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Selective Cleavage of Ethers Using Silica-Alumina Gel Catalysts Prepared by the Sol-Gel Method

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Abstract: The selective cleavage of tetrahydropyranyl (THP), methoxymethyl (MOM), 1-ethoxyethyl (EE), 1-methyl-1-methoxyethyl (MME) and trimethylsilyl (TMS) ether groups with silica-alumina gels prepared by the sol-gel method has been investigated. The deprotection rate follows the order: TMS > MME » EE > THP » MOM. The selective deprotection of diol derivatives with mixed protecting groups was achieved efficiently. Bis-THP and bis-MOM ether derivatives of a substrate which contained a primary and a tertiary hydroxyl groups were mono-deprotected with moderate selectivity. The selective deprotection of glycerol ethers was also examined. The silica-alumina gels prepared by the sol-gel method are thus shown to be a good catalyst for selective cleavage of ether protecting groups giving the product in a simple manner under mild conditions. Copyright © 1996 Published by Elsevier Science Ltd

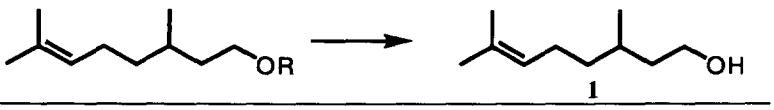
Solid acid catalysts, especially silica gels and zeolites, have received much attention in organic synthesis for their ease in handling and use.[1] However, due to their insufficient acidity, prolonged reaction time[2] or a large quantity of them are usually necessary,[3] and they are often modified by Lewis acid to increase catalytic activity.[4]

In the course of our investigation on the catalytic property of the silica-alumina gels prepared by the sol-gel method,[5] we found that they are effective as a catalyst for the Diels-Alder reaction between isoprene and acrylaldehyde.[6] Among the silica-alumina gels SA-1, SA-2 and SA-3, which are prepared by the sol-gel method under the addition of 2-propanol, 2-propanol and dodecane, and 2-propanol and oxalic acid, respectively, SA-3 gave the best results in yield and selectivity of the Diels-Alder reaction, and this fact was shown to relate with the population of strongly acidic sites on the catalyst surface. Generally, the material prepared by the sol-gel method is chemically more homogeneous[7] and has better surface properties[6] such as surface area, pore size and pore volume, and these could be controlled variously by preparative methods. Thus, while the silica-alumina gels prepared by the sol-gel method are potentially as a convenient catalyst in selective organic reactions, exploration of their application in this direction has been very limited. In this paper we report our studies aiming at application of such silica-alumina gel catalysts to the selective deprotection of ether protecting groups for alcohols.[8]

1. *Scope and Limitation of Deprotection Reactions with the Silica-Alumina Gel Catalysts*

Firstly, cleavage reactions with our catalysts (SA-1, SA-2 and SA-3) and commercial silica gel were tested for tetrahydropyranyl (THP), methoxymethyl (MOM), 1-ethoxyethyl (EE), 1-methyl-1-methoxyethyl (MME) and trimethylsilyl (TMS) ethers of citronellol (**1**). The results are shown in Table 1. When ether derivatives of **1** (compounds **1a**, **1b**, **1c** and **1d**) in methanol were allowed to react at room temperature in the presence of

Table 1. Cleavage Reaction of Citronellol Derivatives with an Ether Protecting Group in the Presence of Silica-Alumina Catalysts Prepared by the Sol-Gel Method



1

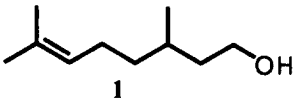
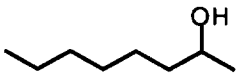
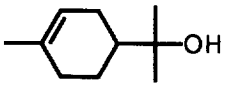
Substrate	R	Catalyst[a] SA-3	SA-2	SA-1	SiO_2
1a	THP	130 min /120 °C (98% yield)	150 min /140 °C (98%)	140 min /140 °C (97%)	230 min /160 °C (97%)
1b	EE	80 min /120 °C (98%)	60 min /140 °C (97%)	110 min /140 °C (97%)	210 min /160 °C (97%)
1c	MME	120 min /rt (95%)	190 min /rt (97%)	250 min /rt (95%)	15 h /rt (97%)
1d	TMS	70 min /rt (97%)	110 min /rt (97%)	100 min /rt (97%)	340 min /64 °C (97%)

[a] SA-1, SA-2 and SA-3 indicate the silica-aluminas which are prepared by the sol-gel method under the addition of 2-propanol, 2-propanol and dodecane, and 2-propanol and oxalic acid, respectively.

SA-3 (25 mg for 0.6 mmol of substrate), the reactions of **1c** and **1d** were completed within a few hours. While no sign of the reactions was observed for **1a** and **1b** at room temperature, the reactions came to completion at 120 °C within admissible time. In every case the reaction was clean and no byproduct was detected on TLC analyses. The catalysts SA-1 and SA-2 are less effective than SA-3. Thus, catalytic activity decreases in the order of SA-3 > SA-2 ≈ SA-1 > SiO_2. For comparison with the silica-alumina gels prepared by the sol-gel method, commercially available silica-alumina (denoted SA-4) was tested for the cleavage reaction. SA-4 was a little more effective than SA-1 (for **1d**, 90 min at room temperature). Since the cleavage reaction of ether or acetal is decidedly catalyzed by acids, a significant contribution by the number of the strongly acidic sites ($pK_a \leq -3.0$) is reasonably conceived as in the case of the Diels-Alder reaction, which is in an order of SA-3 > SA-4 > SA-2 > SA-1.[6] The acidic sites with $pK_a \leq -3.0$ are reported not to exist in silica gel. [9] These facts agree with the observed activity of the catalysts in the deprotection reactions. In addition, the remarkably large surface area of the SA-3 might contribute to its high activity to some extent, while the pore volume would be less significant, since those of SA-3 and SA-4 were comparable.

Deprotection of MOM ether **1e** with SA-3 (see Table 2) did not complete at 160 °C within an acceptable time. Ease of the deprotection reactions is in the order: TMS > MME » EE > THP » MOM. The efficiency of the silica-alumina gel catalysts prepared by the sol-gel method, especially SA-3, in comparison with that of the commercial silica gel is evident. In four kinds of ether derivatives **1a-1d**, deprotection with SA-3 could be performed at tolerable temperatures and within a short time. Moreover, the amount of the catalysts used was one-tenth of the substrate weight. In a recent report[10] neutral alumina was utilized for selective cleavage of silyl ether protecting groups, in which 50-fold of the substrate weight was used.

