

Supporting Information

Novel Conversion of 1,2-Disubstituted *cis*-Epoxides to One Carbon Homologated Allylic Alcohols Using Dimethyl Sulfonium Methylide

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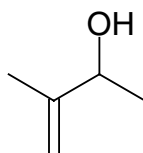
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General

ⁿBuLi solutions and anhydrous THF were purchased from Aldrich. All reactions were conducted in heat-dried glassware under an atmosphere of high purity nitrogen. Solvent removal was carried out using a rotary evaporator connected to a dry ice condenser. Column chromatography was performed on silica cartridges. ¹H and ¹³C NMR spectra were obtained from either a 300 MHz (¹H: 300 MHz, ¹³C: 75 MHz) or 400 MHz (¹H: 400 MHz, ¹³C: 100 MHz) Varian Unity Inova spectrometer. ¹H and ¹³C shifts are given in ppm, δ scale and are measured relative to tetramethylsilane as standard. Mass spectra were recorded on a Hewlett Packard HP 6890 or HP5973 MSD instrument. Optical rotation were recorded on an Optical Activity Ltd AA-1000 polarimeter.

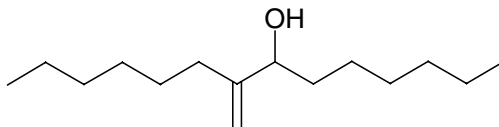
3-methyl-3-buten-2-ol¹



Colorless liquid; 91% yield; ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 4.97 (s, 1H, C=CHH), 4.80 (s, 1H, C=CHH), 4.25 (apparent quintet, 1H, J = 5.8 Hz, CHOH), 1.75 (s, 3H, CCH₃), 1.45 (d, 1H, J = 4.0 Hz, OH), 1.29 (d, 3H, J = 6.5 Hz, CHCH₃); ¹³C NMR (CDCl₃, 100 MHz): δ_{ppm} 148.9, 109.5, 71.5, 21.7, 17.8.

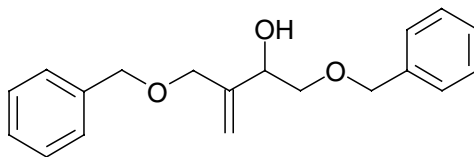
In agreement with reference 1.

8-methylene tetradecan-7-ol



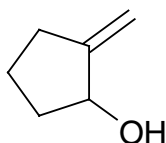
Colorless oil; 88% yield; ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 5.00 (s, 1H, C=CHH), 4.83 (d, 1H, J = 1.3 Hz, C=CHH), 4.06 (dt, 1H, J = 7.2 and 4.7 Hz, CHOH), 2.02 (apparent nontuplet, 2H, J = 8.0 Hz, CH₂C=CH₂), 1.62-1.40 (m, 6H, 3CH₂), 1.34-1.29 (m, 12H, 6CH₂), 0.89-0.86 (m, 6H, 2CH₃); ¹³C NMR (CDCl₃, 75 MHz): δ_{ppm} 152.4, 109.0, 75.5, 35.5, 31.8, 31.76, 31.4, 29.2(2C), 28.0, 25.7, 22.6(2C), 14.1(2C). MS (EPCI) m/z (rel %) 226 (1), 208 (1), 141 (54), 71 (100). Anal. Calc. for C₁₅H₃₀O C, 79.58; H, 13.36. Found: C, 79.65; H, 13.39.

1-(benzyloxy)-3-[(benzyloxy)methyl]-3-buten-2-ol



Colorless oil; 90% yield; ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 7.38-7.28 (m, 10H, Ar-H), 5.32 (s, 1H, $\text{C}=\text{CHH}$), 5.24 (s, 1H, $\text{C}=\text{CHH}$), 4.56 (s, 2H, ArCH_2), 4.49 (s, 2H, ArCH_2), 4.45 (app. quint., 1H, $J=4.1$ Hz, CHOH), 4.06 (s, 2H, $\text{CH}_2\text{C}=\text{CH}_2$), 3.64 (dd 1H, $J = 3.6$ and 9.5 Hz, CHHCHOH), 3.49 (dd, 1H, $J = 9.5$ and 8.7 Hz, CHHCHOH), 2.70 (d, 1H, $J = 2.4$ Hz, OH); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ_{ppm} 144.4, 138.0, 137.9, 128.5 (2C), 128.4 (2C), 127.8 (3C), 127.8 (2C), 127.7, 114.9, 73.5, 73.4, 72.3, 72.0, 71.3. HRMS Calcd. for $\text{C}_{19}\text{H}_{23}\text{O}_3$ m/z 299.1647, found: 299.1654.

