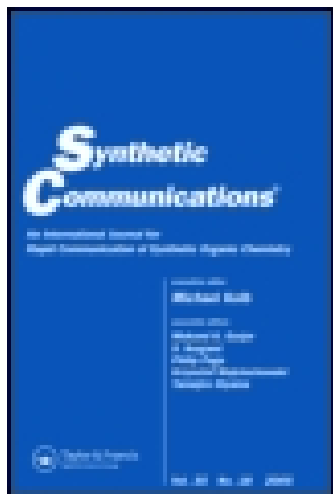


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## CONVENIENT SYNTHESIS OF MONOPROTECTED 1,2-DIOLS

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**Abstract:** Reaction of the protected glycidol derivatives (1A-C) with a wide variety of Grignard reagents (2a-h) in the presence of catalytic amount of CuCN provided the corresponding monoprotected diol derivatives (3) in a highly regioselective manner.

1,2-Diols either in racemic or in enantiomerically pure form are important structural units or synthetic building blocks for numerous biologically active natural or synthetic compounds, and for this reason, they are subject of many recent interests. In the course of our investigations on biocatalytic enantiomer-separation of diverse 1,2-diol derivatives, e.g. 1,2-diol diacetates<sup>1</sup>, a need for a general synthetic procedure for the production of such compounds was recognised.

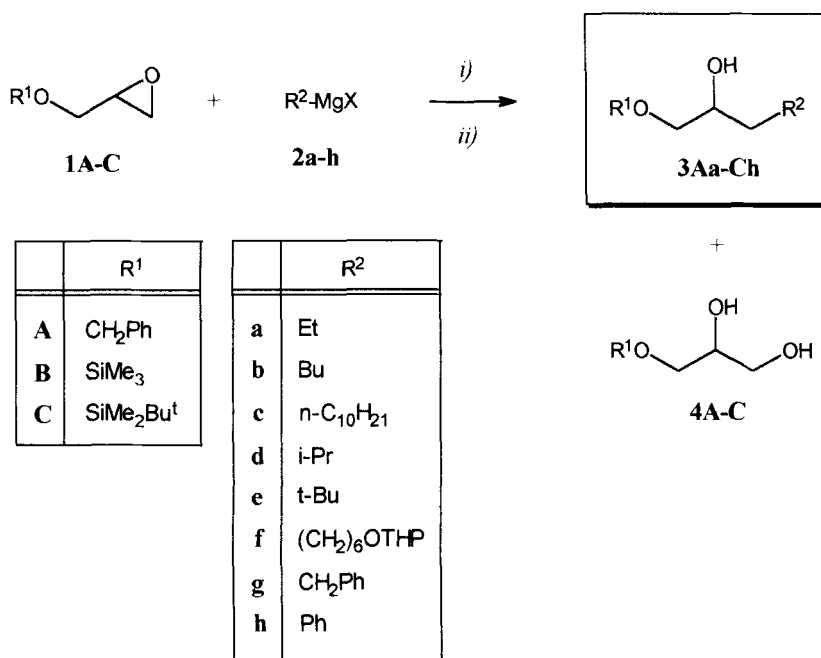
The utility of Grignard reagents for oxirane ring-opening reactions is well known<sup>2</sup>. Ring-opening reaction of oxirane with Grignard reagents in absence<sup>3</sup> or in presence of CuI catalyst<sup>4</sup> was used for two carbon chain elongation. Similar ring-opening reaction of methyloxirane<sup>5</sup> in the presence of CuCN proceeded regioselectively, the oxirane ring was attacked predominantly from the

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unsubstituted side. Grignard reagents, mostly in the presence of Cu(I) salt catalysts, opened the oxirane ring of alkyloxiranes<sup>6</sup>, vinyloxiranes<sup>7</sup>,  $\beta$ -epoxi-sulphones, -sulphoxides or esters<sup>8</sup> or dianhydro sugars<sup>9</sup> also in a regioselective manner. Although, scattered examples for reaction of Grignard reagents with enantiomers of benzyl glycidyl ether (**1A**) exist<sup>10</sup>, usefulness and generality of ring opening reaction of protected glycidol derivatives with Grignard reagents for preparation of 1,2-diol derivatives has not been systematically studied.