Table 2. Cleavage Reaction of the Protected Mono-alcohols Using SA-3 as Catalyst

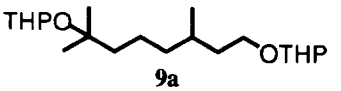
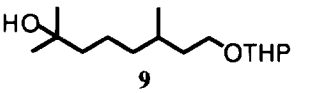
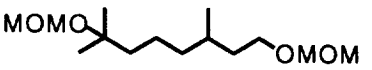
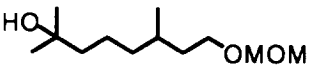
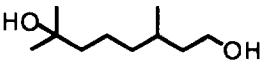
Alcohol	Protecting Groups				
	THP	EE	MME	TMS	MOM
 1	**1a** 130 min 120 °C (98% yield)	**1b** 80 min 120 °C (98%)	**1c** 120 min rt (95%)	**1d** 70 min rt (97%)	**1e** 10 h 160 °C (70%)
 2	**2a** 140 min 120 °C (96%)	**2b** 210 min 64 °C (98%)	- - -	**2d** 80 min rt (96%)	**2e** 140 min 160 °C (97 %)
 3	**3a** 150 min 64 °C (98%)	- - -	- - -	**3d** 30 min 64 °C (96%)	**3e** 52 h 64 °C (95%)

Subsequently, the cleavage reaction of SA-3 catalyst was tested for the ether derivatives of two other representative alcohols, 2-octanol (**2**, secondary) and α-terpineol (**3**, tertiary). The results are reproduced in Table 2 together with those of citronellol derivatives for comparison. The secondary alcohol ethers **2a**, **2b**, **2d** and **2e** could be cleaved under the conditions similar to those for primary alcohol ethers **1a**, **1b**, **1d** and **1e**. Interestingly, THP derivative **3a** and MOM derivative **3e** of tertiary alcohol were deprotected at temperature lower than those used for **1a** and **2a** and for **1e** and **2e**, respectively, while for the deprotection of TMS derivative **3d**, warming of the reaction mixture to 64 °C was necessary in contrast to reaction at room temperature for **1d** and **2d**. The reversed reactivity, in THP and MOM ethers on the side and TMS on the other, depending upon the class of alcohols concerned, would be ascribed to the difference in the reaction mechanism. In the cleavage of the former ethers, the protonation of ether oxygen atom followed by the fission of the alkoxyether oxygen-carbon bond affords the deprotected alcohols and the oxonium ions derived from THP and MOM ethers to which solvent methanol add. Therefore, the ether of the tertiary alcohol would have greater reactivity than those of the ethers derived from primary and secondary alcohols, since the release of strain energy should be larger for the tertiary ether in the rate-determining C-O cleavage step.[11] In the reaction of TMS ether, the ease in the attack of the nucleophilic methanol molecule to the silicone atom determines the rate; thus, the more sterically hindered tertiary ether show decreased reactivity. The results obtained suggested the possible selective cleavage of the polyol ether derivatives which contain a tertiary hydroxyl function and those of the other classes (see section 3).

2. *Selective Cleavage of Diol Derivatives with Different Ether Protecting Groups*

Based on data obtained in the preceding section, we studied the selective cleavage of differently protected hydroxyl groups in a symmetrical diol using SA-3 catalyst. As indicated in Table 3, in the combinations of THP and MME ether groups (**4a** and **7a**), EE and MME ether groups (**5a** and **8a**), MOM and MME ether

Table 3. Selective Deprotection Reaction of the Protected Diols Using SA-3 as the Catalyst

Protected alcohols	Products	Reac. cond. (selectivity)	Yield
$THPO(CH_2)_5OMME$ **4a**	$THPO(CH_2)_5OH$ **4**	90 min / rt (100%)	97%
$EEO(CH_2)_5OMME$ **5a**	$EEO(CH_2)_5OH$ **5**	80 min / rt (100%)	96%
$MOMO(CH_2)_6OMME$ **6a**	$MOMO(CH_2)_6OH$ **6**	70 min / rt (100%)	97%
$THPO(CH_2)_6OMME$ **7a**	$THPO(CH_2)_6OH$ **7**	140 min / rt (100%)	98%
$EEO(CH_2)_6OMME$ **8a**	$EEO(CH_2)_6OH$ **8**	50 min / rt (100%)	98%
$THPO(CH_2)_6OTMS$ **7b**	**7**	20 min / rt (100%)	96%
 **9a**	 **9**	80 min / 64 °C (80 : 20[a])	**9a**: 19% **9** : 76%
 **10a**	 **10**	21 h / 64 °C (85 : 15[a])	**10a**: 14% **10** : 82%
	 **11**		

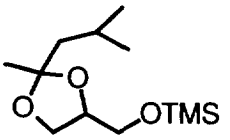
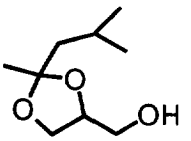
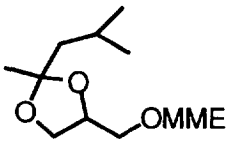
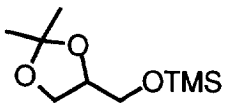
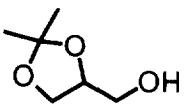
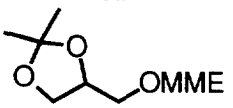
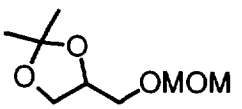
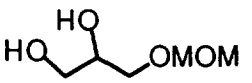
[a] Ratio of mono-alcohol to starting material.

groups (**6a**), selective removal of the MME group could be attained quantitatively. In the case of 1-trimethylsilyloxy-6-tetrahydropyranyloxyhexane (**7b**), the silyl group was cleaved predominantly. Thus, the excellent utility of SA-3 catalyst for selective cleavage of ether protecting groups is demonstrated.

3. *Selective Cleavage of Ether-protecting Groups in Diol Containing Different Classes of Hydroxyl Groups*

Next, we explored the selective cleavage of the same ether protecting groups in a diol derivative which has different classes of hydroxyl groups. Bis-THP ether **9a** and bis-MOM ether **10a** of 3,7-dimethyl-1,7-octanediol (**11**) were used as substrates. Although the protective groups of the tertiary hydroxyl functions were removed preferentially upon the reaction at 64 °C in both cases, the achieved selectivity remained at best in ratios (mono-alcohol : substrate) of 80 : 20 and 85 : 15, respectively, since longer treatment resulted in the formation of diol **11**. Attempts to mono-deprotect bis-THP and bis-MOM ethers of 1,4-pentanediol and 1,5-hexanediol using SA-3 catalyst failed.

Table 4. Selective Deprotection Reaction of the Protected Glycerol Derivatives Using SA-3 as Catalyst

Protected alcohols	Products	Reac. cond. (selectivity)	Yield
 **12a**	 **12**	90 min / rt (100%)	97%
 **12b**	**12**	280 min / rt (100%)	96%
 **13a**	 **13**	50 min / rt (100%)	94%
 **13b**	**13**	110 min / 64 °C (100%)	95%
 **13c**	 **14**	330 min / 64 °C (68%)	64% (glycerol 30%)

4. *Selective Cleavage of Glycerol Derivatives with Ether Protecting Groups*

Selective cleavage of glycerol derivatives with ether protection is a critical problem in the synthesis of glycerides containing different ester groups. We therefore investigated the selective deprotection of etherderivatives obtained from glycerol 1,2-acetals (see Table 4). When TMS and MME derivatives (**12a**, **13a** and **12b**, **13b**) of 1,2-isobutylethylideneglycerol (**12**) and 1,2-isopropylideneglycerol (**13**) were treated with SA-3 catalyst, both TMS and MME groups were cleaved exclusively. Selective deprotection of EE or THP ethers of **12** and **13** could not be achieved. In the reaction of MOM derivative **13c**, the isopropylidene group of **13c** was removed preferentially over the MOM group affording diol **14** without formation of **13**, with concomitant complete hydrolysis to glycerol.

