CH_2), 48.70 (CH_2), 49.83 (CH_2), 49.85 (CH_2), 55.22 (CHCl), 71.74 (COH); IR (CCl_4 soln) 3606 (OH), 2929, 1462, 1346, 1321, 1117, 1014, 704; MS (EI, 70 eV) *m/z* (rel intensity %) 188 (1), 173 (7), 153 (16), 145 (73), 135 (9), 111 (100), 95 (14), 69 (12), 55 (23). Recrystallization from hexane gave a sample for elemental analysis and crystals suitable for X-ray analysis: mp 69.5-70.0 ^{o}C; Anal. Calcd for $C_{10}H_{17}ClO$ (188.69): C, 63.65; H, 9.08; Cl, 18.79. Found: C, 63.76; H, 9.29; Cl, 18.28. Physical data for α-chlorohydrin **12** was taken from the 8:1 mixture of chorohydrins: TLC R_f = 0.68 (65:35 EtOAc:hexane); t_R = 10.98 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08 (s, 3H, C5-CH_3), 1.13 (ddd, 1H, *J* = 12.1, 2.5, 1.5 Hz) 1.40 (s, 1H, exch. D_2O, OH), 1.48-1.53 (m, 3H), 1.68-1.75 (m, 2H), 1.79-1.85 (m, 2H), 1.90 (tdd, 1H, *J* = 13.3, 6.4, 3.0 Hz), 1.97 (d, 1H, *J* = 12.2 Hz), 2.06 (dd, 1H, *J* = 16.1, 6.4 Hz), 2.46 (dddd, 1H, *J* = 16.1, 13.7, 6.0, 4.5 Hz), 4.02 (app. d, 1H, *J* = 4.3 Hz, CHCl); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.33 (CH_2), 30.34 (C5-CH_3), 32.77 (CH_2), 33.71 (CH_2), 35.75 (CH_2), 38.53 (CH_2), 40.45 (C5), 43.33 (CH_2), 68.79 (CHCl), 70.26 (COH); IR (CCl_4 soln) 3606 (OH), 3359 (OH, H-bond) 2931, 2856, 1466, 1356, 1230, 1140, 1065, 1012, 692; MS (EI, 70 eV) *m/z* (rel intensity %) 188 (1), 173 (4), 145 (100), 111

(88), 95 (7), 55 (16). Recrystallization from hexane gave a sample for elemental analysis: mp 89-93 ^{o}C; Anal. Calcd for $C_{10}H_{17}ClO$ (188.69): C, 63.65; H, 9.08; Cl, 18.79. Found: C, 64.07; H, 9.74; Cl, 18.00. HRMS (EI, 70 eV) Calcd for $C_{10}H_{17}ClO$: 188.0968. Found: 188.0964 (Δ = 2.2).

(1R*,5R*)-5-Methylbicyclo[3.3.1]non-2-en-1-ol (S10): TLC R_f = 0.42 (30:70 EtOAc:hexane); t_R = 7.22 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (s, 3H, C5-CH_3), 1.10 (tdd, 1H, *J* = 13.3, 5.4, 1.7 Hz, H6), 1.32-1.40 (m, 3H), 1.45-1.61 (m, 3H), 1.59 (dt, 1H, *J* = 10.9, 2.3 Hz), 1.64 (s, 1H, exch. D_2O, OH), 1.77 (app. dm, 1H, *J* = 18.9 Hz, H4), 1.91 (app. dq, 1H, *J* = 18.9, 2.2 Hz, H4), 5.49 (app. dq, 1H, *J* = 10.1, 2.1 Hz, H2), 5.74 (ddd, 1H, *J* = 10.0, 3.9, 3.1 Hz, H3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.56 (C7), 31.67 (C5-CH_3), 33.67 (C5), 36.63 (C8), 38.86 (C4), 40.40 (C6), 48.07 (C9), 71.91 (COH), 128.74 (C3), 133.14 (C2); IR (neat) 3350 (OH), 2947, 2868, 2102, 1454, 1036; MS (EI, 70 eV) *m/z* (rel intensity %) 152 (7), 137 (3), 109 (100), 95 (9), 79 (5); HRMS (EI, 70 eV) Calcd for $C_{10}H_{16}O$: 152.1201. Found: 152.1202 (Δ = -0.6).

(1R*,5R*)-5-Methylbicyclo[3.3.1]non-3-en-1-ol (S11): TLC R_f = 0.42 (30:70 EtOAc:hexane); t_R = 7.12 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 3H, C5-CH_3), 5.25 (dm, 1H, *J* = 10.7 Hz, =CH), 5.66 (dt, 1H, *J* = 10.1, 3.5 Hz, =CH).

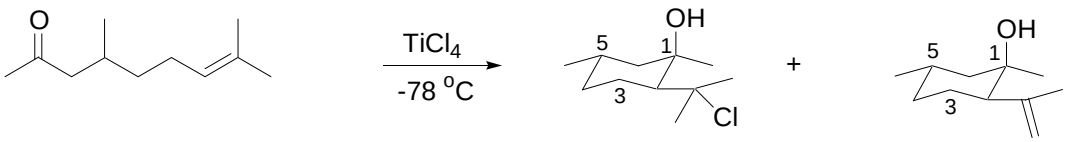
Method B. (Solvent: CH_2Cl_2) The procedure for this cyclization was carried out as described for the preparation of **5b** (Method C), except CH_2Cl_2 was used as solvent and the reaction time was increased to 15 min. A solution of keto olefin **10a** (107 mg, 0.70 mmol) in CH_2Cl_2 (5 mL) and an aliquot of 1.0 M $TiCl_4$ in CH_2Cl_2 (0.70 mL, 0.70 mmol) was stirred and cooled at –78 ^{o}C for 15 min which upon workup gave 103 mg pale yellow oil that was a 7.5:6:3.8:1 mixture of β-chlorohydrin, α-chlorohydrin, starting material, and allylic alcohol. Column purification (1:15:84 Et_3N:EtOAc:hexane) afforded 10 mg (9%) of keto olefin starting material and 58 mg (44%, 48% Corr. for rec. SM) of colorless solid that was a 1.3:1 mixture of β-chlorohydrin and α-chlorohydrin. The physical data matched those obtained above.



