Regioselective Coupling Reaction of Allylic Barium Reagents with Epoxides

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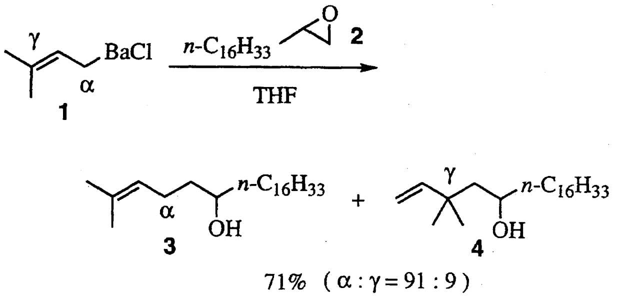
The regioselective coupling reaction of epoxides with allylic barium reagents was achieved. All reactions resulted in high yields with remarkable α-selectivities. 2-Propynylbarium reagent afforded exclusively the corresponding acetylenic alcohol.

Unsaturated alcohols and their derivatives are valuable synthetic intermediates of various natural products. One straightforward way to obtain 4-alken-1-ols is the allylation of epoxides. Although a large number of cross-coupling methods using allylic organometallics have been developed for the selective synthesis of 4-alken-1-ols[1,2] and other olefinic compounds including 1,5-dienes,[3] most of these suffered from the problems of α/γ regioselectivity of allylic reagents and *E*/*Z* stereoselectivity of the products. Described herein is a solution of these problems. The highly α-selective cross-coupling reaction of epoxides was first achieved using allylic barium reagents.[4] For example, when 1,2-epoxyoctadecane (**2**) was treated with prenylbarium reagent **1**, the cross-coupling products were obtained with an α/γ ratio of 91 : 9 in 71% combined yield (Eq. 1).



(1)

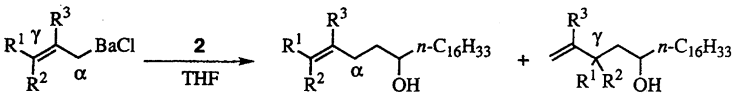
Results and Discussion

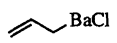
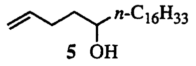
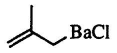
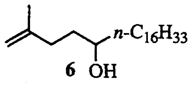
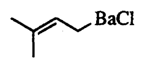
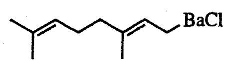
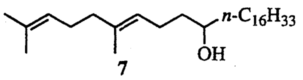
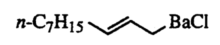
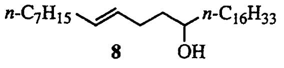
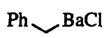
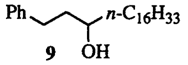
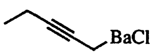
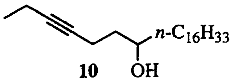
Allylic barium reagents can be directly prepared by reaction of in situ generated barium with various allylic chlorides; they are then allowed to react with various electrophiles in a highly α-selective manner without losing the double bond geometry.[4—6] We have examined various kinds of allylic barium reagents thus obtained for cross-coupling reaction with epoxide **2**. Allylic barium reagent was treated with a solution of **2** in THF at −78 °C and stirred for 12 h at 20 °C. The results are summarized in Table 1. Several characteristic features of the reaction have been noted: (1) Allylic barium reagents generated from a variety of 3-substituted and 3,3-disubstituted allyl chlorides showed high α-selectivities without exception (Entries 3—5). (2) The nucleophilic attack of the barium reagents took place at the carbon atom carrying no substitutent of epoxide **2**. (3) Though the reaction was carried out at 20 °C over a long period, the double bond geometry of the starting 3-substituted allyl chloride was retained to some extent (Entries 4 and 5).[7] (4) Benzyl barium reagent was also reacted with epoxide **2** to afford the coupling product **9** (Entry 6).[8] (5) The coupling of 2-propynylbarium reagent with **2** afforded the corresponding acetylenic alcohol (α-adduct, **10**) without contamination of homoallenylic alcohol (Entry 7).