5. *Conclusion*

The silica-aluminas prepared by the sol-gel method are shown to be effective catalysts for selective cleavage of ether protecting groups. The SA-3 catalyst, which is prepared using oxalic acid and 2-propanol as

organic additives and has a relatively high contribution of strongly acidic sites, was the most potent. The reaction is performed simply by keeping the methanol solution of the substrate in the presence of the catalyst at requisite temperatures. Removal of the catalyst by filtration and evaporation of the solvent afford the deprotected product cleanly. Ratio of One-tenth of catalyst to substrate (w / w) is enough to make the reaction rate practical. This fact is remarkable in contrast to the large amount of solid catalysts used in the reported procedures.[10] In this way THP, EE, MME and TMS derivatives of primary, secondary and tertiary alcohols are cleaved within a few hours at temperatures ranging from ambient to 120 °C. Although cleavage of primary MOM ether is slow even at higher temperature (160 °C), MOM ethers of secondary and tertiary alcohols are practically cleaved. Since conventional methods for cleaving an ether protecting group with protonic or Lewis acids are sometimes accompanied by byproducts,[12] the mild condition and simplicity of our procedure using the SA-3 catalyst would be valuable. The protecting groups examined can be divided into three classes according to ease of the cleavage using our catalyst SA-3: (1) those cleaved on the reaction at 64 °C (TMS, MME and tertiary MOM), (2) those cleaved on treatment at 120 °C (EE and THP) and (3) those not cleaved on treatment at 120 °C (primary and secondary MOM). Thus, clear differentiation among these classes of protecting groups in the cleavage reaction is reasonably expected and this was demonstrated in the selective deprotection of ether derivatives of diols. The difference in ease of the cleavage of the same protecting groups dependent upon the class of the hydroxyl groups concerned is noted. On the reaction of bis-THP and bis-MOM ethers, derived from the diols which has a primary and a tertiary hydroxyl groups, the selective mono-deprotection at the tertiary ether groups was observed in both cases. Finally, selective cleavage of TMS and MME ether groups in glycerol derivatives with 1,2-acetal groups was successful. Although the reaction of those containing EE or THP groups was found to be non-selective, the isopropyridene group was removed selectively for the substrate containing the MOM group.

Experimental Section

The preparation of silica-alumina gels used as catalysts by the sol-gel method was reported.[6] SA-1, SA-2, and SA-3 are the silica-aluminas which are prepared under the addition of 2-propanol, and 2-propanol and dodecane, and 2-propanol and oxalic acid, respectively. Silica gel on the market (Kanto Chemical Co. Ltd., for chromatography, 60 ~ 80 mesh) and silica-alumina gel on the market (Fuji Silysia Co. Ltd., No. 93386) were used as control catalysts. The catalysts were used after drying at 180 °C for 3 h under reduced pressure.

IR spectra were recorded on a Shimadzu DR 8000 FT-IR apparatus. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ on a JEOL JNM-EX270 FT NMR spectrometer, operating at 270 MHz for proton, and 67.5 MHz for carbon, respectively. Chemical shifts are reported in δ scale relative to the chloroform signal of $CDCl_3$ in the ^{1}H NMR and to the $CDCl_3$ triplet in the ^{13}C NMR spectra. The mass spectra were determined on a JEOL JMS-DX303H apparatus.

Preparation of THP ethers 1a, 2a, 3a and 9a

Compounds **1a**, **2a**, **3a** and **9a** were prepared by Bernady's procedure.[13] After work-up the compounds were purified by column chromatography on silica gel (hexane : ethyl acetate = 25 : 1).

3,7-Dimethyl-1-tetrahydropyranyloxy-6-octene (1a)

THP ether **1a** was prepared from citronellol (**1**) (17.5 mmol, 2.73g) to give 4.07g of product (97% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2940 (s), 1458 (m), 1377 (m), 1136 (m), 1078 (m), 1034 (m); ^{1}H NMR ($CDCl_3$): δ = 0.91 (d, 3H, J = 6.6 Hz), 1.13-2.05 (m, 13H), 1.60 (s, 3H), 1.68 (s, 3H), 3.34-3.57 (m, 2H), 3.72-3.93 (m, 2H), 4.56-4.59 (m, 1H), 5.10 (br, t, 1H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) 62.21, a pair at 65.82 and 65.91, a pair at 98.73 and 98.85, 124.80, 130.99; MS (70eV): m/z = 240 (M^+, 0.5), 156 (14), 136 (16), 123 (28), 109 (16), 95 (49), 65 (69), 69 (85), 55 (100); HRMS: Calc. for $C_{11}H_{20}O_2$ (M - C_4H_8), 184.1463: found, 184.1445.

2-Tetrahydropyranyloxyoctane (2a)

THP ether **2a** was prepared from 2-octanol (**2**) (20.4 mmol, 2.66g) to give 4.15g of product as a mixture

of 1 : 1 diastereomers (95% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2932 (s), 2859 (s), 1446 (m), 1375 (m), 1078 (m), 1022 (m), 990 (m); ^1H NMR ($CDCl_3$): δ = 0.88 (t, 3H, *J* = 7.9 Hz), a pair of doublet (3H) at 1.10, 1.21 (*J* = 5.9 and 6.3 Hz, respectively), 1.28-1.42 (m, 10H), 1.52-1.85 (m, 6H), 3.45-3.52 (m, 1H), 3.68-3.86 (m, 1H), 3.88-3.98 (m, 1H), a pair of triplet (1H) at 4.63, 4.70 (*J* = 4.3 and 3.3 Hz, respectively); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) a pair at 62.36 and 62.79, a pair at 71.10 and 73.89, a pair at 95.52 and 98.56; MS (70eV): *m/z* = 214 (M^+, 0.5), 170 (3), 129 (17), 112 (34), 97 (27), 85 (100), 69 (34), 55 (100); HRMS: Calc. for $C_{13}H_{25}O_2$ (M - H), 213.1855: found, 213.1862.

4-(1-Methyl-1-tetrahydropyranyloxyethyl)-1-methylcyclohexene (3a)

THP ether **3a** was prepared from α-terpineol (**3**) (9.7 mmol, 1.50g) to give 2.13g of product (92% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2938 (m), 2868 (m), 1641 (m), 1458 (m), 1379 (m), 1200 (m), 1034 (m), 883 (m); ^1H NMR ($CDCl_3$) δ = 1.23 (s, 3H), 1.28 (s, 3H), 1.13-1.82 (m, 13H), 2.03-2.12 (m, 1H), 3.32-3.67 (m, 2H), 3.70-3.88 (m, 2H), 4.53-4.69 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) 62.12, 67.43, a pair at 73.14 and 74.34, 98.65, 108.09, 149.61; MS (70eV): *m/z* = 206 (6), 177 (5), 154 (9), 136 (67), 121 (100), 107 (26), 93 (80), 79 (26), 55 (43); HRMS: Calc. for $C_{10}H_{15}O_2$ (M - C_5H_{11}), 167.1072: found, 167.1060.

3,7-Dimethyl-1,7-bis(tetrahydropyranyloxy)octane (9a)

Bis-THP ether **9a** was prepared from 3,7-dimethyl-1,7-octanediol (**11**) (6.72 mmol, 1.17g) to give 1.61g of product (70% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2942 (s), 1460 (m), 1360 (m), 1130 (m), 1076 (m), 1024 (s), 991 (m); ^1H NMR ($CDCl_3$) δ = 0.90 (d, 3H, *J* = 6.3 Hz), 1.19 (s, 3H), 1.21 (s, 3H), 1.13-1.92 (m, 21H), 3.31-3.58 (m, 3H), 3.70-3.98 (m, 3H), 4.55-4.61 (m, 1H), 4.68-4.74 (m, 1H) ; ^{13}C NMR ($CDCl_3$): δ = (selected peaks) a pair at 42.21 and 44.20, a pair at 62.28 and 62.86, 63.32, 76.24, a pair at 93.87 and 94.59, a pair at 98.78 and 98.96; MS (70eV): *m/z* = 267 (0.4), 252 (8), 235 (4), 140 (9), 101 (41), 63 (100), 69 (100), 57 (100); HRMS: Calc. for $C_{11}H_{23}O_2$ (M - $C_9H_{15}O_2$), 187.1698: found, 187.1688.