10b **S12** **S13**

3,5-Dimethylbycyclo[3.3.1]non-3-en-1-ol and 3,5-Dimethylbicyclo[3.3.1]non-2-en-1-ols (S12 and S13). The procedure for the cyclization of keto olefin **10b** (0.50 g, 3.0 mmol) was carried out as described for the preparation of **5b** (Method A) in CH_2Cl_2 (20 mL) using 1.0 M $TiCl_4$ in CH_2Cl_2 (3.0 mL, 3.0 mmol), except the reaction was stirred for 30 s after the $TiCl_4$ was added to give 481 mg of white solid that was a 6.1:2.5:1.4:1 mixture of homoallylic alcohol:unknown olefin:unknown olefin:allylic alcohol. Column purification (1:32:67 Et_3N:Et_2O:hexane) afforded 149 mg of colorless oil that was a 1.6:1 mixture of olefins, 8 mg (2%) of allylic alcohol as a colorless oil, 78 mg (15%) of white powder that was a 2.5:1 mixture of homoallylic and allylic alcohols, and 157 mg (31%) of homoallylic alcohol as a white powder. Physical data for unknown olefin mixture: TLC R_f = 0.59 (hexane); t_R = 9.52 min (major), 9.83 min (minor) (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (s, 3H), 1.67 (s, 3H), 2.06 (dm, 1H, *J* = 12.6 Hz), 2.33 (app. d, 1H, *J* = 17.8 Hz), 2.65 (app. d, 1H, *J* = 17.8 Hz), 5.00 (app. sext., 1H, *J* = 1.1 Hz); Minor: δ 0.96 (s, 3H), 1.69 (s, 3H), 5.45 (app. sext., 1H, *J* = 0.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.05 (CH_2), 22.23 (CH_3), 22.35 (CH_3), 28.82 (CH_3), 31.52 (CH_3), 34.37 (C), 35.90 (CH_2), 37.30 (C), 39.56 (CH_2), 40.34 (CH_2), 43.11 (CH_2), 43.88 (CH_2), 47.23 (CH_2), 49.98 (CH_2), 50.16 (CH_2), 70.26 (C), 70.38 (C), 127.19 (CH), 128.79 (CH), 133.99 (C), 137.19 (C); IR (neat) 2931, 2866, 1448, 910, 827, 735; GC-MS (EI, 70 eV) *m/z* (rel intensity %) Major: 186 (2), 184 (8), 149 (71), 141 (3), 119 (6), 107 (100), 91 (16); Minor 186 (4), 184 (11), 149 (24), 141 (100), 105 (24), 91 (17). Homoallylic alcohol **S12**: TLC R_f = 0.52 (Et_2O); t_R = 9.24 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (s, 3H, C5-CH_3), 1.07 (td, 1H, *J* = 12.6, 4.5 Hz, H6), 1.20 (dm, 1H, *J* = 11.8 Hz, H6), 1.31 (d, 1H, *J* = 11.1 Hz, H9), ~1.35 (m, 1H, H8), 1.43 (s, 1H, Exch. D_2O, OH), 1.44 (qt, 1H, *J* = 13.1, 4.3 Hz, H7), 1.50-1.55 (m, 1H, H7), 1.55 (dt, 1H, *J* = 11.1, 2.5 Hz, H9), 1.67 (s, 3H, =CCH_3), 1.69 (m, 1H, H7), 2.01 and 2.12 (ABq, 2H, *J* = 17.4 Hz, H2), 4.96 (app. dd, 1H, *J* = 2.1 1.3 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.92

(C7), 22.47 (=C*C*H$_3$), 28.96 (C5-CH$_3$), 36.42 (C6), 37.02 (C5), 41.27 (C8), 45.47 (C2), 48.29 (C9), 70.76 (COH), 129.13 (=CH), 133.56 (=C); IR (CCl_4 soln) 3610 (OH), 2927, 1450, 1350, 1041, 895; MS (EI, 70 eV) *m/z* (rel intensity) 166 (19), 151 (18), 133 (2), 123 (100), 109 (7). Recrystallization from hexane gave an analytical sample: mp 74-75 ^{o}C; Anal. Calcd for $C_{11}H_{18}O$ (166.25): C, 79.46, H, 10.91. Found: C, 79.20; H, 10.93. HMQC (500 MHz, $CDCl_3$): (20.92) δ 1.50-1.55, 1.69; (22.47) δ 1.67; (28.96) δ 1.01; (36.42) δ 1.20, 1.07; (41.27) δ ~1.35, 1.44; (45.47) δ 2.01, 2.12; (48.29) δ 1.31, 1.55; (129.13) δ 4.96. HMBC (500 MHz, $CDCl_3$): (20.92) δ 1.07, 1.20, ~1.35; (22.47) δ 2.01, 4.96; (28.96) δ 1.07, 1.31, 1.55, 4.96; (36.42) δ 1.01, 1.69; (37.02) δ 1.01, 1.07, 1.20, 1.31, 4.96; (41.27) δ 1.20, 1.31, 1.50-1.55, 1.55, 2.01, 2.12; (45.47) δ 1.31, ~1.35, 1.44, 1.55, 1.67, 4.96; (48.29) δ 1.01, 1.07, 1.20, ~1.35, 1.44, 2.01, 4.96; (70.76) δ 1.31, ~1.35, 1.44, 1.50-1.55, 1.55, 2.01, 2.12; (129.13) δ 1.01, 1.07, 1.31, 1.67, 2.01, 2.12; (133.56) δ 1.67, 2.01, 2.12. Allylic alcohol **S13**: TLC R_f = 0.60 (Et_2O); t_R = 9.42 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (s, 3H, C5-CH$_3$), 1.09 (tdd, 1H, *J* = 13.2, 4.9, 1.7 Hz), 1.31-1.46 (m, 4H), 1.50 (s, 1H, Exch. D_2O, OH), 1.50-1.59 (m, 3H), 1.66 and 1.84 (ABq, 2H, *J* = 18.4 Hz), 1.67 (s, 3H, =CCH$_3$, 5.23 (app. quint., 1H, *J* = 1.7 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.71 (CH_2), 22.39 (CH_3), 31.65 (CH_3), 33.86 (C), 37.13 (CH_2), 40.31 (CH_2), 43.88 (CH_2), 48.33 (CH_2), 72.21 (COH), 127.99 (=CH), 136.63 (=C); IR (neat) 3369 (OH), 2922, 1456, 1138, 1011, 735; MS (EI, 70 eV) *m/z* (rel intensity %)166 (7), 151 (4), 123 (100), 109 (10), 95 (4); HRMS (EI, 70 eV) Calcd for $C_{11}H_{18}O$: 166.1358. Found: 166.1351 (Δ = 4.0).