Table 2 shows a general overview of the α-selective allylation of various epoxides with prenylbarium reagent **1**, which has the following characteristic features: (1) The coupling occurred at the less-substituted carbon of the epoxides without exception. (2) The reaction of *trans*-disubstituted epoxide provided a higher α-selectivity than that of *cis*-epoxide (compare Entry 3 with Entries 2 and 4). Prenylation of 2,2-disubstituted or trisubstituted epoxide produced the α-product nearly exclusively (Entries 5 and 6). (3) The substitution reaction proceeds with complete inversion. Thus, (*RS*,*SR*)-isomer is predominantly formed from *cis*-epoxide (Entries 2, 4 and 6), whereas (*RS*,*RS*)-isomer is obtained from *trans*-epoxide (Entry 3).

Next, we investigated the possibility of an intramolecular version of the present cross-coupling reaction of allylic barium reagent with epoxides, which is one significant challenge from the viewpoint of macrocyclic synthesis. This is not a simple problem, since the occurrence of the accompanying homocoupling reactions of the starting allylic chlorides cannot be suppressed and low cross/homo selectivities are anticipated for the coupling reaction. In fact, Corey and coworkers applied this intramolecular cross-coupling method to the synthesis of cembrol A,[6b)] although the yield of the cyclization product was not satisfactory. Thus, we examined a Barbier-type cross-coupling reaction of epoxides with allylic chloride using reactive barium prior to our study of

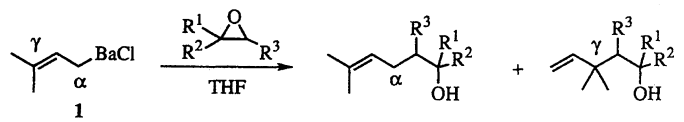
Table 1. Regioselective Coupling Reaction of 1,2-Epoxyoctadecane (**2**) with Various Barium Reagents[a)]

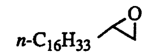
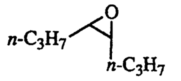
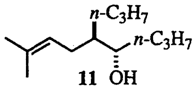
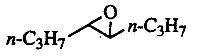
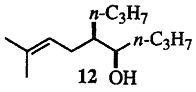
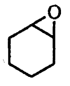
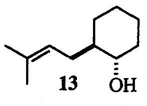
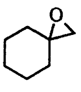
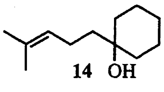
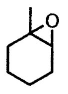
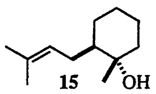


Entry	Barium reagent	Major product	Yield/%[b)]	Ratio (α : γ)[c)]
1		 **5**	81	—
2		 **6**	90	—
3	 **1**	**3**	71	91 : 9
4		 **7**	96	86 : 14[d)]
5		 **8**	91	92 : 8[e)]
6		 **9**	34	—
7		 **10**	58	>95 : 5

a) The reaction was carried out using a barium reagent (2 molar amounts) and 1,2-epoxyoctadecane (**2**) at 20 °C for 12 h. b) Isolated yield. c) Determined by ^{1}H NMR analysis. d) The $E:Z$ ratio of the α-product was 94 : 6. e) The $E:Z$ ratio of the α-product was 78 : 22.

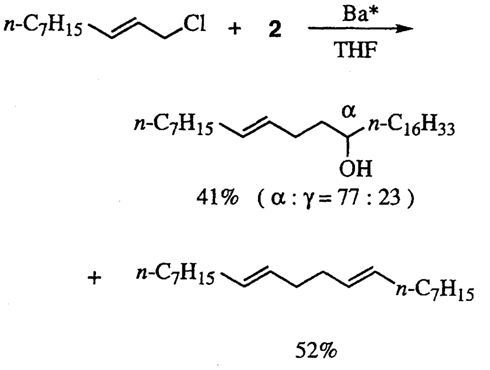
Table 2. Regioselective Coupling Reaction of Various Epoxides with Prenylbarium Reagent **1**[a)]



Entry	Epoxide	Major product	Yield/%[b)]	Ratio (α : γ)[c)]
1	 **2**	**3**	71	91 : 9
2		 **11**	81	86 : 14[d)]
3		 **12**	78	>95 : 5[d)]
4		 **13**	78	91 : 9[d)]
5		 **14**	75	>95 : 5
6		 **15**	99	>95 : 5[d)]

a) The reaction was carried out using prenylbarium reagent **1** (2 molar amounts) and epoxide at 20 °C for 12 h. b) Isolated yield. c) Determined by ^{1}H NMR analysis. d) The ratios of **11**, **12**, **13**, and **15** to their diastereomers were >95 : 5.