Preparation of EE ethers 1b and 2b

Compounds **1b** and **2b** were prepared by Fukuzawa's procedure.[14] After work-up the compounds were purified by column chromatography on silica gel (hexane : ethyl acetate = 25 : 1).

3,7-Dimethyl-1-(1-ethoxyethoxy)-6-octene (1b)

EE ether **1b** was prepared from citronellol (**1**) (17.6 mmol, 2.75g) to give 3.56g of product as a mixture of 1 : 1 diastereomers (89% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2928 (s), 2966 (s), 1460 (m), 1377 (m), 1134 (m), 1063 (m); ^1H NMR ($CDCl_3$): δ = 0.90 (d, 3H, *J* = 6.6 Hz), 1.20 (t, 3H, *J* = 7.1 Hz), a pair of doublet (3H) at 1.28 and 1.30 (*J* = 5.3 and 5.6 Hz, respectively), 1.60 (s, 3H), 1.68 (s, 3H), 1.14-1.71 (m, 5H), 1.90-2.05 (m, 2H), 3.38-3.54 (m, 2H), 3.56-3.72 (m, 2H), 4.58-4.72 (m, 1H), 5.10 (t, 1H, *J* = 5.0 Hz); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) 60.56, a pair at 63.38 and 63.49, a pair at 99.48 and 99.64, 124.76, 131.02; MS (70eV): *m/z* = 228 (M^+, 0.15), 182 (7), 167 (10), 156 (12), 138 (29), 123 (68), 109 (41), 95 (98), 61 (100), 67 (95), 55(100); HRMS: Calc. for $C_{12}H_{23}O$ (M - C_2H_5O), 183.1749: found, 183.1770.

2-(1-Ethoxyethoxy)octane (2b)

EE ether **2b** was prepared from 2-octanol (**2**) (9.31 mmol, 1.21g) to give 1.82g of product as a mixture of 1 : 1 diastereomers (91% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2961 (s), 2934 (s), 1375 (m), 1334 (m), 1240 (s), 1200 (s); ^1H NMR ($CDCl_3$): δ = 0.88 (t, 3H, *J* = 7.6 Hz), a pair of doublet (3H) at 1.11 and 1.18 (*J* = 6.6 and 5.9 Hz, respectively), 1.20 (t, 3H, *J* = 7.1 Hz), 1.30 (d, 3H, *J* = 7.6 Hz), 1.29-1.54 (m, 10H), 3.43-3.54 (m, 1H), 3.58-3.71 (m, 2H), 4.68-4.78 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) a pair at 59.68 and 59.80, a pair at 71.61 and 72.94, a pair at 97.66 and 99.03; MS (70eV): *m/z* = 201 (M^+-1, 0.2), 187 (14), 157 (22), 141 (13), 112 (58), 97 (13), 63 (34), 73 (100), 57 (100); HRMS: Calc. for $C_{10}H_{21}O$ (M - C_2H_5O), 157.1592: found, 157.1575.

Preparation of MME ethers 1c, 4a, 7a and 13b

Compounds **1c**, **4a**, **7a** and **13b** were prepared by George's procedure.[15] After work-up the compounds were purified by vacuum distillation.

3,7-Dimethyl-1-(1-methyl-1-methoxyethoxy)-6-octene (1c)

MME ether **1c** was prepared from citronellol (**1**) (16.4 mmol, 2.56g) to give 3.45g of product (85 °C, 0.3 Torr.; 92% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2930 (s), 1455 (m), 1380 (m), 1240 (m), 1061 (m) ; ^1H NMR ($CDCl_3$): δ = 0.89 (d, 3H, *J* = 6.9 Hz), 1.33 (s, 6H), 1.60 (s, 3H), 1.68 (s, 3H), 1.10-1.72 (m, 5H), 1.91-2.02 (m, 2H), 3.19 (s, 3H), 3.34-3.50 (m, 2H), 5.04-5.13 (m, 1H) ; ^{13}C NMR ($CDCl_3$): δ = (selected

peaks) 48.39, 58.99, 99.80, 124.89, 131.10; MS (70eV): *m/z* = 228 (M^+, 0.5) 181 (11), 156 (8), 136 (71), 123 (86), 109 (43), 95 (90), 82 (100), 69 (85), 55 (100); HRMS: Calc. for $C_{13}H_{25}O$ (M - CH_3O), 197.1906: found, 197.1896.

5-(1-Methyl-1-methoxyethoxy)-1-tetrahydropyranyloxypentane (4a)

MME ether **4a** was prepared from 1-tetrahydropyranyloxy-5-pentanol (**4**) (7.56 mmol, 1.53g) to give 1.88g of product (90 °C, 0.15 Torr.; 91% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2942 (s), 2990 (s), 1455 (m), 1367 (m), 1283 (m), 1184 (m), 1123 (m), 1078 (m); ^1H NMR ($CDCl_3$): δ = 1.33 (s, 6H), 1.36-1.88 (m, 12H), 3.19 (s, 3H), 3.35-3.43 (m, 3H), 3.46-3.54 (m, 1H), 3.62-3.79 (m, 1H), 3.83-3.89 (m, 1H), 4.56-4.59 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) 48.25, 60.49, 62.18, 67.39, 98.73, 99.66; MS (70eV): *m/z* = 260 (M^+, 1), 101 (12), 84 (94), 69 (35), 56 (100); HRMS: Calc. for $C_{11}H_{20}O_4$ (M - C_3H_8), 216.1362: found, 216.1350.

6-(1-Methyl-1-methoxyethoxy)-1-tetrahydropyranyloxyhexane (7a)

MME ether **7a** was prepared from 1-tetrahydropyranyloxy-6-hexanol (**7**) (10.0 mmol, 2.04g) to give 2.54g of product (104 °C, 0.18 Torr.; 92% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2992 (s), 2940 (s), 1466 (m), 1379 (m), 1259 (m), 1185 (m), 1145 (s), 1080 (s), 1035 (s), 989 (m), 908 (m) ; ^1H NMR ($CDCl_3$): δ = 1.33 (s, 6H), 1.36-1.44 (m, 4H), 1.48-1.66 (m, 9H), 1.70-1.86 (m, 1H), 3.19 (s, 1H), 3.33-3.43 (m, 3H), 3.46-3.54 (m, 1H), 3.61-3.79 (m, 1H), 3.83-3.92 (m, 1H), 4.56-4.59 (m, 1H) ; ^{13}C NMR ($CDCl_3$): δ = (selected peaks) 48.27, 60.56, 62.23, 67.49, 98.76, 99.66; MS (70eV): *m/z* = 274 (M^+, 0.4), 252 (3), 157 (5), 113(5), 101 (30), 85 (84), 67 (28), 55 (100) ; HRMS: Calc. for $C_{14}H_{26}O_4$ (M - H_2), 258.1831: found, 258.1914.