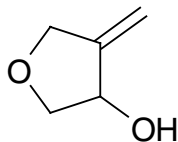
2-methylene cyclopentanol²



Colorless oil; 91% yield; ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 5.14 (d, 1H, $J = 2.4$ Hz, $\text{C}=\text{CHH}$), 5.02 (d, 1H, $J = 2.4$ Hz, $\text{C}=\text{CHH}$), 4.42 (app. q, 1H, $J = 4.8$ Hz, CHOH), 2.56-2.41 (m, 1H, $\text{CHHC}=\text{CH}_2$), 2.38-2.25 (m, 1H, $\text{CHHC}=\text{CH}_2$), 2.01-1.75 (m, 2H, CH_2CHOH), 1.74-1.50 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.42 (d, 1H, $J=5.4$ Hz, OH); ^{13}C NMR (CDCl_3 , 100 MHz): δ_{ppm} 155.3, 107.5, 75.1, 35.6, 30.3, 21.7.

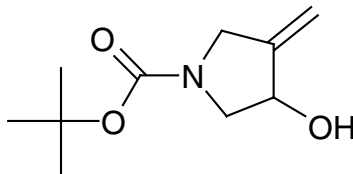
In agreement with reference 2.

Tetrahydro-4-methylene-3-furanol



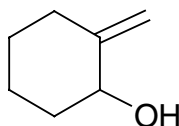
Colorless oil; 92 % yield; ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 5.35-5.33 (m, 1H, $\text{C}=\text{CHH}$), 5.15 (app. q, 1H, $J = 2.0$ Hz, $\text{C}=\text{CHH}$), 4.62-4.56 (m, 1H, CHOH), 4.50 (dt, 1H, $J = 13.5$ and 2.0 Hz, $\text{CHHC}=\text{CH}_2$), 4.28 (dt, 1H, $J = 13.5$ and 2.4 Hz, $\text{CHHC}=\text{CH}_2$), 3.93 (dd, 1H, $J = 5.0$ and 9.9 Hz, CHHCHOH), 3.78 (dd, 1H, $J = 9.9$ and 3.3 Hz, CHHCHOH), 1.74 (d, 1H, $J = 6.5$ Hz, OH); ^{13}C NMR (CDCl_3 , 75 MHz): δ_{ppm} 150.4, 107.9, 75.1, 72.7, 70.0. Anal. Calc. for $\text{C}_5\text{H}_8\text{O}_2$ C, 59.98; H, 8.05. Found: C, 60.14; H, 8.21.

tert-butyl 3-hydroxy-4-methylene-1-pyrrolidinecarboxylate



Colorless oil; 83% yield; ^1H NMR (300 MHz, $\text{D}_6\text{-DMSO}$): δ_{ppm} 5.34 (d, 1H, $J = 5.2$ Hz, OH), 5.13 (s, 1H, $\text{C}=\text{CHH}$), 5.05 (s, 1H, $\text{C}=\text{CHH}$), 4.44 (app. q, 1H, $J = 6.5$ Hz, CHOH), 3.94-3.82 (m, 2H, $\text{CH}_2\text{C}=\text{CH}_2$), 3.57-3.51 (m, 1H, CHHCHOH), 3.04-2.98 (m, 1H, CHHCHOH), 1.40 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR ($\text{D}_6\text{-DMSO}$ (90°C), 75 MHz): δ_{ppm} 153.7, 148.6, 107.3, 78.5, 70.3, 53.2, 48.8, 28.2(3C). MS (EPCI) m/z (rel %) 199 (1), 143 (22), 126 (19), 82 (19), 57 (100). Anal. Calc. for $\text{C}_{10}\text{H}_{17}\text{NO}_3$ C, 60.28; H, 8.60; N, 7.03. Found: C, 60.11; H, 8.64; N, 6.99.