13 **14** **S18**

(1R*,2S*,5S*)-2-(1-Chloro-1-methylethyl)-1,5-dimethylcyclohexanol (14).

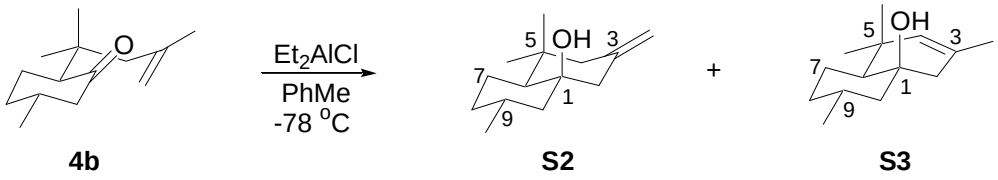
Method A. (Solvent: CH_2Cl_2) The procedure for the cyclization of keto olefin **13** (118 mg, 0.70 mmol) in CH_2Cl_2 (5 mL) was carried out as described for the preparation of **5b** (Method C) using 1.0 M $TiCl_4$ in CH_2Cl_2 (0.70 mL, 0.70 mmol) that upon work up gave

113 mg of colorless oil that 23:3.7:1 mixture of chlorohydrin (69%), homoallylic alcohol (11%), and starting material (3%). The physical data for the chlorohydrin and homoallylic alcohol matched those obtained below.

Method B. (Solvent: pentane) The procedure for this cyclization was carried out as described for the preparation of **5a** (Method C), except the reaction was stirred for 30 s after the $TiCl_4$ was added. A solution of keto olefin **13** (118 mg, 0.70 mmol) in pentane (8 mL) and 1.0 M $TiCl_4$ in pentane (0.70 mL, 0.70 mmol) at –78 ^oC was stirred for 30 s which upon work up gave 97 mg of colorless oil that was a 2.6:1 mixture of starting material (60%) and chlorohydrin (23%, 57% Corr. for rec. SM). The physical data for the chlorohydrin and homoallylic alcohol matched those obtained below.

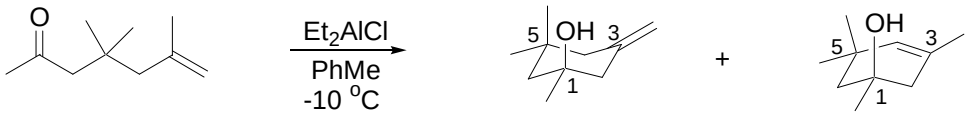
Method C. (Solvent: PhMe) A solution of keto olefin **13** (421 mg, 2.5 mmol) in PhMe (20 mL) was stirred and cooled at –78 ^oC as an aliquot of 1.0 M $TiCl_4$ in PhMe (2.5 mL, 2.5 mmol) was added dropwise over 1 min. After 30 s, a solution of Et_3N (1.74 mL, 12.5 mmol) and MeOH (0.56 mL, 12.5 mmol) was added dropwise over 30 s. The heterogeneous mixture was stirred 5 min at –78 ^oC, warmed to rt (rt H_2O bath, 2 min), and diluted with Et_2O (15 mL). The organic layer was washed with 10% HCl (2 x 15 mL), satd. $NaHCO_3$ (15 mL), and satd. NaCl (15 mL); dried ($MgSO_4$); and evaporated to give 524 mg of colorless oil that was a 9.0:1.1:1 mixture of chlorohydrin (79%, 87% Corr. for rec. SM), homoallylic alcohol (10%, 11% Corr. for rec. SM), and starting keto olefin (9%). **14**: ^1H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, 3H, *J* = 6.4 Hz, C5-CH_3), 1.10 (dd, 1H, *J* = 13.7, 12.2 Hz, H6α), 1.49 (s, 3H, C1-CH_3), 1.55 (ddd, 1H, *J* = 13.5, 3.8, 2.7 Hz, H6β), 1.59-1.80 (m, 5H), 1.73 (s, 6H, $CCl(CH_3)_2$), 1.90 (s, 1H, exch. D_2O, OH), 1.92 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.82 (C5-CH_3), 24.91 (C3), 27.60 (C5), 32.25 (Cl-CH_3), 33.52 ($CCl\mathit{C}H_3$), 34.49 ($CCl\mathit{C}H_3$), 35.13 (C4), 52.58 (C6), 56.28 (C2), 73.37 (COH), 76.15 (CCl); IR (neat) 3475 (OH), 2922. A crude sample from an identical run was used for MS and elemental analysis because the chlorohydrin was not stable to silica gel column purification or storage: MS (FI, 70 eV) *m/z* (rel intensity %) 204 (0.7), 169 (12), 168 (100); Anal. Calcd for $C_{11}H_{21}ClO$ (204.73): C, 64.53; H, 10.34; Cl, 17.32. Found: C, 68.23; H, 10.98; Cl, 12.81. HMQC (500 MHz, $CDCl_3$): (21.82) δ 0.85; (32.25) δ 1.49; (52.58) δ 1.10, 1.55. HMBC (500 MHz, $CDCl_3$): (27.60) δ 0.85, 1.10;