It was our aim, therefore, to investigate the applicability of the ring opening reaction of various protected glycidol derivatives (**1A-C**) with a selection of Grignard reagents (**2a-h**) yielding the corresponding monoprotected diols (**3**).



Conditions: *i.*) cat. CuCN, ether type solvent; *ii.*) saturated NH<sub>4</sub>Cl  
(for details see Table and Experimental)

Benzyl-, trimethylsilyl-, and *tert*-butyldimethylsilyl derivatives of glycidol (**1A-C**, respectively); and Grignard reagents prepared from primary alkyl halides of different lengths, secondary and tertiary alkyl halides, phenyl and benzyl halides, or  $\omega$ -functionalized alkyl halide (**2a-h**, respectively) were chosen as reaction partners in the present study.

First, the reaction between (*tert*-butyldimethylsilyloxy)methyl oxirane (**1C**) and butylmagnesium bromide (**2b**) (Table, Entries 18-23) was chosen as a typical probe on which effects of solvent, temperature, and amount of CuCN catalyst were examined. It was found that the reaction can be conveniently carried out in ether type solvents in the presence of catalytic amount of CuCN at -15°C within 15 min.

Diethyl ether, tetrahydrofuran and 2-methyltetrahydrofuran were investigated as solvents (Entries 18, 19 and 23, respectively). The desired diol derivative (**3Cb**) was obtained in all three solvents in satisfactory yield. The reaction in diethylether (Entry 18), however, gave a slightly lower yield and more diol byproduct (**4C**). Considering yield, cost, safety, and extractability from water 2-methyl-tetrahydrofuran was chosen as solvent. Next, the effect of amount of CuCN catalyst was studied in tetrahydrofuran at -15°C (Entries 19-21). It was concluded that CuCN should be applied in catalytic (ca. 2 mole%) amount (Entry 19); reactions either in the presence of higher amount of CuCN (Entry 21, 25 mole%) or in the absence of CuCN (Entry 20) gave disappointing results: i.e. much slower reaction and appearance of diverse unidentified byproducts were observed in both cases. Finally, the reaction was carried out at higher temperature (0°C to RT for 2 h, Entry 22) but under this condition a reasonable proportion of ring cleavage product diol (**4C**) was produced parallel with a significant drop in yield of the desired diol derivative (**3Cb**). Consequently, reaction in 2-methyltetrahydrofuran in the presence of 2 mole% CuCN at -15°C for 15 min was chosen as general method for further study with protected glycidol derivatives (**1A-C**) and Grignard reagents (**2a-h**).

Each reaction in the present study performed between glycidol derivatives (**1A-C**) and several Grignard reagents (**2a-h**) (see Table) proved to be highly regioselective, a regioisomeric product arising from attack at the carbon of the oxirane ring bearing substituent was never isolated or detected. A concomitant formation of the corresponding diol byproduct (**4A-C**), however, was observed in the majority of the cases, even if the reaction was conducted under strictly water-free conditions. Our preliminary investigations showed that the relative amount of the diols can be reduced by lowering the temperature from RT or 0°C to -15°C, hence, most of the reactions were investigated at this temperature. Results of ring cleavage reactions of the glycidol derivatives (**1A-C**) with Grignard reagents (**2a-h**) indicate (see Table) that the process is more influenced by the nature of the Grignard reagent and much less sensitive to the kind of protecting group in the glycidol derivative. These reactions seem to be widely applicable, since ring opening with short, medium or long primary alkylmagnesium bromides (**2a, b, c**; Entries 1-3, 9-11, 17-24; respectively) as well as with secondary or tertiary alkylmagnesium halides (**2d, e**; Entries 4,5; 12,13; 25,26; respectively) proceeded with satisfactory to good yields. In the case of the reactions with isopropylmagnesium bromide (**2d**, Entries 4, 12 and 25), however, higher temperature and prolonged time (0°C to RT, 2 h) was needed to obtain