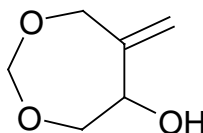
2-methylene cyclohexanol³



Colorless oil; 86% yield; ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 4.89 (s, 1H, $\text{C}=\text{CHH}$), 4.76 (s, 1H, $\text{C}=\text{CHH}$), 4.09-4.07 (m, 1H, CHOH), 2.41-2.39 (m, 1H, CH_2), 2.03-2.00 (m, 2H, CH_2), 1.83-1.79 (m, 1H, CH_2), 1.68-1.64 (m, 1H, CH_2), 1.55 (d, 1H, $J = 4.2$ Hz, OH), 1.51-1.27 (m, 3H, CH_2); ^{13}C NMR (CDCl_3 , 100 MHz): δ_{ppm} 151.6, 105.0, 72.6, 36.6, 33.5, 27.7, 23.7. MS (EPCI) m/z (rel %) 112 (54), 97 (94), 83 (100).

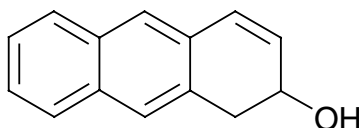
In agreement with reference 3.

6-methylene-1,3-dioxepan-5-ol



Colorless oil; 81% yield; ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 5.16 (s, 1H, $\text{C}=\text{CHH}$), 5.04 (s, 1H, $\text{C}=\text{CHH}$), 4.99 (d, 1H, $J = 6.7$ Hz, OCHHO), 4.64 (d, 1H, $J = 6.7$ Hz, OCHHO), 4.54 (d, 1H, $J = 14.0$ Hz, $\text{CHHC}=\text{CH}_2$), 4.33 (bd, 1H, $J = 4.0$ Hz, CHOH), 4.26 (dd, 1H, $J = 1.5$ and 14.0 Hz, $\text{CHHC}=\text{CH}_2$), 3.95 (dd, 1H, $J = 4.0$ and 11.9 Hz, CHHCHOH), 3.66 (dd, 1H, $J = 1.7$ and 11.9 Hz, CHHCHOH), 2.66 (bs, 1H, OH); ^{13}C NMR (CDCl_3 , 75 MHz): δ_{ppm} 148.1, 114.3, 95.6, 74.6, 72.7, 70.5. Anal. Calc. for $\text{C}_6\text{H}_{10}\text{O}_3$ C, 55.37; H, 7.74. Found: C, 55.48; H, 7.79.

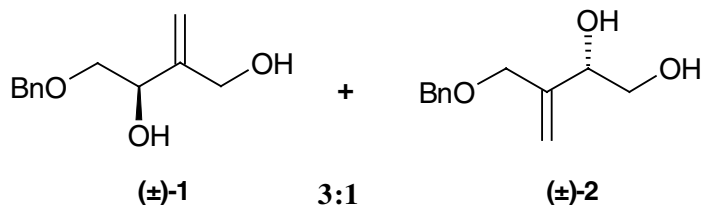
1,2-dihydro-2-anthracenol⁴



White crystals; 75% yield; ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 7.79-7.73 (m, 2H, Ar-H), 7.62 (s, 1H, Ar-H), 7.56 (s, 1H, Ar-H), 7.48-7.38 (m, 2H, Ar-H), 6.73 (d, 1H, $J = 9.6$ Hz, $\text{ArCH}=\text{CH}$), 6.21 (dd, 1H, $J = 4.2$ and 9.6 Hz, $\text{ArCH}=\text{CH}$), 4.60 (app. quint., 1H, $J = 6.0$ Hz, CHOH), 3.20 (d, 2H, $J = 6.0$ Hz, CH_2).

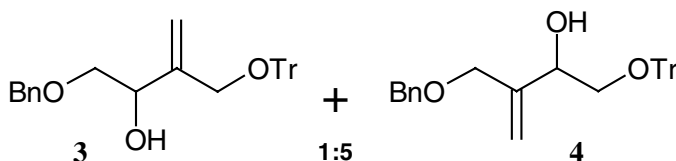
See reference 4.