1,2-Isopropylidene-3-(1-methyl-1-methoxyethoxy)glycerol (13b)

MME ether **13b** was prepared from 1,2-isopropylideneglycerol (**13**) (11.7 mmol, 1.54g) to give 2.02g of product (65 °C, 0.6 Torr.; 85% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2990 (s), 2939 (m), 1458 (m), 1371 (s), 1215 (s), 1157 (m), 1084 (s), 1055 (s), 841 (m); ^1H NMR ($CDCl_3$): δ = 1.33 (s, 3H), 1.35 (s, 3H), 1.36 (s, 3H), 1.42 (s, 3H), 3.20 (s, 3H), 3.40-3.53 (m, 2H), 3.67-3.76 (m, 1H), 4.03-4.11 (m, 1H), 4.20-4.27 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 23.85, 24.49, 25.43, 26.70, 48.35, 62.17, 66.95, 74.93, 100.14, 109.33; MS (70eV): *m/z* = 203 (M^+-1, 0.45), 189 (4), 157 (29), 117 (67), 101 (58), 83 (24), 73 (94), 57 (100); HRMS: Calc. for $C_9H_{17}O_3$ (M - CH_3O), 173.1178: found, 173.1140.

Preparation of TMS ethers 1d, 2d, 3d, 7b and 13a

Compounds **1d**, **2d**, **3d**, **7b** and **13a** were prepared by Corey's procedure.[16] After work-up the compounds were purified by vacuum distillation.

3,7-Dimethyl-1-trimethylsilyloxy-6-octene (1d)

TMS ether **1d** was prepared from citronellol (**1**) (6.93 mmol, 1.08g) to give 1.43g of product (68 °C, 0.39 Torr.; 91% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2957 (s), 2920 (s), 1728 (m), 1450(m), 1377 (m), 1250 (s), 1093 (m), 966 (m); ^1H NMR ($CDCl_3$): δ = 0.11 (s, 9H), 0.88 (d, 3H, *J* = 6.6 Hz), 1.09-1.70 (m, 5H), 1.60 (s, 3H), 1.68 (s, 3H), 1.85-2.05 (m, 2H), 3.56-3.66 (m, 2H), 5.10 (br, t, 1H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$): δ = 0.48, 18.56, 20.52, 26.41, 26.64, 30.13, 38.16, 40.75, 61.85, 125.82, 132.01; MS (70eV): *m/z* = 226 (M^+, 6), 213 (8), 143 (26), 123 (26), 109 (18), 95 (47), 82 (69), 69 (100), 55 (14); HRMS: Calc. for $C_{12}H_{25}OSi$ (M - CH_3), 213.1675: found, 213.1590.

2-Trimethylsilyloxyoctane (2d)

TMS ether **2d** was prepared from 2-octanol (**2**) (21.9 mmol, 2.85g) to give 3.89g of product (55 °C, 0.51 Torr.; 88% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2959 (s), 2860 (s), 1375 (m), 1250 (s), 1084 (m), 1049 (m), 841 (s); ^1H NMR ($CDCl_3$): δ = 0.11 (s, 9H), 0.88 (t, 3H, *J* = 7.9 Hz), 1.12 (d, 3H, *J* = 6.3 Hz), 1.27-1.37 (m, 10H), 3.70-3.82 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 0.05, 13.89, 22.44, 23.70, 25.75, 29.15, 31.70, 39.46, 68.43; MS (70eV): *m/z* = 202 (M^+, 4), 187 (40), 129 (13), 119 (100), 101 (17), 75 (82), 61 (27), 55 (19); HRMS: Calc. for $C_{10}H_{23}OSi$ (M - CH_3), 187.1518: found, 187.1518.

4-(1-Methyl-1-trimethylsilyloxyethyl)-1-methylcyclohexene (3d)

TMS ether **3d** was prepared from α-terpineol (**3**) (15.6 mmol, 2.41g) to give 3.47g of product (63 °C, 0.21 Torr.; 98% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2963 (s), 1381 (m), 1363 (m), 1250 (s), 1161 (m), 1039 (s), 839(s); ^1H NMR ($CDCl_3$): δ = 0.09 (s, 9H), 1.16 (s, 3H), 1.18 (s, 3H), 1.64 (s, 3H), 1.21-2.22 (m, 7H), 5.38 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 2.59, 23.36, 23.99, 26.92, 26.99, 27.69, 31.18, 45.77, 121.06, 133.84; MS (70eV): *m/z* = 226 (M^+, 2), 207 (26), 181 (5), 131 (100), 117 (13), 73 (17); HRMS: Calc. for

$C_{12}H_{23}OSi$ (M - CH_3), 211.1518: found, 211.1543.

6-Trimethylsilyloxy-1-tetrahydropyranyloxyhexane (7b)

TMS ether **7b** was prepared from 1-tetrahydropyranyloxy-5-pentanol (**7**) (20.2 mmol, 4.09g) to give 5.06g of product (95 °C, 0.41 Torr.; 91% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2940 (s), 2863 (s), 1250 (s), 1095 (m), 1035 (m), 841 (m) ; ^1H NMR ($CDCl_3$): δ = 0.11 (s, 9H), 1.30-1.44 (m, 4H), 1.50-1.88 (m, 10H), 3.34-3.43 (m, 1H), 3.46-3.66 (m, 3H), 3.69-3.78 (m, 1H), 3.83-3.91 (m, 1H), 4.56-4.60 (m, 1H) ; ^{13}C NMR ($CDCl_3$): δ = -0.48, 19.62, 25.48, 25.66, 26.04, 29.71, 30.73, 32.56, 62.23, 62.57, 67.51, 98.78; MS (70eV): *m/z* = 274 (M^+, 0.2), 189 (4), 173 (13), 157 (5), 129 (4), 105 (15), 93 (5), 83 (100), 75 (39), 55 (80); HRMS: Calc. for $C_8H_{17}O_2Si$ (M - $C_6H_{13}O$), 173.0998: found, 173.1049.

1,2-Isopropylidene-3-trimethylsilyloxyglycerol (13a)

TMS ether **13a** was prepared from 1,2-isopropylideneglycerol (**13**) (23.5 mmol, 3.11g) to give 4.31g of product (35 °C, 0.15 Torr.; 80% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2988 (s), 2874 (s), 1371 (m), 1252 (s), 1217(m), 1147 (m), 1093 (m), 881 (m), 843 (m); ^1H NMR ($CDCl_3$): δ = 0.12 (s, 9H), 1.36 (s, 3H), 1.41 (s, 3H), 3.54 (dd, 1H, *J* = 10.1, 6.3 Hz), 3.65 (dd, 1H, *J* = 10.1, 4.6 Hz), 3.75 (dd, 1H, *J* = 7.3, 5.9 Hz), 4.04 (dd, 1H, *J* = 8.3, 7.3 Hz), 4.16 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 0.16, 26.13, 27.49, 64.38, 67.53, 78.27, 109.99; MS (70eV): *m/z* = 203 (M^+-1, 0.2), 189 (58), 131 (80), 129(100), 115 (2), 101 (74), 87 (11), 73 (60), 59 (22); HRMS: Calc. for $C_8H_{17}O_3Si$ (M - CH_3), 189.0947: found, 189.0983.

Preparation of MOM ethers 1e, 2e, 3e, 10a and 13c

Compounds **1e**, **2e**, **3e**, **10a** and **13c** were prepared by Stork's procedure.[17] After work-up the compounds were purified by column chromatography on silica gel (hexane : ethyl acetate = 25 : 1).