Table: Reaction of protected glycidol derivatives (1) with Grignard reagents (2)

Entry	1	2	(X)	Conditions <sup>a</sup>			3 (4) <sup>b</sup> Yield (%)
				(solvent <sup>c</sup> ;	CuCN [equiv.];	temp., time.)	
1	A	a	Br	Me-THF	0.02	-15°C, 15 min	89
2	A	b	Br	Me-THF	0.02	-15°C, 15 min	87(5)
3	A	c	Br	Me-THF	0.02	-15°C, 15 min	80(9)
4	A	d	Br	Me-THF	0.02	-15°C-RT, 120 min	44(46)
5	A	e	Cl	Me-THF	0.02	-15°C, 15 min	61(20)
6	A	f	Br	Me-THF	0.02	-15°C-RT, 120 min	65(6) <sup>d</sup>
7	A	g	Cl	Me-THF	0.02	-15°C, 15 min	88(3)
8	A	h	Br	Me-THF	0.02	-15°C, 15 min	85(4)
9	B	a	Br	Me-THF	0.02	-15°C, 15 min	83
10	B	b	Br	Me-THF	0.02	-15°C, 15 min	82(7)
11	B	c	Br	Me-THF	0.02	-15°C, 15 min	71(9)
12	B	d	Br	Me-THF	0.02	-15°C-RT, 120 min	57(24)
13	B	e	Cl	Me-THF	0.02	-15°C, 15 min	58(19)
14	B	f	Br	Me-THF	0.02	-15°C to RT, 60 min	59(13) <sup>d</sup>
15	B	g	Cl	Me-THF	0.02	-15°C, 15 min	87
16	B	h	Br	Me-THF	0.02	-15°C, 15 min	88
17	C	a	Br	Me-THF	0.02	-15°C, 15 min	93
18	C	b	Br	Et <sub>2</sub> O	0.02	-15°C, 15 min	75(12)
19	C	b	Br	THF	0.02	-15°C, 15 min	88
20	C	b	Br	THF	0	-15°C, 15 min	<sup>e</sup>
21	C	b	Br	THF	0.25	-15°C, 15 min	<sup>e</sup>
22	C	b	Br	THF	0.02	0°C-RT, 120 min	54(38)
23	C	b	Br	Me-THF	0.02	-15°C, 15 min	92
24	C	c	Br	Me-THF	0.02	-15°C, 15 min	79(12)
25	C	d	Br	Me-THF	0.02	-15°C-RT, 120 min	62(29)
26	C	e	Cl	Me-THF	0.02	-15°C, 15 min	65(18)
27	C	f	Br	Me-THF	0.02	-15°C-RT, 120 min	63(9) <sup>f</sup>
28	C	g	Cl	Me-THF	0.02	-15°C, 15 min	89
29	C	h	Br	Me-THF	0.02	-15°C, 15 min	91

<sup>a</sup> For details on preparation of Grignard reagents and reaction conditions see Experimental.

<sup>b</sup> Isolated yields of product(s) separated by chromatography on silica gel. Yield of diol 4 is given between brackets. Single number indicates that no diol (4) was isolated. <sup>c</sup> Me-THF: 2-methyltetrahydrofuran. <sup>d</sup> Beside a minor amount of diol (4) further unidentified byproducts were observed. <sup>e</sup> TLC investigation of the raw product revealed rather low conversion and presence of unidentified byproducts.

satisfactory yields. Similarly good results were achieved in reactions with phenyl- or benzylmagnesium halides (**2g, h**; Entries 7,8; 15,16 and 28,29; respectively). The reactions of glycidol derivatives (**1A-C**) with a Grignard reagent prepared from 1-bromo-6-(2-tetrahydropyranyl)oxy-hexane (**2f**) (Entries 6, 14, 27) affording skeletons functionalized at both ends further illustrate the synthetic usefulness of this process. In reactions with Grignard compound **2f** a prolonged reaction time and higher temperature (-15°C to RT, 2 h) were also required for acceptable yield.