4-(benzyloxy)-2-methylene-1,3-butanediol ($\pm$)-1 and 3-[(benzyloxy)methyl]-3-butene-1,2-diol ($\pm$)-2



Inseparable mixture of isomers in ratio 3:1 (based on crude NMR); 85% yield; **1**: ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 7.37-7.29 (m, 5H, Ar-H), 5.19 (s, 1H, $\text{C}=\text{CHH}$), 5.17 (s, 1H, $\text{C}=\text{CHH}$), 4.59 (s, 2H, PhCH_2), 4.55-4.45 (m, 1H, CHOH), 4.21-4.18 (m, 2H, CH_2OH), 3.63 (dd, 1H, $J = 9.6$ and 3.8 Hz, BnOCHH), 3.55 (dd, 1H, $J = 9.6$ and 7.7 Hz, BnOCHH), 2.73 (d, 1H, $J = 3.8$ Hz, OH), 2.21 (t, 1H, $J = 6.2$ Hz, OH); and **2**: ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 7.37-7.29 (m, 5H, Ar-H), 5.31 (s, 1H, $\text{C}=\text{CHH}$), 5.25 (s, 1H, $\text{C}=\text{CHH}$), 4.54 (s, 2H, PhCH_2), 4.33 (app. q, 1H, $J = 6.0$ Hz, CHOH), 4.11 (dd, 1H, $J = 11.7$ and 1.8, $\text{CHHC}=\text{CH}_2$), 4.03 (dd, 1H, $J = 11.7$ and 1.8 Hz, $\text{CHHC}=\text{CH}_2$), 3.73-3.64 (m, 2H, CH_2OH), 2.66 (d, 1H, $J = 5.6$ Hz, OH), 2.36 (t, 1H, $J = 6.0$ Hz, OH). HRMS Calcd. for $\text{C}_{12}\text{H}_{17}\text{O}_3$ m/z 209.1178, found: 209.1164.

1-(benzyloxy)-3-[(trityloxy)methyl]-3-buten-2-ol **3 and 3-[(benzyloxy)methyl]-1-(trityloxy)-3-buten-2-ol **4****

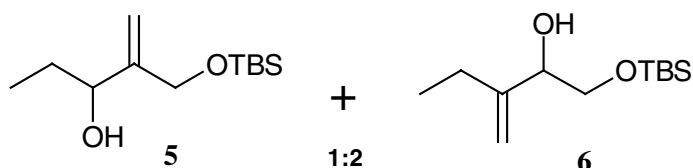


Two isomers in ratio 1:5 (based on crude NMR). Purification yielded two thick yellow oils:

3 (11% yield): ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 7.42 (d, 6H, $J = 8.4$ Hz, Ar-H), 7.31-7.24 (m, 14H, Ar-H), 5.36 (s, 1H, $\text{C}=\text{CHH}$), 5.30 (s, 1H, $\text{C}=\text{CHH}$), 4.48 (s, 2H, PhCH_2), 4.41-4.37 (m, 1H, CHOH), 3.68 (d, 1H, $J = 11.0$ Hz, $\text{CHHC}=\text{CH}_2$), 3.61 (d, 1H, $J = 11.0$ Hz, $\text{CHHC}=\text{CH}_2$), 3.50 (dd, 1H, $J = 9.9$ and 3.7 Hz, BnOCHH), 3.36 (dd, 1H, $J = 9.9$ and 7.9 Hz, BnOCHH), 2.57 (d, 1H, $J = 3.8$ Hz, OH); ^{13}C NMR (CDCl_3 , 100 MHz): δ_{ppm} 144.1, 143.9 (3C), 138.9, 128.6 (6C), 128.4 (2C), 127.8 (6C), 127.7 (2C), 127.1, 127.0 (3C), 113.1, 87.2, 73.4, 73.2, 71.9, 64.9. Anal. Calc. for $\text{C}_{31}\text{H}_{30}\text{O}_3$ C, 82.64; H, 6.71. Found: C, 82.58; H, 6.72.