intramolecular cross-coupling. Treatment of a 1 : 1 mixture of (E)-2-octenyl chloride and epoxide **2** with 1 equimolar amount of reactive barium in THF at 0 °C for 20 min and then at 20 °C for 12 h afforded a 44 : 56 mixture of the cross-coupling product and the homocoupling product of the allylic chloride in 93% combined yield (Eq. 2). The cross-coupling product indicated an α/γ ratio of 77/23. The low yield of the cross-coupling product is due to the low reactivity of the epoxide toward the in situ generating allylic barium reagent relative to that of the allylic chloride as an electrophile. The reaction at a lower reaction temperature showed a significant decrease in the yield of the coupling adducts.



(2)

In summary, the extraordinary α-selectivity of the cross-coupling of epoxides with allylic barium reagents provided an unprecedented route to 4-alken-1-ols and is broadly applicable in organic synthesis.

Experimental

General. Analytical TLC was done on E. Merck precoated (0.25 mm) silica gel 60 F$_{254}$ plates. Column chromatography was conducted using silica gel 60 (E. Merck 9385, 230—400 mesh). Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini-300 (300 MHz) spectrometer. ^{13}C NMR spectra were measured on a Varian Gemini-300 (75 MHz) spectrometer. Chemical shifts of ^{1}H NMR spectra were reported relative to tetramethysilane (δ=0) or chloroform (δ=7.26). Chemical shifts of ^{13}C NMR spectra were reported relative to CDCl$_3$ (δ=77.0). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Analytical gas-liquid phase chromatography (GLC) was performed on a Shimadzu GC-8A instrument equipped with a flame ionization detector and a capillary column of PEG-HT (0.25×25000 mm) using nitrogen as carrier gas. Microanalyses were accomplished at the Faculty of Agriculture, Nagoya University.

All experiments were carried out in a Schlenk tube under an atmosphere of standard grade argon gas (oxygen <10 ppm). Dry THF was used as purchased from Aldrich (anhydrous, 99.9%). Anhydrous BaI$_2$ was prepared by drying BaI$_2$·2H$_2$O (extra pure reagent, Nacalai Tesque) at 150 °C for 2 h under reduced pressure (<10 Torr, 1 Torr=133.322 Pa). Products of Aldrich, Fluka, Kishida Chemical, and Wako Pure Chemical could be used with equal efficiency. Lithium (wire, 99.9%) was purchased from Aldrich and was cut into 20—30 mg pieces, which were rinsed with dry hexane before use. Biphenyl (guaranteed reagent) was used as purchased from Nacalai Tesque. Stereochemically pure (>99%) allylic chlorides were prepared by treatment of the corresponding allylic alcohols with a mixture of N-chlorosuccinimide and dimethyl sulfide in CH$_2$Cl$_2$.[9)] Epoxides were synthesized from the corresponding alkenes by epoxidation with m-chloroperbenzoic acid in CH$_2$Cl$_2$. Other chemicals were used as purchased.

Typical Procedure for Reaction of Allylic Barium Reagents with Epoxides: Synthesis of 2-Methyl-2-docosen-6-ol (3) (Eq. 1 and Entry 3 in Table 1). An oven-dried, 20-ml Schlenk tube equipped with a Teflon®-coated magnetic stirring bar was flushed with argon. Freshly cut lithium (14 mg, 2.0 mmol) and biphenyl (320 mg, 2.1 mmol) were put into the apparatus and covered with dry THF (5 ml), and the mixture was stirred for 2 h at 20—25 °C (lithium was completely consumed). Anhydrous BaI$_2$ (470 mg, 1.2 mmol) was placed into a separate oven-dried, 50 ml Schlenk tube equipped with a Teflon®-coated magnetic stirring bar under argon atmosphere; this was covered with dry THF (3 ml), and stirred for 5 min at room temperature. To the suspension of BaI$_2$ in THF was added at room temperature a solution of the biphenylyllithium (lithium biphenylide) in THF through a stainless steel cannula under an argon stream. The reaction mixture was stirred for 30 min at room temperature. A solution of prenyl chloride (107 mg, 1.0 mmol) in THF (2 ml) was slowly added to the resulting dark brown suspension of reactive barium (1.0 mmol) in THF (10 ml) at −78 °C. After being stirred for 20 min, the mixture was treated with a solution of 1,2-epoxyoctadecane (**2**, 135 mg, 0.50 mmol) in THF (1 ml) at −78 °C and again stirred for 12 h at 20 °C. A saturated NH$_4$Cl aqueous solution (10 ml) was added to the mixture and the aqueous layer was extracted with ether (10 ml). The combined organic extracts were washed with 1 mol dm^{-3} sodium thiosulfate solution (20 ml), dried over anhydrous MgSO$_4$, and concentrated in vacuo after filtration. The crude product was purified by flush-column chromatography on silica gel (1 : 20 to 1 : 5 ether/hexane as the eluant) to afford 2-methyl-2-docosen-6-ol (**3**, α-adduct, 110 mg, 65% yield) and 3,3-dimethyl-1-henicosen-5-ol (**4**, γ-adduct, 11 mg, 6% yield).