In summary, the highly regioselective ring opening reaction between Grignard reagents (**2a-h**) and protected glycidol derivatives (**1A-C**) proved to be generally applicable yielding 1,2-diol derivatives protected at the primary hydroxyl group (**3Aa-Ch**). These products may conveniently be manipulated further at the free secondary hydroxyl moiety or may provide the corresponding 1,2-diols after deprotection.

## EXPERIMENTAL

NMR spectra were measured on Bruker AW-80 or Varian VXR 400 spectrometers operating at 80 and 400 MHz for <sup>1</sup>H and 101 MHz for <sup>13</sup>C in CDCl<sub>3</sub> containing TMS as internal standard. IR spectra (ν, film) were recorded on a Spekord IR 20M spectrometer. GLC chromatography was performed on a HP 5890 Series II gas chromatograph equipped with a HP-1 25 m x 0.20 mm, 0.20 μm column and FID (V<sub>hydrogen</sub> = 1.6 ml/min, t<sub>i</sub> = 140°C, t<sub>d</sub> = 230°C, 100°C: 1 min, 100-200°C: 5°C/min). Preparative vacuum-chromatography<sup>11</sup> was carried out using Merck Kieselgel 60 (60-200 μm). All isolated products were homogenous by TLC on Merck Kieselgel 60 F<sub>254</sub> plates and gave satisfactory elemental analysis (C,H) data. Halogen compounds for Grignard reagents **2a-e,g,h** were commercial products from Fluka or Aldrich. Magnesium and 1,2-dibromoethane were supplied by Merck. The protected glycidol derivatives (**1A-C**) and bromide for Grignard reagent **2f** were prepared by known procedures. Dry diethyl ether was obtained from Fluka, tetrahydrofuran and 2-methyltetrahydrofuran were freshly distilled from LiAlH<sub>4</sub> and stabilized with 2,6-di-*tert*-butyl-*p*-cresol.

### *General procedure for ring cleavage of glycidol derivatives by Grignard reagents*

*A) Preparation of Grignard reagents:* A four necked flask containing Mg (0.6 g, 25 mmol) and small pieces of I<sub>2</sub> was flamed out by a burner, connected to a dry reflux condenser and cooled down under a slight positive pressure of nitrogen. After cooling, the flask was equipped with a dropping funnel filled with a solution of halogen compound (25 mmol) in 15 ml of solvent indicated in Table and with a second dropping funnel containing 25 ml of pure solvent. A small portion (2-3 ml) of solvent followed by 0.1 ml of 1,2-dibromoethane were introduced into the flask, and after the gas evolution was ceased, pure solvent and solution of the halide were dropped simultaneously. The Grignard reactions were performed at the boiling point of the lowest boiling component or at 50-55°C for 45 min.

*B) Ring cleavage of glycidol derivatives (1A-C) by Grignard reagents (2a-h):* To the resulting solution of the Grignard reagent (2), CuCN catalyst (amount indicated in Table) was added at 0°C followed by addition of a solution of the corresponding glycidol derivative (1, 20 mmol) in 15 ml of solvent (for temperature and reaction time see Table). The reaction mixture was worked up by pouring into 40 ml of saturated NH<sub>4</sub>Cl solution IR: 3300-3750, 3030, 3000, 2935, 1470, 1245, 1090, 845, 805, 710 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.11 (s, 9H, SiCH<sub>3</sub>), 0.87 (t, 3H, CH<sub>3</sub>), 1.23-1.50 (br m, 8H, 4CH<sub>2</sub>), 3.34 and 3.58 (mc, 2x1H, OCH<sub>2</sub>), 3.62 (m, 1H, O-CH).