4 (57% yield): ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 7.42 (d, 6H, $J = 8.4$ Hz, Ar-H), 7.31-7.20 (m, 14H, Ar-H), 5.25 (s, 1H, $\text{C}=\text{CHH}$), 5.19 (s, 1H, $\text{C}=\text{CHH}$), 4.37 (s, 2H, PhCH_2), 4.38-4.32 (m, 1H, CHOH), 3.94 (s, 2H, BnOCH_2), 3.32 (dd, 1H, $J = 9.4$ and 4.4 Hz, CHHOTr), 3.24 (dd, 1H, $J = 9.4$ and 7.1 Hz, CHHOTr), 2.71 (d, 1H, $J = 4.6$ Hz, OH); ^{13}C NMR (CDCl_3 , 75 MHz): δ_{ppm} 144.5, 143.8 (3C), 137.9, 128.7 (6C), 128.4 (2C), 127.9 (6C), 127.7, (2C), 127.6, 127.1 (3C), 114.9, 86.8, 72.6, 72.3, 71.3, 66.7. Anal. Calc. for $\text{C}_{31}\text{H}_{30}\text{O}_3$ C, 82.64; H, 6.71. Found: C, 82.73; H, 6.78.

2-([*tert*-butyl(dimethyl)silyl]oxy)methyl)-1-penten-3-ol **5 and 1-([*tert*-butyl(dimethyl)silyl]oxy)-3-ethyl-3-buten-2-ol **6****

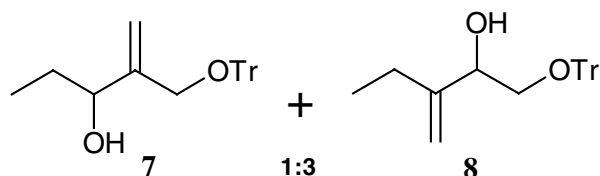


Purification yielded two colourless oils in ratio 1:2 (based on crude NMR):

5 (24% yield): ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 5.10 (s, 1H, $\text{C}=\text{CHH}$) 5.05 (s, 1H, $\text{C}=\text{CHH}$), 4.30 (d, 1H, $J = 13.1$, CHHO), 4.19 (d, 1H, $J = 13.1$ Hz, CHHO), 4.08 (dt, 1H, $J = 5.4$ and 6.0 Hz, CHOH), 2.43 (d, 1H, $J = 5.4$ Hz, OH), 1.65 (app. quintet, 2H, $J = 7.3$ Hz, CH_2CH_3), 0.91 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.85 (t, 3H, $J = 6.4$ Hz, CH_3), 0.09 (s, 6H, $\text{Si}(\text{CH}_3)_2$; ^{13}C NMR (CDCl_3 , 100 MHz): δ_{ppm} 149.2, 111.3, 75.7, 64.5, 28.5, 25.8(3C), 18.2, 10.0, -5.5(2C). Anal. Calc. for $\text{C}_{12}\text{H}_{26}\text{O}_2$ Si C, 62.55; H, 11.37. Found: C, 62.76; H, 11.25.

6 (53% yield): ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 5.10 (s, 1H, $\text{C}=\text{CHH}$), 4.92 (s, 1H, $\text{C}=\text{CHH}$), 4.14 (dt, 1H, $J = 8.2$ and 4.1 Hz, CHOH), 3.70 (dd, 1H, $J = 10.0$ and 3.5 Hz, CHHCHOH), 3.46 (dd, 1H, $J = 10.0$ and 8.3 Hz, CHHCHOH), 2.64 (d, 1H, $J = 2.9$ Hz, OH), 2.18-1.95 (m, 2H, CH_2CH_3), 0.91 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.85 (t, 3H, $J = 6.3$ Hz, CH_3), 0.10 (s, 3H, SiCH_3), 0.08 (s, 3H, SiCH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ_{ppm} 150.8, 108.5, 74.1, 68.7, 25.0, 25.8(3C), 18.3, 12.7, -5.5(2C). Anal. Calc. for $\text{C}_{12}\text{H}_{26}\text{O}_2$ Si C, 62.55; H, 11.37. Found: C, 62.5; H, 11.36.