(35.13) δ 0.85, 1.10; (52.58) δ 0.85, 1.49; (73.37) δ 1.49. ^{1}H NMR NOE (500 MHz, $CDCl_3$): Irrad. δ 1.10, obs. δ 0.85 (1.4%), 1.49 (0.6%), 1.55 (22%).



4b **S2** **S3**

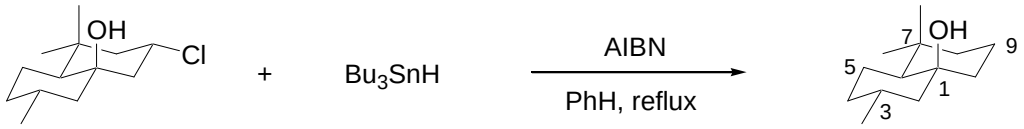
(1R,6S,9R)-3-Methylene-5,5,9-trimethylbicyclo[4.4.0]decan-1-ol (S2). The procedure for this cyclization was based on that described by Snider.[15] A solution of keto olefin **4b** (208 mg, 1.0 mmol) in PhMe (1 mL) was stirred and cooled at –78 °C as an aliquot of 1.8 M Et_2AlCl in PhMe (0.56 mL, 1.0 mmol) was added dropwise over 30 s. After 10 min, the solution was warmed to 0 °C and neutralized by the careful addition of satd. $NaHCO_3$ (3 mL). The resultant mixture was diluted with Et_2O (15 mL) and the organic layer was washed with H_2O (3 mL) and satd. NaCl (3 mL), dried ($MgSO_4$), and evaporated to give 171 mg of colorless oil that was 7.7:1 mixture of exocyclic and endocyclic olefins. Column purification (5:95 Et_2O:pentane) gave 130 mg (63%) of colorless oil that was a 7.7:1 mixture of exocyclic and endocyclic olefins. **S2**: TLC R_f = 0.62 (15:85 EtOAc:hexane); t_R = 10.87 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (s, 3H, C5–CH_3), 0.86 (d, 3H, *J* = 6.2 Hz, C9–CH_3), 0.90 (dd, 1H, *J* = 13.5, 3.6 Hz), 0.93 (s, 3H, C5–CH_3), 0.97 (dd, 1H, *J* = 13.1, 12.0 Hz), 1.07 (dd, 1H, *J* = 12.6, 3.4 Hz), 1.35 (br. s, 1H, OH, exch. D_2O), 1.43 (qd, 1H, *J* = 12.8, 3.3 Hz), 1.55-1.60 (m, 2H), 1.75-1.84 (m, 2H), 1.98 and 1.99 (ABq, 2H, *J* = 13.0 Hz), 2.11 (app. s, 2H), 4.80 (m, 2H, =CH_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.84 (CH_3), 22.09 (CH_2), 22.30 (CH_3), 27.94 (CH_3 or CH), 31.63 (CH_3 or CH), 35.43 (C5), 35.65 (CH_2), 49.50 (CH_2), 49.88 (CH_2), 50.83 (CH_2), 51.45 (CH), 73.09 (COH), 111.56 (=CH_2), 144.19 (=C); IR (neat) 3485 (OH), 3072, 2947, 1653, 1456, 1367, 891, 874; MS (EI, 70 eV) *m/z* (rel intensity %) 208 (5), 190 (64), 175 (38), 153 (100), 112 (29), 97 (36), 81 (50); HRMS (EI, 70 eV) Calcd for $C_{14}H_{24}O$: 208.1827. Found: 208.1826 (Δ = 0.4). Kugelrohr distillation at 85-90 °C (1.4 torr) gave an analytical sample: Anal. Calcd for $C_{14}H_{24}O$ (208.18): C, 80.71; H, 11.61. Found: C, 80.71; H, 12.16. The physical data for endocyclic olefin **S3** matched that obtained above.