*1-Trimethylsilyloxytridecan-2-ol (3Bc)*

IR: 3300-3750, 3030, 3000, 2935, 1470, 1245, 1090, 845, 805, 705 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.10 (s, 9H, SiCH<sub>3</sub>), 0.87 (t, 3H, CH<sub>3</sub>), 1.28 (mc, 18H, 9 CH<sub>2</sub>), 1.43 (m, 2H, CH<sub>2</sub>), 3.35 and 3.60 (mc, 2x1H, OCH<sub>2</sub>), 3.62 (m, 1H, OCH).

*1-Trimethylsilyloxy-4-methylpentan-2-ol (3Bd)*

IR: 3350-3750, 3030, 3000, 2925, 1470, 1370, 1250, 1100, 810 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.09 (s, 9H, SiCH<sub>3</sub>), 0.94 (d, 6H, 2 CH<sub>3</sub>), 1.14 and 1.41 (mc, 2x1H, CH<sub>2</sub>-Pr<sup>i</sup>), 1.73 (mc, 1H, CH), 3.35 and 3.61 (mc, 2x1H, CH<sub>2</sub>-O), 3.71 (mc, 1H, CH-O).

*1-Trimethylsilyloxy-4,4-dimethylpentan-2-ol (3Be)*

IR: 3350-3750, 3030, 3000, 2905, 1465, 1370, 1250, 1100, 805 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.06 (s, 6H, SiCH<sub>3</sub>), 0.89 (s, 9H, SiCCH<sub>3</sub>), 0.95 (s, 9H, CCH<sub>3</sub>), 1.17 and 1.32 (mc, 2x1H, CH<sub>2</sub>-Bu<sup>t</sup>), 3.30 and 3.50 (mc, 2x1H, SiOCH<sub>2</sub>), 3.75 (mc, 1H, CH-OH).

*1-Trimethylsilyloxy-9-(tetrahydro-2H-pyran-2-yloxy)nonan-2-ol (3Bf)*

IR: 3750-3350, 3010, 2990, 2920, 1470, 1360, 1100, 1060, 1005, 805, 750 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.13 (s, 9H, SiCH<sub>3</sub>), 1.30-1.65 (m, 16H, 8CH<sub>2</sub>), 1.70 and 1.83 (mc, 2x1H, CH<sub>2</sub>), 3.37 and 3.49 (mc, 2x1H, CH<sub>2</sub>O), 3.35 and 3.58 (mc, 2x1H, CH<sub>2</sub>O), 3.63 (mc, 1H, CH-O), 3.73 and 3.87 (mc, 2x1H, CH<sub>2</sub>O), 4.57 (mc, 1H, OCHO).

*1-Trimethylsilyloxy-4-phenylbutan-2-ol (3Bg)*

IR: 3300-3750, 3175, 3155, 3105, 3025, 2990, 2920, 1510, 1490, 1455, 1385, 1355, 1240, 1095, 805 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.11 (s, 9H, 2 SiCH<sub>3</sub>), 1.71 (mc, 2H, CH<sub>2</sub>Ph), 2.68 and 2.81 (mc, 2x1H CH<sub>2</sub>-CH<sub>2</sub>Ph), 3.40 and 3.59 (mc, 2x1H, CH<sub>2</sub>-O), 3.64 (mc, 1H, CH-O), 7.15-7.35 (m, 5H, ArH).

*1-Trimethylsilyloxy-3-phenylpropan-2-ol (3Bh)*

IR: 3300-3750, 3195, 3160, 3115, 3040, 3005, 2930, 1470, 1250, 1100, 810 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.06 (br s, 6H, 2SiCH<sub>3</sub>), 0.89 (s, 9H, SiC(CH<sub>3</sub>)), 2.77 (dd, 2H, CH<sub>2</sub>Ph), 3.46 and 3.60 (mc, 2x1H, OCH<sub>2</sub>), 3.85 (mc, 1H, CH-OH), 7.15-7.35 (m, 5H ArH).