2-([trityloxy]methyl)-1-penten-3-ol (7**) and 3-ethyl-1-(trityloxy)-3-buten-2-ol **8****



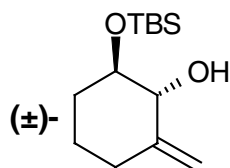
Purification yielded two colourless oils in ratio 1:3 (based on crude NMR):

7 (20 yield%): ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 7.47 (d, 6H, $J = 10$ Hz, Ar-H), 7.33-7.22 (m, 9H, Ar-H), 5.30 (d, 1H, $J = 1.3$ Hz, $\text{C}=\text{CHH}$), 5.17 (s, 1H, $\text{C}=\text{CHH}$), 4.05 (dt, 1H, $J = 5.0$ and 6.0 Hz, CHOH), 3.69 (bs, 2H, CH_2OTr), 2.07 (d, 1H, $J = 5.0$ Hz, OH), 1.47 (apparent quin, 2H, $J = 7.4$ Hz, CH_2CH_3), 0.84 (t, 3H, $J = 7.4$ Hz,

CH₃); ¹³C NMR (CDCl₃, 75.4 Hz): δ_{ppm} 147.9, 143.8 (3C), 128.6 (6C), 127.9 (6C), 127.1 (3C), 112.4, 87.3, 75.5, 64.9, 28.4, 9.9. Anal. Calc. for C₂₅H₂₆O₂ C, 83.76; H, 7.31. Found: C, 83.54; H, 7.45.

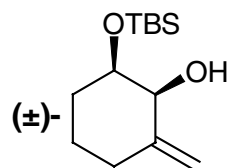
8 (57 yield%): ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 7.45 (d, 6H, *J* = 10 Hz, Ar-H) 7.34-7.24 (m, 9H, Ar-H), 5.06 (s, 1H, C=CHH), 4.88 (s, 1H, C=CHH), 4.18 (dt, 1H, *J* = 7.7 and 3.5 Hz, CHOH), 3.27 (dd, 1H, *J* = 9.6 and 3.7 Hz, CHHOTr), 3.15 (dd, 1H, *J* = 9.6 and 7.7 Hz, CHHOTr), 2.45 (d, 1H, *J* = 3.5 Hz, OH), 2.02-1.78 (m, 2H, CH₂CH₃), 0.97 (t, 3H, *J* = 7.4 Hz, CH₃); ¹³C NMR (CDCl₃, 75.4 MHz): δ_{ppm} 149.8, 143.9 (3C), 128.6 (6C), 127.9 (6C), 127.1 (3C), 109.6, 86.9, 73.9, 67.1, 25.0, 12.1. Anal. Calc. for C₂₅H₂₆O₂ C, 83.76; H, 7.31. Found: C, 83.63; H, 7.28.

2-[[*tert*-butyl(dimethyl)silyl]oxy]-6-methylenecyclohexanol



Purification yielded a pale yellow oil; 80% yield; ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 5.06 (q, 1H, *J* = 1.8 Hz, C=CHH), 4.83 (q, 1H, *J* = 1.8 Hz, C=CHH), 3.84 (dd, 1H, *J* = 1.8 and 8.5 Hz, CHOH), 3.32 (ddd, 1H, *J* = 4.4, 8.5 and 10.4 Hz, CHOSi), 2.52 (d, 1H, *J* = 1.8 Hz, OH), 2.36-2.28 (m, 1H, CH₂), 2.04-1.98 (m, 1H, CH₂), 1.96-1.87 (m, 1H, CH₂), 1.78-1.69 (m, 1H, CH₂), 1.53-1.40 (m, 1H, CH₂CHHCH₂), 1.36-1.21 (m, 1H, CH₂CHHCH₂), 0.91 (s, 9H, C(CH₃)₃), 0.11 (s, 3H, SiCH₃), 0.09 (s, 3H, SiCH₃); ¹³C NMR (CDCl₃, 75.4 MHz): δ_{ppm} 146.8, 106.4, 77.6, 77.5, 33.7, 33.5, 25.8(3C), 24.3, 18.0, -4.2, -4.4. HRMS Calcd. for C₁₃H₂₇O₂ Si *m/z* 243.1780, found: 243.1796.