7b **S14** **S17**

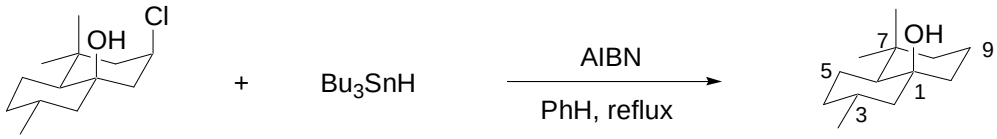
3-Methylene-1,5,5-trimethylcyclohexanol (S14). The procedure for this cyclization was carried out as described above for the preparation of **S2**, except the reaction was allowed to stir for 15 min. A solution of keto olefin (231 mg, 1.5 mmol) and 1.8 M Et_2AlCl in PhMe (0.83 mL, 1.5 mmol) in PhMe (1.5 ml) was stirred for 15 min at –78 °C which upon workup gave 223 mg of colorless oil that was a 3:1 mixture of exocyclic and endocyclic olefin. Column purification (25:75 Et_2O:pentane) gave 106 mg (46%) of colorless oil that was a 3:1 mixture of exocyclic and endocyclic olefins. **S14**: TLC R_f = 0.50 (3:7 EtOAc:hexane); t_R = 5.42 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (s, 3H, C5–CH_3), 1.01 (s, 3H, C5–CH_3), 1.23 (s, 3H, C1–CH_3), 1.40 (app. d, 1H, *J* = 14.2 Hz), 1.49 (br. s, 1H, OH, exch. D_2O), 1.55 (dt, 1H, *J* = 14.2, 1.9 Hz), 1.89 and 1.98 (ABq, 2H, *J* = 13.0 Hz), 2.13 and 2.18 (ABq, 2H, *J* = 13.3 Hz), 4.80 (m, 1H, =CH_2), 4.83 (m, 1H, =CH_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.72, 30.97, 32.75, 32.79, 48.03, 48.45, 50.88, 72.10 (COH), 111.74 (=CH_2), 144.64 (=C); IR (neat) 3402 (OH), 3072, 2953, 1653, 1456, 1369, 1107, 1066, 893;); MS (EI, 70 eV) *m/z* (rel intensity %) 154 (10), 136 (23), 121 (45), 96 (100), 81 (58), 69 (17); HRMS (EI, 70 eV) Calcd for $C_{10}H_{18}O$: 154.1358. Found: 154.1354 (Δ = 2.1). Kugelrohr distillation at 40-45 °C (0.8 torr) gave an analytical sample: Anal. Calcd for $C_{10}H_{18}O$ (154.14): C, 77.87; H, 11.76. Found: C, 76.99; H, 12.16. The physical data for endocyclic olefin **S17** matched that obtained below.

Reductive Dechlorinations



6a **S1**

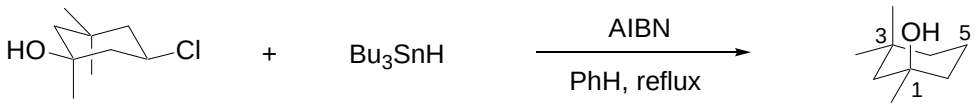
(1R,3R,6S)-3,7,7-Trimethylbicycl[4.4.0]decan-1-ol (S1). The procedure for this reductive dechlorination is based on that described by Colcolough.[16] A solution of trans chlorohydrin **6a** (150 mg, 0.65 mmol), Bu_3SnH (350 μL, 1.3 mmol), and AIBN (21 mg, 0.13 mmol) in degassed PhH (4 mL) was heated at reflux under N_2 for 3 h, cooled to rt, and diluted with Et_2O (10 mL) and satd. KF (5 mL). The organic layer was washed with satd. KF (2 x 5 mL), dried ($MgSO_4$), and evaporated to give 258 mg of white residue. Column purification (2:98 Et_2O:hexane) gave 78 mg (61%) of colorless oil: TLC R_f = 0.56 (15:85 EtOAc:hexane); t_R = 11.28 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (s, 3H, C7–CH_3), 0.86 (d, 3H, *J* = 6.6 Hz, C3–CH_3), 0.86-0.96 (m, 3H), 0.94 (s, 3H, C7–CH_3), 1.08 (s, 1H, OH, exch. D_2O), 1.19 (td, 1H, *J* = 13.5, 3.6 Hz), 1.25 (td, 1H, *J* = 13.5, 4.0 Hz), 1.34 (qd, 1H, *J* = 13.1, 3.4 Hz), 1.37-1.45 (m, 2H), 1.48 (ddd, 1H, *J* = 13.5, 3.6, 2.4 Hz), 1.54 (dq, 1H, *J* = 13.5, 2.8 Hz), 1.60 (dq, 1H, *J* =13.3, 3.3 Hz), 1.68-1.84 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.12, 21.52, 21.75, 22.33, 27.88, 32.10, 32.82, 35.69, 40.72, 42.20, 50.54, 51.48, 71.65 (COH); IR (neat) 3482 (OH), 2945, 2868, 2845, 1454, 1365, 1184, 945, 926; MS (EI, 70 eV) *m/z* (rel intensity %) 196 (25), 181 (100), 163 (12), 153 (35), 135 (4), 126 (8), 111 (20). Kugelrohr distillation at 70-75 ^{o}C (0.30 torr) gave an analytical sample: Anal. Calcd for $C_{13}H_{24}O$ (196.32): C, 79.53; H, 12.32. Found: C, 79.57; H, 12.42.



5a **S1**

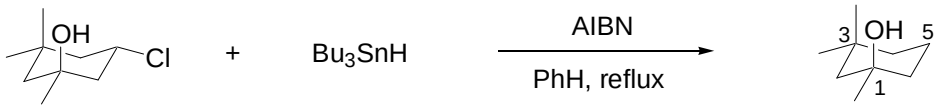
(1R,3R,6S)-3,7,7-Trimethylbicycl[4.4.0]decan-1-ol (S1). The procedure for the reductive dechlorination of cis chlorohydrin **5a** (75 mg, 0.32 mmol) using Bu_3SnH (172 μL, 0.64 mmol) and AIBN (11 mg, 0.064 mmol) in degassed PhH (2 mL) was carried out

as described above for the preparation of **S1** to afford 180 mg of white residue. Column purification (2:98 Et_2O:hexane) gave 44 mg (70%) of colorless oil. The physical data were in agreement with those obtained above.