3,7-Dimethyl-1-methoxymethoxy-6-octene (1e)

MOM ether **1e** was prepared from citronellol (**1**) (6.47 mmol, 1.01g) to give 1.23g of product (94% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2956 (s), 2878 (s), 1742 (m), 1456 (m), 1377 (m), 1154 (s), 1111 (s), 1047 (s), 920 (m); ^1H NMR ($CDCl_3$): δ = 0.90 (d, 3H, *J* = 7.0 Hz), 1.10-1.75 (m, 5H), 1.60 (s, 3H), 1.68 (s, 3H), 1.90-2.07 (m, 2H), 3.36 (s, 3H), 3.51-3.64 (m, 2H), 4.61 (s, 2H), 5.10 (br, s, 1H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$): δ = 17.56, 19.45, 25.45, 25.66, 29.53, 36.69, 37.16, 55.04, 66.04, 96.41, 124.76, 131.11; MS (70eV): *m/z* = 200 (M^+, 2), 168 (23), 155 (6), 137 (34), 121 (12), 112 (16), 95 (100), 81 (71), 69 (80), 55 (30); HRMS: Calc. for $C_{12}H_{24}O_2$, 200.1776: found, 200.1758.

2-Methoxymethoxyoctane (2e)

MOM ether **2e** was prepared from 2-octanol (**2**) (16.3 mmol, 2.12g) to give 2.39g of product (84% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2980 (s), 2957 (s), 1460 (w), 1377 (w), 1146 (m), 1100 (m), 1042 (s), 920 (m) ; ^1H NMR ($CDCl_3$): δ = 0.88 (t, 3H, *J* = 6.6 Hz), 1.16 (d, 3H, *J* = 5.9 Hz), 1.25-1.60 (m, 10H), 3.37 (s, 3H), 3.62-3.73 (m, 1H), 4.65 (ABq, 2H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ = 14.02, 20.24, 22.59, 25.54, 29.33, 31.83, 37.06, 55.17, 73.16, 94.81; MS (70eV): *m/z* = 174 (M^+, 0.15), 159 (8), 129 (15), 112 (32), 98 (22), 89 (75), 83 (21), 70 (80), 56 (100); HRMS: Calc. for $C_9H_{19}O_2$ (M - CH_3), 159.1385: found, 159.1384.

4-(1-Methyl-1-methoxymethoxyethyl)-1-methylcyclohexene (3e)

MOM ether **3e** was prepared from α-terpineol (**3**) (13.4 mmol, 2.07g) to give 2.41g of product (91% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2963 (s), 2889 (s), 1455 (m), 1381 (m), 1147 (m), 1136 (m), 1090 (m), 1040 (s), 918 (m); ^1H NMR ($CDCl_3$): δ = 1.17 (s, 3H), 1.18 (s, 3H), 1.22-1.45 (m, 2H), 1.64 (s, 3H), 1.56-2.10 (m, 5H), 3.36 (s, 3H), 4.72 (s, 2H), 5.36-5.41 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 22.98, 23.31, 23.93, 26.83, 31.07, 38.10, 43.78, 55.06, 78.22, 90.78, 120.77, 133.96; MS (70eV): *m/z* = 198 (M^+, 0.2), 166 (100), 151 (8), 136 (82), 121 (70), 106 (27), 91 (49), 79 (41), 68 (26), 53 (16); HRMS: Calc. for $C_{11}H_{19}O_2$ (M - CH_3), 183.1385: found, 183.1414.

3,7-Dimethyl-1,7-bis(methoxymethoxy)octane (10a)

Bis-MOM ether **10a** was prepared from 3,7-dimethyl-1,7-octanediol (**11**) (11.0 mmol, 1.92g) to give 2.54g of product (88% yield). After work-up the compound was purified by column chromatography on silica gel (hexane : ethyl acetate = 25 : 1): colorless oil; IR (neat, cm^{-1}): ν = 2932 (s), 2822 (m), 1470 (m), 1383 (m), 1147 (m), 1043 (s), 918 (m); ^1H NMR ($CDCl_3$): δ = 0.90 (d, 3H, *J* = 6.6 Hz), 1.21 (s, 6H), 1.13-1.68 (m, 9H), 3.36 (s, 3H), 3.37 (s, 3H), 3.56 (t, 2H, *J* = 6.6 Hz), 4.61 (s, 2H), 4.70 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 19.53, 21.35, 26.32, 29.87, 36.78, 37.63, 42.12, 55.07, 66.05, 76.26, 90.98, 96.42; MS (70eV): *m/z* = 262 (M^+, 0.6), 166 (23), 153 (9), 137 (29), 123 (15), 109 (17), 95 (54), 81 (93), 69 (100), 55 (43); HRMS: Calc.

for $C_{12}H_{24}O_2$ (M - $C_2H_6O_2$), 200.1776: found, 200.1689.

1,2-Isopropylidene-3-methoxymethylglycerol (13c)

MOM ether **13c** was prepared from 1,2-isopropylideneglycerol (**13**) (13.4 mmol, 1.77g) to give 1.79g of product (76% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2998 (m), 2969 (m), 2887 (m), 1371 (m), 1215 (m), 1154 (m), 113(m), 1042 (s), 918 (m); ^1H NMR ($CDCl_3$): δ =1.37 (s, 3H), 1.43 (s, 3H), 3.37 (s, 3H), 3.58 (dd, 2H, *J* = 1.5, 4.8 Hz), 3.73 (dd, 1H, *J* = 8.3, 6.3 Hz), 4.07 (dd, 1H, *J* = 8.3, 6.3 Hz), 4.26-4.36 (m, 1H), 4.65 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 25.30, 26.67, 55.19, 66.61, 68.54, 74.61, 96.60, 109.40; MS (70eV): *m/z* = 161 (M^+-15, 70), 145 (9), 131 (41), 101 (85), 87 (19), 71 (100), 57 (32); HRMS: Calc. for $C_7H_{13}O_3$ (M - CH_3O), 145.0865: found, 145.0860.

Preparation of bis-ethers 5a, 6a and 8a

Compounds **5**, **6** and **8** were prepared by Dickman's procedure.[18] In work-up process, saturated NaCl solution was used instead of HCl solution to avoid hydrolysis of produced monoethers. After work-up the compounds were purified by column chromatography on silica gel (hexane : ethyl acetate = 5 : 1) Compounds **5a**, **6a** and **8a** were prepared by George's procedure.[15] After work-up the compounds were purified by vacuum distillation.

1-(1-Ethoxyethoxy)-5-(1-methyl-1-methoxyethoxy)pentane (5a)

1-(1-Ethoxyethoxy)-5-pentanol (**5**) was prepared from 5-(1-ethoxyethoxy)methyl pentanoate (19.2 mmol, 3.93g) to give 2.62g of product (77% yield).: colorless oil; IR (neat, cm^{-1}): ν = 3480 (br, s), 2986 (s), 2868(s), 1383 (m), 1340(m), 1134 (m), 949 (m), 885 (m); ^1H NMR ($CDCl_3$): δ = 1.20 (t, 3H, *J* = 6.9 Hz), 1.24 (d, 3H, *J* = 7.3 Hz), 1.37-1.52 (m, 2H), 1.53-1.73 (m, 4H), 3.38-3.74 (m, 4H), 4.12 (q, 2H, *J* = 7.3 Hz), 4.58-4.70 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.20, 19.84, 21.02, 22.78, 29.68, 32.43, 60.43, 65.25, 99.69; MS (70eV): *m/z* = 176 (M^+, 0.6), 115 (10), 85 (100), 69 (40), 56 (33); HRMS: Calc. for $C_8H_{17}O_3$ (M - CH_3), 161.1178: found, 161.1195.