*1-(tert-Butyl-dimethylsilyloxy)pentan-2-ol (3Ca)*

GLC: t<sub>R</sub> = 1.28 min; IR: 3300-3750, 3035, 3000, 2940, 1470, 1370, 1250, 1090, 845, 805 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.05 (s, 6H, SiCH<sub>3</sub>), 0.88 (s, 9H, SiCCH<sub>3</sub>), 0.91 (t, 3H, CH<sub>3</sub>), 1.28-1.53 (m, 4H, 2CH<sub>2</sub>), 3.36 and 3.59 (mc, 2x1H, OCH<sub>2</sub>), 3.63 (m, 1H, OCH); <sup>13</sup>C-NMR: -5.34 (SiCH<sub>3</sub>), -5.40 (SiCH<sub>3</sub>), 14.16 (CH<sub>3</sub>), 18.30 (SiC(CH<sub>3</sub>)), 18.81 (CH<sub>2</sub>), 25.89 (SiC(CH<sub>3</sub>)), 34.93 (CH<sub>2</sub>), 67.32 (OCH<sub>2</sub>), 71.56 (OCH).

*1-(tert-Butyl-dimethylsilyloxy)heptan-2-ol (3Cb)*

GLC: t<sub>R</sub> = 2.43 min; IR: 3300-3750, 3035, 3000, 2935, 1475, 1250, 1090, 810, 750 cm<sup>-1</sup>, <sup>1</sup>H-NMR: 0.06 (s, 6H, SiCH<sub>3</sub>), 0.87 (t, 3H, CH<sub>3</sub>), 0.88 (s, 9H, SiCCH<sub>3</sub>), 1.28 (mc 6H, 3CH<sub>2</sub>), 1.40 (m, 2H, CH<sub>2</sub>), 3.37 and 3.60 (mc, 2x1H, OCH<sub>2</sub>), 3.62 (m, 1H, OCH); <sup>13</sup>C-NMR: -5.32 (SiCH<sub>3</sub>), -5.38 (SiCH<sub>3</sub>), 14.06 (CH<sub>3</sub>), 18.31 (SiC(CH<sub>3</sub>)), 22.62 (CH<sub>2</sub>), 25.29 (CH<sub>2</sub>), 25.90 (SiC(CH<sub>3</sub>)), 31.97 (CH<sub>2</sub>), 32.79 (CH<sub>2</sub>), 67.31 (OCH<sub>2</sub>), 71.87 (OCH).



*1-(tert-Butyl-dimethylsilyloxy)tridecan-2-ol (3Cc)*

GLC:  $t_R$  = 11.05 min; IR: 3300-3750, 3035, 3000, 2940, 1470, 1250, 1090, 815  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$ : 0.07 (s, 6H,  $\text{SiCH}_3$ ), 0.88 (t, 3H,  $\text{CH}_3$ ), 0.90 (s, 9H,  $\text{SiCCH}_3$ ), 1.27 (mc, 18H, 9  $\text{CH}_2$ ), 1.43 (m, 2H,  $\text{CH}_2$ ), 3.38 and 3.61 (mc, 2x1H,  $\text{OCH}_2$ ), 3.62 (m, 1H,  $\text{OCH}$ );  $^{13}\text{C-NMR}$ : -5.33 ( $\text{SiCH}_3$ ), -5.39 ( $\text{SiCH}_3$ ), 14.13 ( $\text{CH}_3$ ), 18.30 ( $\text{SiC}(\text{CH}_3)_3$ ), 22.71 and 25.61 ( $2\text{CH}_2$ ), 25.89 ( $\text{SiC}(\text{CH}_3)_3$ ), 25.90, 29.37, 29.60, 29.62, 29.65, 29.68 and 29.77 (8  $\text{CH}_2$ ), 67.31 ( $\text{OCH}_2$ ), 71.86 ( $\text{OCH}$ ).