3: TLC R_f 0.36 (1 : 5 ethyl acetate/hexane); IR (neat) 3347, 3250, 2959, 2917, 2849, 1472, 1464, 1375, 1354, 1109, 1082, 909, 735 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ=0.88 (t, 3 H, J=6.2 Hz, CH$_3$), 1.15—1.59 (m, 33 H, 16 CH$_2$ and OH), 1.63 (s, 3 H, CH$_3$), 1.69 (s, 3 H, CH$_3$), 2.09 (m, 2 H, CH$_2$), 3.60 (m, 1 H, CH), 5.14 (t, 1 H, J=6.5 Hz, vinyl); ^{13}C NMR (75 MHz, CDCl$_3$) δ=14.1, 17.7, 22.7, 24.4, 25.7, 29.4, 29.7 (11 C), 31.9, 37.4, 37.5, 71.8, 124.2, 132.0. Found: C, 81.51; H, 13.85%. Calcd for C$_{23}$H$_{46}$O: C, 81.60; H, 13.70%.

1-Henicosen-5-ol (5, Entry 1 in Table 1): TLC R_f 0.37 (1 : 5 ethyl acetate/hexane); IR (KBr) 3294, 2917, 2849, 2361, 1466, 1356, 1118, 1082, 912, 722 cm^{-1} ; ^{1}H NMR (300 MHz, CDCl$_3$) δ=0.88 (t, 3 H, J=7.5 Hz, CH$_3$), 1.20—1.71 (m, 33 H, 16 CH$_2$ and OH), 2.18 (m, 2 H, CH$_2$), 3.61 (m, 1 H, CH), 4.96 (d, 1 H, J=10.1 Hz, vinyl), 5.05 (d, 1 H, J=17.2 Hz, vinyl), 5.85 (ddt, 1 H, J=6.8, 10.3, 17.1 Hz, vinyl); ^{13}C NMR (75 MHz, CDCl$_3$) δ=14.1, 22.7, 25.6, 29.4, 29.7 (10 C), 30.1, 31.9, 36.4, 37.5, 71.5, 114.7, 138.7. Found: C, 81.21; H, 13.86%. Calcd for C$_{21}$H$_{42}$O: C, 81.22; H, 13.63%.

2-Methyl-1-henicosen-5-ol (6, Entry 2 in Table 1): TLC R_f 0.40 (1 : 5 ethyl acetate/hexane); IR (KBr) 3310, 2917, 2849, 1650, 1474, 1464, 1111, 1086, 835, 720 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ=0.88 (t, 3 H, J=6.7 Hz, CH$_3$), 1.10—1.65 (m, 33 H, 16 CH$_2$ and OH), 1.74 (s, 3 H, CH$_3$), 2.13 (m, 2 H, CH$_2$), 3.61 (m, 1 H, CH), 4.72 (s, 2 H, 2 vinyls); ^{13}C NMR (75 MHz, CDCl$_3$) δ=14.1, 22.5, 22.7, 25.6, 29.4, 29.7 (10 C), 31.9, 34.1, 35.2, 37.5, 70.8, 110.0, 146.0. Found: C, 81.31; H, 14.02%. Calcd for C$_{22}$H$_{44}$O: C, 81.41; H, 13.66%.