8a **S15**

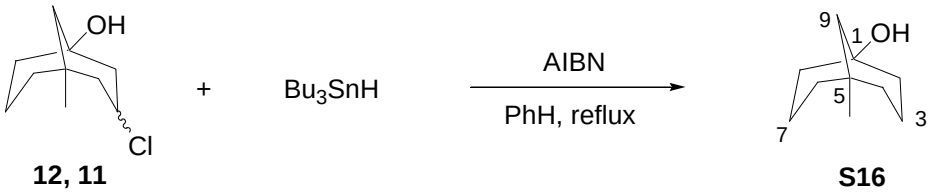
1,3,3-Trimethylcyclohexanol (S15). The procedure for this reductive dechlorination was carried out as described above for the preparation of **S1**, except the reaction solution was heated at reflux for 30 min. A solution of chlorohydrin **8a** (90 mg, 0.51 mmol), Bu_3SnH (274 μL, 1.02 mmol), and AIBN (17 mg, 0.10 mmol) in degassed PhH (3 mL) was heated to gentle reflux for 30 min to give 187 mg of crude. Column purification (8:92 EtOAc:hexane) afforded 33 mg (45%) of alcohol as a white solid: TLC R_f = 0.67 (30:70 EtOAc:hexane); t_R = 4.83 min (Method A); mp 71-72 °C (lit. 72 °C)[14]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (s, 3H, C3-CH_3), 1.02 (s, 1H, exch D_2O, OH), 1.06 (s, 3H, C3-CH_3), 1.09 (td, 1H, *J* = 12.6, 3.6 Hz), 1.19 (s, 3H, Cl-CH_3), 1.25 (d, 1H, *J* = 14 Hz), 1.29 (td, 1H, *J* = 12.9, 4.1 Hz), 1.35-1.47 (m, 3H), 1.58 (dm, 1H, *J* = 13.5 Hz), 1.74 (dtt, 1H, *J* = 13.5, 12.2, 3.4 Hz, H5); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.85, 27.54, 30.80, 32.56, 33.36, 38.96, 39.14, 51.06, 70.81; IR (CCl_4 soln), 3614 (OH), 2951, 1456, 1365, 1196, 1095, 951, 899. The physical data agreed with those reported in the literature.[17]



9a **S15**

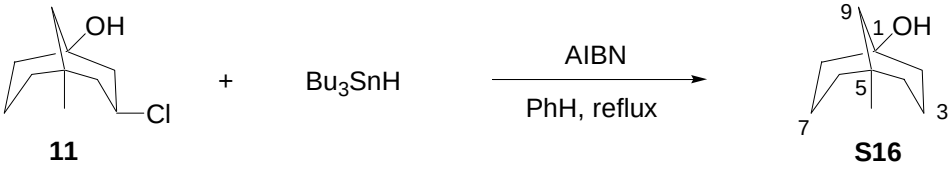
1,3,3-Trimethylcyclohexanol (S15). The procedure for this reductive dechlorination was carried out as described above for the preparation of **S1**, except the reaction solution was heated at reflux for 1.5 h. A solution of chlorohydrin **9a** (65 mg, 0.37 mmol), Bu_3SnH (199 μL, 0.74 mmol), and AIBN (12 mg, 0.074 mmol) in degassed PhH (2 mL)

was heated to gentle reflux for 1.5 h. to give 171 mg of crude. Column purification (8:92 EtOAc:hexane) afforded 13 mg (25%) of alcohol as a white solid. The physical data matched those obtained above.



12, 11 **S16**

5-Methylbicyclo[3.3.1]nonan-1-ol (S16). The procedure for the reductive dechlorination of a 3.8:1 mixture of chlorohydrins **12** and **11** (33 mg, 0.17 mmol) using Bu_3SnH (94 μL, 0.35 mmol) and AIBN (6 mg, 0.035 mmol) in degassed PhH (1 mL) was was carried out as described for for the preparation of **S15** from **8a** to give 74 mg of crude. Column purification (15:85 EtOAc:hexane) afforded 16 mg (62%) of tertiary alcohol. The physical data agreed with those obtained below.

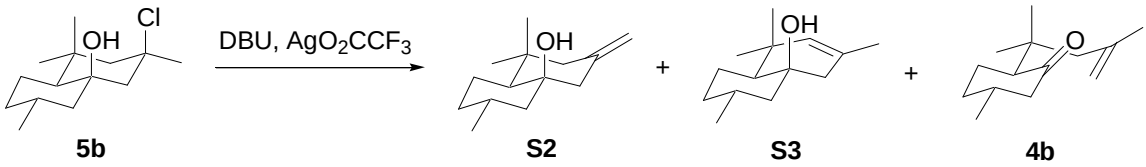


11 **S16**

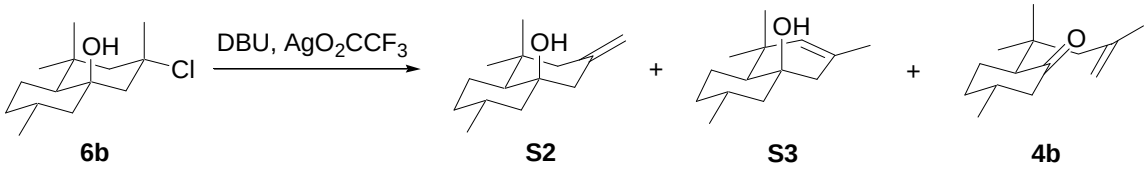
5-Methylbicyclo[3.3.1]nonan-1-ol (S16). The procedure for the reductive dechlorination of chlorohydrin **11** (33 mg, 0.17 mmol) using Bu_3SnH (94 uL, 0.35 mmol) and AIBN (6 mg, 0.035 mmol) in degassed PhH (1 mL) was carried out as described above for the preparation of **S15** from **8a** to give 75 mg of crude alcohol. Column purification (15:85 EtOAc:hexane) afforded 13 mg (50%) of bicyclic alcohol as a white solid: TLC R_f = 0.49 (30:70 EtOAc:hexane); t_R = 7.75 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (s, 3H, CH_3), 1.18-1.26 (m, 2H), 1.32 (s, 2H), 1.33 (s, 1H, exch. D_2O, OH), 1.42-1.51 (m, 4H), 1.58-1.65 (m, 2H), 1.82 (m, 2H), 1.91-2.02 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.66, 32.52, 35.09, 37.38, 38.94, 50.78, 70.99 (COH); IR (CCl_4 soln) 3608 (OH), 3421 (OH, H-bonded), 2925, 2846, 1456, 1138, 1063, 1012. The

physical data agreed with those reported in the literature.[1]