*1-(tert-Butyl-dimethylsilyloxy)-4-methylpentan-2-ol (3Cd)*

GLC:  $t_R$  = 1.50 min; IR: 3300-3750, 3035, 3000, 2940, 1470, 1375, 1250, 1090, 815  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$ : 0.08 (s, 6H,  $\text{SiCH}_3$ ), 0.89 (s, 9H,  $\text{SiCCH}_3$ ), 0.93 (d, 6H,  $2\text{CH}_3$ ), 1.14 and 1.38 (mc, 2x1H,  $\text{CH}_2$ ), 1.79 (m, 1H,  $\text{CH}$ ), 3.36 and 3.60 (mc, 2x1H,  $\text{OCH}_2$ ), 3.72 (m, 1H,  $\text{OCH}$ );  $^{13}\text{C-NMR}$ : -5.32 ( $\text{SiCH}_3$ ), -5.39 ( $\text{SiCH}_3$ ), 18.31 ( $\text{SiC}(\text{CH}_3)_3$ ), 22.21 ( $\text{CH}_3$ ), 23.45 ( $\text{CH}_3$ ), 24.56 ( $\text{CH}$ ), 25.90 ( $\text{SiC}(\text{CH}_3)_3$ ), 41.78 ( $\text{CH}_2\text{-Pr}^1$ ), 67.71 ( $\text{CH}_2\text{O}$ ), 69.97 ( $\text{CH-O}$ ).

*1-(tert-Butyl-dimethylsilyloxy)-4,4-dimethylpentan-2-ol (3Ce)*

GLC:  $t_R$  = 1.70 min; IR: 3350-3750, 3030, 3000, 2925, 1470, 1370, 1250, 1100, 805, 750  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$ : 0.06 (s, 6H,  $\text{SiCH}_3$ ), 0.89 (s, 9H,  $\text{SiCCH}_3$ ), 0.95 (s, 9H,  $\text{CCH}_3$ ), 1.17 and 1.32 (mc, 2x1H,  $\text{CH}_2\text{-Bu}^1$ ), 3.30 and 3.50 (mc, 2x1H,  $\text{SiOCH}_2$ ), 3.75 (mc, 1H,  $\text{CH-OH}$ );  $^{13}\text{C-NMR}$ : -5.30 ( $\text{SiCH}_3$ ), -5.37 ( $\text{SiCH}_3$ ), 18.30 ( $\text{SiC}(\text{CH}_3)_3$ ), 25.91 ( $\text{SiC}(\text{CH}_3)_3$ ), 30.04 ( $\text{CH}_2\text{C}(\text{CH}_3)_3$ ), 30.07 ( $\text{C}(\text{CH}_3)_3$ ), 46.20 ( $\text{CH}_2\text{-Bu}^1$ ), 68.38 ( $\text{CH}_2\text{O}$ ), 69.39 ( $\text{CH-O}$ ).

*1-(tert-Butyl-dimethylsilyloxy)-9-(tetrahydro-2H-pyran-2-yloxy)nonan-2-ol (3Cf)*

GLC:  $t_R$  = 15.84 min; IR: 3750-3350, 3025, 3010, 2940, 1470, 1450, 1375, 1360, 1260, 1110, 1065, 1015, 805, 750  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$ : 0.08 (s, 6H,  $\text{SiCH}_3$ ), 0.90 (s, 9H,  $\text{SiCCH}_3$ ), 1.35-1.65 (m, 16H, 8 $\text{CH}_2$ ), 1.70 and 1.83 (mc, 2x1H,  $\text{CH}_2$ ), 3.37 and 3.50 (mc, 2x1H,  $\text{CH}_2\text{O}$ ), 3.38 and 3.62 (mc, 2x1H,  $\text{CH}_2\text{O}$ ), 3.63 (mc, 1H,  $\text{CH-O}$ ), 3.73 and 3.87 (mc, 2x1H,  $\text{CH}_2\text{O}$ ), 4.57 (mc, 1H,  $\text{OCHO}$ );  $^{13}\text{C-NMR}$ : -5.32 ( $\text{SiCH}_3$ ), -5.38 ( $\text{SiCH}_3$ ), 18.30 ( $\text{SiC}(\text{CH}_3)_3$ ), 19.70, 25.51, 25.54 (3 $\text{CH}_2$ ), 25.90 ( $\text{SiC}(\text{CH}_3)_3$ ), 26.19, 29.41, 29.67, 29.74, 30.79, 32.79 (6 $\text{CH}_2$ ), 62.32, 67.30, 67.64 (3 $\text{CH}_2\text{-O}$ ), 71.82 ( $\text{CH-O}$ ), 98.83 ( $\text{OCHO}$ ).