(*E*)-2,6-Dimethyl-2,6-hexacosadien-10-ol (7, Entry 4 in Table 1): TLC R_f 0.38 (1 : 5 ethyl acetate/hexane); IR (KBr) 3350, 2917, 2849, 1474, 1375, 1350, 1109, 1070, 916, 887, 851, 803, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=0.88 (t, 3 H, J=6.9 Hz, CH_3), 1.20—1.59 (m, 33 H, 16 CH_2 and OH), 1.60 (s, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.95—2.28 (m, 6 H, 3 CH_2), 3.60 (m, 1 H, CH), 5.05—5.22 (m, 2 H, 2 vinyls); ^{13}C NMR (75 MHz, $CDCl_3$) δ=14.1, 16.0, 17.7, 22.7, 24.3, 25.7 (2 C), 26.6, 29.4, 29.7 (10 C), 31.9, 37.3, 37.5, 39.7, 71.8, 124.1, 124.2, 131.4, 135.6. Found: C, 82.69; H, 13.90%. Calcd for $C_{28}H_{54}O$: C, 82.66; H, 13.41%.

(*E*)-8-Octacosen-12-ol (8, Entry 5 in Table 1): TLC R_f 0.40 (1 : 5 ethyl acetate/hexane); IR (KBr) 3320, 2919, 2849, 1478, 1354, 1111, 1079, 1043, 965, 910, 878, 857, 721 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=0.88 (t, 6 H, J=6.8 Hz, 2 CH_3), 1.00—1.82 (m, 43 H, 21 CH_2 and OH), 1.94—2.20 (m, 4 H, 2 CH_2), 3.61 (m, 1 H, CH), 5.38—5.47 (m, 2 H, 2 vinyls); ^{13}C NMR (75 MHz, $CDCl_3$) δ=14.1, 22.7, 25.6, 29.0, 29.1—29.7 (16 C), 31.9 (2 C), 32.6, 37.1, 37.4, 71.6, 129.7, 131.1. Found: C, 82.23; H, 14.24%. Calcd for $C_{28}H_{56}O$: C, 82.28; H, 13.81%.

1-Phenylnonadecan-3-ol (9, Entry 6 in Table 1): TLC R_f 0.33 (1 : 5 ethyl acetate/hexane); IR (KBr) 3305, 2917, 2849, 1559, 1541, 1509, 1474, 1337, 1078, 911, 749, 698 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ=0.88 (t, 3 H, J=6.8 Hz, CH_3), 1.14—1.63 (m, 31 H, 15 CH_2 and OH), 1.77 (m, 2 H, CH_2), 2.73 (m, 2 H, CH_2), 3.62 (m, 1 H, CH), 7.07—7.32 (m, 5 H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ=14.1, 22.7, 25.6, 29.4, 29.7 (10 C), 31.9, 32.1, 37.6, 39.1, 71.4, 125.8, 128.4 (4 C), 142.2. Found: C, 83.28; H, 12.25%. Calcd for $C_{25}H_{44}O$: C, 83.27; H, 12.30%.

3-Tricosyn-7-ol (10, Entry 7 in Table 1): TLC R_f 0.37 (1 : 5 ethyl acetate/hexane); IR (KBr) 3378, 2917, 2849, 1468, 1315, 1111, 1084, 909, 885, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=0.89 (t, 3 H, J=6.9 Hz, CH_3), 1.14 (t, 3 H, J=7.8 Hz, CH_3), 1.15—1.90 (m, 33 H, 16 CH_2 and OH), 2.17 (q, 2 H, J=5.6 Hz, CH_2), 2.30 (t, 2 H, J=5.6 Hz, CH_2) 3.74 (m, 1 H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=12.9, 14.7, 14.8, 16.0, 23.3, 26.2, 29.9, 30.2 (10 C), 32.5, 36.6, 37.9, 71.9, 79.6, 83.1. Found: C, 82.06; H, 13.29%. Calcd for $C_{23}H_{44}O$: C, 82.07; H, 13.18%.