Eliminations

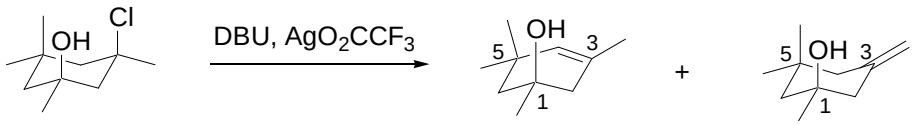


(1R,6S,9R)-3-Methylene-5,5,9-trimethylbicyclo[4.4.0]decan-1-ol and (1R,6S,9R)-3,5,5,9-tetramethylbicyclo[4.4.0]dec-3-en-1-ol (S2 and S3). The procedure for this elimination is based on that described by Majetich.[18] A suspension of AgO_2CCF_3 (66 mg, 0.30 mmol), cis chlorohydrin **5b** (49 mg, 0.20 mmol), and DBU (61 mg, 0.40 mmol) in Et_2O (0.25 mL) was stirred for 2 h at rt then diluted with Et_2O (10 mL) and 10% HCl (3 mL). The organic layer was washed with satd. $NaHCO_3$ (3 mL) and satd. NaCl (3 mL), dried ($MgSO_4$), and evaporated under reduced pressure to afford 27 mg of crude that was a 20:1:1 mixture of endocyclic olefin, exocyclic olefin, and keto olefin. Column purification (9:91 Et_2O:pentane) afforded 15 mg (36%) of colorless oil that was a 18:1 mixture of endo- and exocylic olefins. The physical data matched those obtained above.



(1R,6S,9R)-3-Methylene-5,5,9-trimethylbicyclo[4.4.0]decan-1-ol and (1R,6S,9R)-3,5,5,9-tetramethylbicyclo[4.4.0]dec-3-en-1-ol (S2 and S3). A suspension of AgO_2CCF_3 (56 mg, 0.26 mmol), trans chlorohydrin **6b** (70 mg that is 7:5:1 mixture of trans chlorohydrin (42 mg, 0.17 mmol), exocyclic olefin (24 mg, 0.12 mmol), and endocyclic olefin (5 mg, 0.02 mmol)), and DBU (52 mg, 0.34 mmol) in PhH (0.6 mL) was stirred for 10 min at rt then diluted with Et_2O (10 mL). The organic layer was

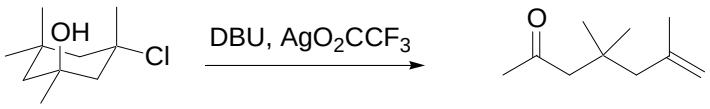
washed with 10% HCl (3 mL), H_2O (3 mL), satd. $NaHCO_3$ (3 mL), and satd. NaCl (3 mL); dried ($MgSO_4$); and evaporated under reduced pressure to afford 51 mg of crude that was a 3.9:2.3:1 mixture of exocyclic olefin, keto olefin, and endocyclic olefin. Column purification (2:98 Et_2O:hexane) afforded 9 mg (26%) of keto olefin and 15 mg (<1%) of exocyclic olefin and 5 mg (<1%) of endocyclic olefin. The physical data matched those obtained above.



8b **S17** **S14**

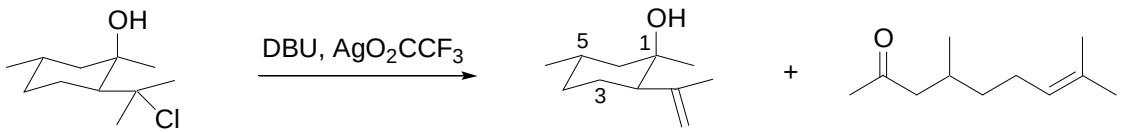
3-Methylene-1,5,5-trimethylcyclohexanol and 1,3,5,5-Tetramethyl-3-cyclohexen-1-ol (S14 and S17). The procedure for the elimination of cis chlorohydrin **8b** (56 mg, 0.29 mmol) was carried out as described above for the preparation of **S3** from **5b** using a suspension of AgO_2CCF_3 (96 mg, 0.44 mmol) and DBU (89 mg, 0.58 mmol) in Et_2O (0.5 mL) to afford 28 mg of crude that was a 20:1 mixture of endo- and exocyclic olefins. Column purification (23:77 Et_2O:pentane) afforded 11 mg (24%) of colorless oil that was a 18:1 mixture of endocyclic and exocylic olefins. The physical data for the exocyclic olefin matched those obtained above. Physical data for endocyclic olefin **S17**: TLC R_f = 0.58 (30:70 EtOAc:hexane); t_R = 5.40 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (s, 3H, C5-CH_3), 1.10 (s, 3H, C5-CH_3), 1.26 (s, 3H, C1-CH_3), 1.41 (d, 1H, *J* = 13.9, H6), 1.51 (s, 1H, OH, Exch D_2O), 1.62 (ddd, 1H, *J* = 13.7, 2.1, 0.9 Hz, H6), 1.67 (s, 3H, =CCH_3), 1.92 and 2.04 (ABq, 2H, *J* = 17.4 Hz, H2), 5.22 (d, 1H, *J* = 1.1 Hz, =CH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.81 (C3-CH_3), 30.06 (C1-CH_3), 30.72 (C5-CH_3), 32.25 (C5-CH_3), 32.75 (C5), 43.99 (C2), 48.48 (C6), 70.39 (COH), 128.27 (=C), 131.38 (=CH); IR (neat) 3392 (OH), 2956, 2916, 1450, 1373, 1107, 904; MS (EI, 70 eV) *m/z* (rel intensity) 154 (19), 139 (31), 121 (60), 96 (100), 81 (51), 57 (37); HRMS (EI, 70 eV) Calcd for $C_{10}H_{18}O$: 154.1358. Found: 154.1361 (Δ = -1.90 ppm). HMQC (500 MHz, $CDCl_3$): (23.81) δ 1.67; (30.06) δ 1.26; (30.72) δ 1.10; (32.25) δ 0.97; (43.99) δ 1.92, 2.04; (48.48) δ 1.41, 1.62; (131.38) δ 5.22. HMBC (500 MHz, $CDCl_3$): (23.81) δ 1.92,