*1-(tert-Butyl-dimethylsilyloxy)-4-phenylbutan-2-ol (3Cg)*

GLC:  $t_R$  = 7.04 min; IR: 3300-3750, 3175, 3155, 3105, 3025, 2990, 2920, 1610, 1490, 1455, 1385, 1355, 1240, 1095, 805, 740  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$ : 0.06 (br s, 6H, 2  $\text{SiCH}_3$ ), 0.89 (s, 9H,  $\text{CCH}_3$ ), 1.71 (mc, 2H,  $\text{CH}_2\text{Ph}$ ), 2.67 and 2.81 (mc, 2x1H  $\text{CH}_2\text{-CH}_2\text{Ph}$ ), 3.42 and 3.61 (mc, 2x1H,  $\text{CH}_2\text{-O}$ ), 3.64 (mc, 1H,  $\text{CH-O}$ ), 7.15-7.32 (m, 5H,  $\text{ArH}$ );  $^{13}\text{C-NMR}$ : -5.33 ( $\text{SiCH}_3$ ), -5.39 ( $\text{SiCH}_3$ ), 18.30 ( $\text{SiC}(\text{CH}_3)_3$ ), 25.90 ( $\text{SiC}(\text{CH}_3)_3$ ), 31.87 ( $\text{CH}_2$ ), 34.52 ( $\text{CH}_2$ ), 67.19 ( $\text{CH}_2\text{O}$ ), 71.07 ( $\text{CH-O}$ ), 125.80 ( $\text{ArC}$ ), 128.36 ( $\text{ArC}$ ), 128.45 ( $\text{ArC}$ ), 142.07 ( $\text{ArC-CH}_2$ ).

*1-(tert-Butyl-dimethylsilyloxy)-3-phenylpropan-2-ol (3Ch)*

GLC:  $t_R$  = 5.28 min; IR: 3300-3750, 3195, 3160, 3115, 3030, 3005, 2930, 1500, 1480, 1465, 1250, 1100, 810, 750  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$ : 0.06 (br s, 6H, 2 $\text{SiCH}_3$ ), 0.89 (s, 9H,  $\text{SiC}(\text{CH}_3)_3$ ), 2.77 (dd, 2H,  $\text{CH}_2\text{Ph}$ ), 3.47 and 3.60 (mc, 2x1H,  $\text{OCH}_2$ ), 3.88 (mc, 1H,  $\text{CH-OH}$ ), 7.18-7.34 (m, 5H  $\text{ArH}$ );  $^{13}\text{C-NMR}$ : -5.35 ( $\text{SiCH}_3$ ), -5.37 ( $\text{SiCH}_3$ ), 18.28 ( $\text{SiC}(\text{CH}_3)_3$ ), 25.88 ( $\text{SiC}(\text{CH}_3)_3$ ), 39.57 ( $\text{CH}_2$ ), 66.19 ( $\text{CH}_2\text{O}$ ), 72.78 ( $\text{CH-O}$ ), 126.33 ( $\text{ArC}$ ), 128.42 ( $\text{ArC}$ ), 129.29 ( $\text{ArC}$ ), 138.26 ( $\text{ArC-CH}_2$ ).

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