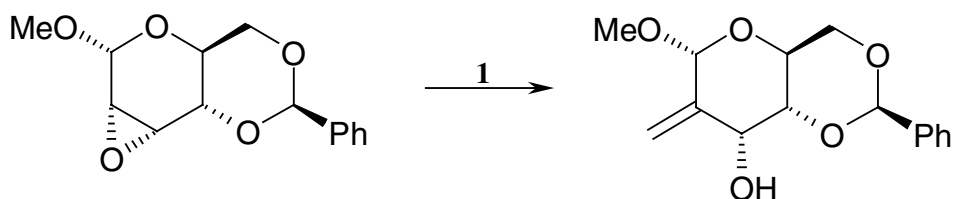
2-[[*tert*-butyl(dimethyl)silyl]oxy]-6-methylenecyclohexanol



Pale yellow oil; 71% yield; ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 4.94 (s, 1H, C=CHH), 4.86 (s, 1H, C=CHH), 4.02 (app t, 1H, *J* = 4.0 Hz, CHOH), 3.78 (dt, 1H, *J* = 8.3 and 3.8 Hz, SiOCH), 2.40 (d, 1H, *J* = 4.4 Hz, OH), 2.36-2.28 (m, 1H, CHHC=CH₂), 2.02 (dt, 1H, *J* = 5.4 and 13.6 Hz, CHHC=CH₂), 1.80-1.65 (m, 2H, CH₂), 1.63-1.56 (m, 1H, CH₂CHHCH₂), 1.36-1.28 (m, 1H, CH₂CHHCH₂), 0.90 (s, 9H, C(CH₃)₃), 0.08 (d, 6H, *J* = 3.1 Hz, Si(CH₃)₂); ¹³C NMR (CDCl₃, 100 MHz): δ_{ppm} 147.8, 110.5, 75.1, 73.3, 30.8, 30.0, 25.7(3C), 23.1, 18.1, -4.2, -4.4. HRMS Calcd. for C₁₃H₂₇O₂ Si *m/z* 243.1780, found: 243.1766.

Relevant signals for the TBS migrated compound (5 to 10 % unseparable): ^1H NMR (300 MHz, CDCl_3): δ_{ppm} 4.92 (s, 1H, $\text{C}=\text{CHH}$), 4.84 (s, 1H, $\text{C}=\text{CHH}$), 4.14 (d, 1H, $J = 3.0$ Hz, SiOCH), 3.78 (app sept, 1H, $J = 3.0$ Hz, CHOH), 2.20 (d, 1H, $J = 6.0$ Hz, OH); ^{13}C NMR (CDCl_3 , 100 MHz): δ_{ppm} 147.8, 109.8, 75.8, 72.4, 31.6, 30.1, 25.7(3C), 22.9, 18.1, -4.2, -4.4.

α -L-*ribo*-hexopyranoside, methyl 2-deoxy-2-methylene-4,6-O-(phenylmethylene)



Thick oil; 91% yield; $[\alpha]_{\text{D}}^{27} +62.4^\circ$ (c 0.23, CHCl_3); ^1H NMR (300 MHz, CD_3OD): δ_{ppm} 7.55-7.51 (m, 2H, Ar-H), 7.38-7.33 (m, 3H, Ar-H), 5.66 (s, 1H, CHPh), 5.33 (d, 1H, $J = 1.0$ Hz, $\text{C}=\text{CHH}$), 5.27 (d, 1H, $J = 1.0$ Hz, $\text{C}=\text{CHH}$), 5.00 (s, 1H, CHOCH_3), 4.49 (d, 1H, $J = 3.1$ Hz, CHOH), 4.33-4.27 (m, 2H, CHCH_2 and CHH_{eq}), 3.75 (app t, 1H, $J = 11.8$ Hz, CHH_{ax}), 3.63 (dd, 1H, $J = 3.1$ and 9.0 Hz, CHCHOH), 3.42 (s, 3H, OCH_3); ^{13}C NMR (CDCl_3 , 75 MHz): δ_{ppm} 144.1, 139.3, 130.0, 129.1(2C), 127.7(2C), 119.5, 103.4, 103.2, 82.0, 71.8, 70.4, 59.3, 55.4. HRMS Calcd. for $\text{C}_{15}\text{H}_{19}\text{O}_5$ m/z 279.1232, found: 279.1238.

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