5.22; (30.06) δ 1.41, 1.62; (30.72) δ 0.97, 1.41, 1.62; (32.25) δ 1.10; (32.75) δ 0.97, 1.10, 1.41, 1.62; (43.99) δ 1.26, 1.41, 1.62, 1.67, 5.22; (48.48) δ 0.97, 1.10, 1.26, 1.92, 5.22; (70.39) δ 1.26, 1.41, 1.62, 1.92, 2.04; (128.27) δ 1.67, 1.92, 2.04; (131.38) δ 0.97, 1.10, 1.41, 1.62, 1.67, 1.92, 2.04. The physical data were similar to those reported in the literature (IR, CCl_4 soln).[19] The physical data for exocyclic olefin **S14** matched those obtained above.



9b **7b**

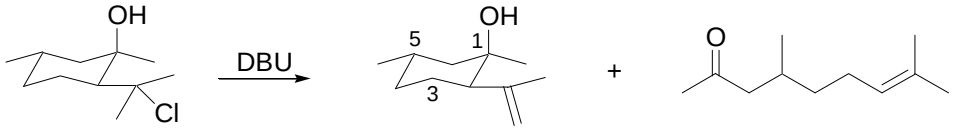
4,4,6-Trimethyl-hept-6-en-2-one (7b). The procedure for the elimination of trans chlorohydrin **9b** (123 mg that was 3.5:1.3:1 mixture of trans chlorohydrin (80 mg, 0.42 mmol), endocyclic olefin (24 mg, 0.16 mmol), and exocyclic olefin (19 mg, 0.12 mmol)) was carried out as described above for the preparation of **S3** from **5b** using a suspension of AgO_2CCF_3 (139 mg, 0.63 mmol) and DBU (128 mg, 0.84 mmol) in Et_2O (0.7 mL) to afford 57 mg of crude that was a 3.4:2.6:1 mixture of endocyclic olefin, exocyclic olefin, and keto olefin. Column purification (23:77 Et_2O:pentane) afforded 3 mg (5%) of keto olefin and 25 mg (<1%) of colorless oil that was a 1.5:1 mixture of endo- and exocyclic olefins. The physical data matched those obtained above.



14 **S18** **13**

(1R*,2R*,5S*)-2-Isopropenyl-1,5-dimethylcyclohexanol (S18). The procedure for the elimination of citronnal chlorohydrin **14** (101 mg that was a 9.0:1.1:1 mixture of chlorohydrin (78 mg, 0.38 mmol), homoallylic alcohol (8 mg, 0.05 mmol), and ketone (7 mg, 0.04 mmol)) using AgO_2CCF_3 (221 mg, 1.0 mmol) and DBU (152 mg, 1.0 mmol) in PhH (2 mL) was carried out as described above for the preparation of **S3** from **6b** which upon workup gave 59 mg of colorless oil that was a 1.9:1 mixture of ketone and

homoallylic alcohol. Column purification (7:93 Et_2O:hexane) afforded 38 mg of colorless oil that was a 2.5:1 mixture of ketone (31%) and alcohol (4%). The physical data for the ketone matched those obtained above. Physical data for homoallylic alcohol **S18**: TLC R_f = 0.48 (15:85 EtOAc:hexane); t_R = 7.17 min (Method A); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (d, 3H, *J* = 6.4 Hz, C5-CH_3), 1.01 (ddd, 1H, *J* = 13.7, 12.2, 1.3 Hz, H6α), 1.13 (s, 3H, C1-CH_3), 1.44 (m, 1H), 1.50 (d, 1H, *J* = 1.5 Hz, exch. D_2O, OH), 1.67-1.79 (m, 5H), 1.82 (dd, 3H, *J* = 1.5, 0.9 Hz, =CCH_3), 1.85 (dd, 1H, *J* = 12.6, 3.4 Hz), 4.75 (m, 1H, =CH_2), 4.89 (quint., 1H, *J* = 1.5 Hz, =CH_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.24 (CH_3), 24.83 (CH_3), 27.78 (CH_3), 27.81 (CH_2), 29.93 (CH), 34.94 (CH_2), 48.68 (CH_2), 53.05 (CH), 70.81 (COH), 111.88 (=CH_2), 148.39 (=C); IR (neat) 3539 (OH), 2920. The physical data matched those reported in the literature.[15]



14 **S18** **13**

(1R*,2R*,5S*)-2-Isopropenyl-1,5-dimethylcyclohexanol (S18). A mixture of crude chlorohydrin **14** (61 mg that was a 9.0:1.1:1 mixture of chlorohydrin (47 mg, 0.23 mmol), olefin (5 mg, 0.03 mmol), and ketone (4 mg, 0.02 mmol)) and DBU (91 mg, 0.60 mmol) was stirred for 3 h at rt then diluted with Et_2O (10 mL). The ammonium salts were hydrolyzed by washing with 10% HCl (3 mL). The organic layer was washed with satd. $NaHCO_3$ (3 mL) and satd. NaCl (3 mL), dried ($MgSO_4$), and evaporated to give 42 mg of crude that was a 1.9:1 mixture of olefin and ketone. Column purification (7:93 Et_2O:hexane) afforded 21 mg of colorless oil that was a 1.8:1 mixture of olefin (23%) and ketone (8%). The physical data matched those obtained above.

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