MME ether **5a** was prepared from alcohol **5** (10.3 mmol, 1.82g) to give 2.26g of product (85 °C, 0.8 Torr.; 88% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2990 (s), 2930 (s), 1455 (m), 1378 (m), 1283 (m), 1213 (m), 1136 (m), 849 (m); ^1H NMR ($CDCl_3$): δ = 1.20 (t, 3H, *J* = 6.9 Hz), 1.29 (d, 3H, *J* = 7.3 Hz), 1,33 (s, 6H), 1.36-1.43 (m, 2H), 1.53-1.68 (m, 4H), 3.19 (s, 3H), 3.36-3.67 (m, 6H), 4.59-4.72 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) 48.25, 52.19, 60.52, 65.12, 99.48, 100.31; MS (70eV): *m/z* = 248 (M^+, 0.2), 170 (6), 127 (10), 99 (21), 85 (69), 69 (100), 55 (90); HRMS: Calc. for $C_{10}H_{21}O_2$ (M - $C_3H_7O_2$), 173.1542: found, 173.1526.

1-Methoxymethoxy-6-(1-methyl-1-methoxyethoxy)hexane (6a)

1-Methoxymethoxy-6-hexanol (**6**) was prepared from 6-(1-methoxymethoxy)methyl hexanoate (16.7 mmol, 3.18g) to give 2.21g of product (82% yield).: colorless oil; IR (neat, cm^{-1}): ν = 3460 (br, s), 2936 (s), 2862 (s), 1461 (m), 1150 (m), 1111 (m), 1051 (m), 920 (m); ^1H NMR ($CDCl_3$): δ = 1.41-1.50 (m, 2H), 1.55-1.69 (m, 4H), 3.36 (s, 3H), 3.54 (t, 2H, *J* = 6.3 Hz), 3.63 (t, 2H, *J* = 6.6 Hz), 4.62 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 25.45, 25.88, 29.54, 32.51, 54.97, 62.54, 67.64, 96.23; MS (70eV): *m/z* = 162 (M^+, 0.2), 131 (4), 117 (27), 98 (65), 83 (80), 81 (100), 71 (70), 55 (90); HRMS: Calc. for $C_8H_{16}O_2$ (M - H_2O), 144.1150: found, 144.1134.

MME ether **6a** was prepared from alcohol **6** (10.2 mmol, 1.66g) to give 2.22g of product (98 °C, 0.25 Torr.; 93% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2930 (s), 2872 (s), 1460 (m), 1379 (m), 1213 (s), 1153 (s), 1047 (s), 920 (m), 849 (m); ^1H NMR ($CDCl_3$): δ = 1.33 (s, 6H), 1.39-1.48 (m, 4H), 1.54-1.65 (m, 4H), 3.19 (s, 3H), 3.35 (s, 3H), 3.40 (t, 2H, *J* = 6.6 Hz), 3.53 (t, 2H, *J* = 6.6 Hz), 4.61 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 20.74, 22.10, 22.66, 27.15, 27.31, 27.56, 45.99, 52.71, 58.20, 65.36, 94.05, 97.32; MS (70eV): *m/z* = 234 (M^+, 0.3), 187 (7), 144 (5), 127 (11), 99 (39), 63 (44), 71 (50), 59 (70), 55 (100); HRMS: Calc. for $C_{10}H_{21}O_2$ (M - $C_2H_5O_2$), 173.1542: found, 173.1526.

1-Ethoxyethoxy-6-(1-methyl-1-methoxyethoxy)hexane (8a)

1-Ethoxyethoxy-6-hexanol (**8**) was prepared from 6-(1-ethoxyethoxy)methyl hexanoate (18.7 mmol, 4.08g) to give 2.98g of product (84% yield).: colorless oil; IR (neat, cm^{-1}): ν = 3360 (br, s), 2936 (s), 2864 (s), 1381 (m), 1134 (s), 1085 (m), 1059 (m); ^1H NMR ($CDCl_3$): δ = 1.22 (t, 3H, *J* = 6.9 Hz), 1.30 (d, 3H, *J* = 5.6 Hz), 1.33-1.42 (m, 4H), 1.52-1.64 (m, 4H), 3.31-3.72 (m, 6H), 4.65-4.69 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 15.31, 18.29, 19.85, 25.56, 26.07, 29.85, 32.58, 62.53, 65.33, 99.69; MS (70eV): *m/z* = 234 (M^+-15, 0.15), 129 (32), 116 (24), 99 (100), 83 (47), 67 (56), 55 (100); HRMS: Calc. for $C_9H_{19}O_3$ (M - CH_3), 175.1334: found, 175.1248.

MME ether **8a** was prepared from alcohol **8** (7.70 mmol, 1.47g) to give 1.85g of product (90 °C, 0.37

Torr.; 92% yield).: colorless oil; IR (neat, cm^{-1}): ν = 2879 (s), 1458 (m), 1376 (m), 1213 (s), 1140 (s), 1080 (s); ^1H NMR ($CDCl_3$): δ = 1.20 (t, 3H, *J* = 6.9 Hz), 1.30 (d, 3H, *J* = 5.3 Hz), 1.33 (s, 6H), 1.35-1.44 (m, 4H), 1.46-1.60 (m, 4H), 3.18 (s, 3H), 3.30-3.70 (m, 6H), 4.60-4.71 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) 48.34, 60.65, 65.19, 99.57, 99.75; MS (70eV): *m/z* = 262 (M^+, 0.4), 155 (15), 112 (41), 97 (4), 83 (48), 70 (100), 57 (88); HRMS: Calc. for $C_{11}H_{23}O_2$ (M - $C_3H_7O_2$), 187.1698: found, 187.1748.

1,2-(*iso*-Butylethylidene)glycerol (12)

Alcohol **12** was prepared from glycerol (46.6 mmol, 4.29g) by common ketalization method[19] using *iso*-butyl methyl ketone to give 7.90g of product as a mixture of 1 : 1 diastereomers (97% yield). After work-up the compound was purified by column chromatography on silica gel (hexane : ethyl acetate = 2 : 1).: colorless oil; IR (neat, cm^{-1}): ν = 3460 (br, s), 2955 (s), 2872 (s), 1377 (m), 1186 (m), 1094 (m), 1045 (m); ^1H NMR ($CDCl_3$): δ = a pair of doublet (6H) at 0.95 and 0.96 (*J* = 6.6 and 6.6 Hz, respectively), a pair of singlet (3H) at 1.32 and 1.38, a pair of doublet (2H) at 1.55 and 1.57 (*J* = 6.3 and 6.6 Hz, respectively), 1.70-1.86 (m, 1H), 3.56-3.63 (m, 1H), 3.64-3.80 (m, 2H), 3.98-4.06 (m, 1H), 4.13(4.26 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) a pair at 48.14 and 49.42, a pair at 64.30 and 64.42, 66.91, a pair at 78.38 and 78.85, a pair at 112.53 and 112.65; MS (70eV): *m/z* = 159 (M^+-15, 31), 143 (12), 117 (100), 99 (17), 85 (31), 69 (13), 57 (100); HRMS: Calc. for $C_9H_{17}O_2$ (M - OH), 157.1229: found, 157.1149.