(5*RS*,6*SR*)-2-Methyl-5-propyl-2-nonen-6-ol (11, Entry 2 in Table 2): TLC R_f 0.33 (1 : 5 ethyl acetate/hexane); IR (neat) 3391, 2959, 2930, 2872, 1672, 1466, 1456, 1377, 1225, 1115, 1059, 1005, 908, 843, 776, 737 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=0.88—1.04 (m, 6 H, 2 CH_3), 1.19—1.80 (m, 10 H, 4 CH_2 and CH and OH), 1.62 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 2.03 (m, 2 H, CH_2), 3.63 (m, 1 H, CH), 5.16 (t, 1 H, J=7.5 Hz, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ=14.2, 14.5, 17.8, 19.5, 20.6, 25.9, 27.8, 32.4, 36.3, 44.0, 73.5, 123.3, 132.3. Found: C, 78.65; H, 13.44%. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21%.

(5*RS*,6*RS*)-2-Methyl-5-propyl-2-nonen-6-ol (12, Entry 3 in Table 2): TLC R_f 0.34 (1 : 5 ethyl acetate/hexane); IR (neat) 3382, 2959, 2930, 2872, 1672, 1466, 1456, 1377, 1117, 1063, 1005, 970, 909, 835, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=0.89—1.00 (m, 6 H, 2 CH_3), 1.19—1.59 (m, 10 H, 4 CH_2, CH, and OH), 1.63 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 1.95—2.17 (m, 2 H, CH_2), 3.61 (m, 1 H, CH), 5.16 (t, 1 H, J=7.5 Hz, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ=14.2, 14.5, 17.8, 19.6, 20.8, 25.9, 28.9, 31.2, 36.2, 43.9, 73.6, 123.3, 132.6. Found: C, 78.55; H, 13.49%. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21%.

(1*RS*,2*SR*)-2-(3-Methyl-2-butenyl)-1-cyclohexanol (13, Entry 4 in Table 2): TLC R_f 0.26 (1 : 5 ethyl acetate/hexane): IR (neat) 3353, 2926, 2857, 1675, 1449, 1377, 1365, 1235, 1129, 1071, 1059, 1034, 929, 841, 700 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ=0.88—1.80 (m, 9 H, 4 CH_2 and OH), 1.65 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 1.86—1.98 (m, 2 H, CH_2), 2.35 (dt, 1 H, J=7.5, 15.0 Hz, CH) 3.28 (m, 1 H, CH), 5.23 (t, 1 H, J=7.5 Hz, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ=17.8, 24.9, 25.6, 25.9, 30.7, 31.7, 35.4, 45.7, 75.2, 123.0, 132.9. Found: C, 78.53; H, 11.79%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

1-(4-Methyl-3-pentenyl)-1-cyclohexanol (14, Entry 5 in Table 2): TLC R_f 0.33 (1 : 5 ethyl acetate/hexane); IR (neat) 3412, 2967, 2930, 2857, 2245, 1674, 1449, 1377, 1343, 1260, 1171, 1148, 1109, 1078, 1042, 967, 926, 909, 835, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=1.20—1.68 (m, 13 H, 6 CH_2 and OH), 1.63 (s, 3 H, CH_3), 1.69 (s, 3 H CH_3), 2.06 (dt, 2 H, J=6.4, 9.7 Hz, CH_2) 5.14 (t, 1 H, J=9.7 Hz, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ=17.6, 21.7, 22.2 (2 C), 25.8 (2 C), 37.4 (2 C), 42.1, 71.5, 124.7, 131.6. Found: C, 79.05; H, 12.10%. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%.

(1*RS*,2*SR*)-1-Methyl-2-(3-methyl-2-butenyl)-1-cyclohexanol (15, Entry 6 in Table 2): TLC R_f 0.28 (1 : 5 ethyl acetate/hexane); IR (neat) 3371, 2969, 2928, 2859, 1675, 1447, 1375, 1337, 1262, 1130, 1113, 983, 918, 843 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=0.89—1.45 (m, 9 H, CH_3 and 3 CH_2), 1.58—1.81 (m, 11 H, 2 CH_3, 2 CH_2, and OH), 2.33 (m, 1 H, CH), 5.16 (t, 1 H, J=7.5 Hz, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ=17.8, 21.1, 24.1, 25.7, 25.8, 28.6, 29.3, 41.9, 48.7, 73.3, 124.0, 132.3. Found: C, 79.06; H, 12.25%. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%.

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