1,2-(*iso*-Butylethylidene)-3-trimethylsilylglycerol (12a)

TMS ether **12a** was prepared from alcohol **12** (21.6 mmol, 3.75g) by Corey's procedure[16] to give 4.49g of product as a mixture of 1 : 1 diastereomers (65 °C, 0.31 Torr.; 84% yield). After work-up the compound was purified by vacuum distillation.: colorless oil; IR (neat, cm^{-1}): ν = 2957 (s), 2872 (m), 1375 (m), 1252 (s), 1145 (m), 1096 (s), 843 (s); ^1H NMR ($CDCl_3$): δ = 0.11 (s, 9H), 0.93 (d, 6H, *J* = 6.6 Hz), a pair of singlet (3H) at 1.29 and 1.34, 1.50-1.58 (m, 2H), 1.70-1.88 (m, 1H), 3.49-3.58 (m, 1H), 3.63-3.77 (m, 2H), 3.99-4.06 (m, 1H), 4.08-4.17 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = -0.59, 23.79, 23.95, a pair at 24.10 and 24.42, 25.11, a pair at 47.05 and 48.14, a pair at 63.63 and 63.76, 66.76, a pair at 75.73 and 76.21, a pair at 111.11 and 111.20; MS (70eV): *m/z* = 245 (M^+-1, 0.2), 231 (17), 189 (80), 143 (27), 131 (100), 101 (43), 87 (41), 73 (70), 59 (33); HRMS: Calc. for $C_{11}H_{22}O_3Si$ (M - CH_4), 230.1338: found, 230.1281.

1,2-(*iso*-Butylethylidene)-3-(1-methyl-1-methoxyethyl)glycerol (12b)

MME ether **12b** was prepared from alcohol **12** (13.0 mmol, 2.27g) by George's procedure[15] to give 2.65g of product as a mixture of 1 : 1 diastereomers (90 °C, 0.80 Torr.; 83% yield). After work-up the compound was purified by vacuum distillation.: colorless oil; IR (neat, cm^{-1}): ν = 2990 (s), 2955 (s), 2872 (m), 1460 (m), 1380 (m), 1215 (m), 1186 (m), 1157 (m), 1084 (m), 1053 (s); ^1H NMR ($CDCl_3$): δ = 0.94 (d, 6H, *J* = 6.6 Hz), a pair of singlet at 1.31 and 1.36, 1.33 (s, 3H), 1.34 (s, 3H), a pair of doublet (2H) at 1.55 and 1.57 (*J* = 5.9 and 6.6 Hz, respectively), 1.73-1.87 (m, 1H), a pair of singlet (3H) at 3.19 and 3.20, 3.35-3.56 (m, 2H), 3.65-3.78 (m, 1H), 4.00-4.09 (m, 1H), 4.15-4.28 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = (selected peaks) a pair at 47.15 and 48.34, a pair at 62.19 and 62.32, 66.97, 67.08, a pair at 74.48 and 75.00, a pair at 100.11 and 111.27; MS (70eV): *m/z* = 246 (M^+, 0.5), 214 (5), 199 (14), 157 (100), 143 (19), 117 (80), 99 (39), 85 (47), 72 (38), 57 (65); HRMS: Calc. for $C_{12}H_{23}O_3$ (M - CH_3O), 215.1647: found, 215.1580.

Typical procedure of cleavage reaction for ethers

To a solution of 0.6 mmol of ether in 20 ml of methanol was added 25 mg of catalyst and the mixture was stirred. The progress of the reaction was monitored by TLC analysis. When heating temperature exceeded 64 °C the reactions were performed in a 100 ml autoclave. When the reaction was over, the mixture was filtered through a sintered glass funnel (No. 4) and washed with methanol followed by evaporation of the solvent. When the unaltered compound was detected the mixture was purified by column chromatography on silica gel eluting with a hexane : ethyl acetate mixture.

Cleavage reaction for 3,7-dimethyl-1,7-bis(tetrahydropyranyloxy)octane (9a)

Bis-THP ether **9a** (2.05g, 6.00 mmol) in 200 ml of methanol was allowed to react in the presence of 250 mg of SA-3 to give 0.388g of bis-THP ether **9a** (19% yield) and 1.17g 3,7-Dimethyl-1-tetrahydropyranyloxy-7-octanol (**9**) (76% yield) were obtained.: colorless oil; IR (neat, cm^{-1}): ν = 3450 (br, m), 2940 (s), 2872 (s), 1465 (m), 1380 (m), 1136 (m), 1120 (m), 1078 (m), 1026 (s); ^1H NMR ($CDCl_3$): δ = 0.91 (d, 3H, *J* = 6.3 Hz), 1.08-1.20 (m, 1H), 1.21 (s, 6H), 1.26-1.48 (m, 6H), 1.51-1.84 (m, 9H), 3.35-3.52 (m, 2H), 3.72-3.90 (m, 2H), 4.55-4.59 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = (selected peak) 44.22, 62.32, a pair at 65.88 and 66.00, 70.99, a pair at 98.78 and 98.99; MS (70eV): *m/z* = 252 (5), 219(4), 179 (4), 138 (48), 123 (77), 109 (34), 95 (91), 81 (100), 69 (81), 55 (68); HRMS: Calc. for $C_{12}H_{20}O_2$ (M - $C_3H_{10}O$), 196.1463: found, 196.1425.

Cleavage reaction for 3,7-dimethyl-1,7-bis(methoxymethoxy)octane (10a)

Bis-MOM ether **10a** (1.57g, 6.00 mmol) in 200 ml of methanol was allowed to react in the presence of 250 mg of SA-3 to give 0.226g of bis-MOM ether **10a** (14% yield) and 1.07g 3,7-Dimethyl-1-methoxymethoxy-7-octanol (**10**) (82% yield).: colorless oil; IR (neat, cm^{-1}): ν = 3475 (br, s), 2980 (s), 2960 (s), 2900 (s), 1466 (m), 1379 (m), 1213 (m), 1155 (m), 1111 (m), 1040 (m), 918 (m); ^1H NMR ($CDCl_3$): δ = 0.91 (d, 3H, J = 6.6 Hz), 1.13-1.21 (m, 1H), 1.21 (s, 6H), 1.28-1.51 (m, 6H), 1.58-1.70 (m, 2H), 1.74-1.77 (m, 1H), 3.36 (s, 3H), 3.56 (t, 2H, J = 6.3 Hz), 4.62 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 19.53, 21.69, 29.18, 29.29, 29.85, 36.75, 37.59, 44.20, 55.11, 66.07, 70.98, 96.04; MS (70eV): m/z = 217 (M^+-1, 0.5), 168 (18), 155 (9), 137 (28), 123 (20), 111 (19), 95 (65), 81 (78), 67 (100), 55 (71); HRMS: Calc. for $C_{11}H_{21}O_2$ (M - CH_5O), 185.1542: found, 185.1528.

Cleavage reaction of 1,2-Isopropylidene-3-methoxymethylglycerol (13c)

MOM ether **13c** (1.06g, 6.00 mmol) in 200 ml of methanol was allowed to react in the presence of 250 mg of SA-3 to give 0.556g of **1-(methoxymethyl)glycerol (14)** (68% yield).: colorless oil; IR (neat, cm^{-1}): ν = 3350(br, s), 2987 (s), 2889 (s), 1455 (m), 1213 (m), 1152 (s), 1113(s), 1038 (s), 920 (m); ^1H NMR ($CDCl_3$): δ = 3.38 (s, 3H), 3.53-3.76 (m, 4H), 3.84-3.93 (m, 1H), 4.65 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 55.42, 63.86, 69.74, 71.01, 96.98; MS (70eV): m/z = 136 (M^+, 0.2), 105 (67), 88 (46), 73 (100), 61 (59); HRMS: Calc. for $C_4H_9O_3$ (M - CH_3O), 105.0552: found, 105.0555.

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