Counterattack Reagent Bis(trimethylsilyl)acetamide in the Disilylation of Diols

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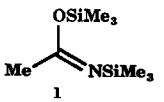
The counterattack method was applied to the disilylation of diols. Treatment of various diols with 0.3 or 1.1 equivalents of potassium hydride and 1.1 equivalents of bis(trimethylsilyl)-acetamide in THF gave the corresponding disilyl ethers in good to excellent yields (60–95%). The diols may contain other functionalities, such as amide, amine, ether, and thioether. The diols used in the disilylation were **2a–14a**. The newly developed disilylation proceeded in one flask by a sequential deprotonation-silylation-deprotonation-silylation pathway. This disilylation also represents an example of a "tandem double-counterattack process". Bis(trimethylsilyl)-acetamide acted as a counterattack reagent; it provided two Me_3Si groups to diols and produced amides as bases.

Trimethylsilylation is useful in the protection of functional groups bearing labile protons[1]. Silylation of alcohols, especially diols, polyols, and carbohydrates, can increase their volatility and thermal stability[2–5]. Consequently, the silylated species are more suitable than the parent alcohols for the analysis by GC and mass spectrometry. The silylating agents *N,O*-bis(trimethylsilyl)acetamide (BSA, **1**)[6–8], *N,N'*-bis(trimethylsilyl)urea[9], and *N*-(trimethylsilyl)acetamide[10] are particularly attractive, because they can efficiently donate the Me_3Si group and produce neutral by-products[5,9].



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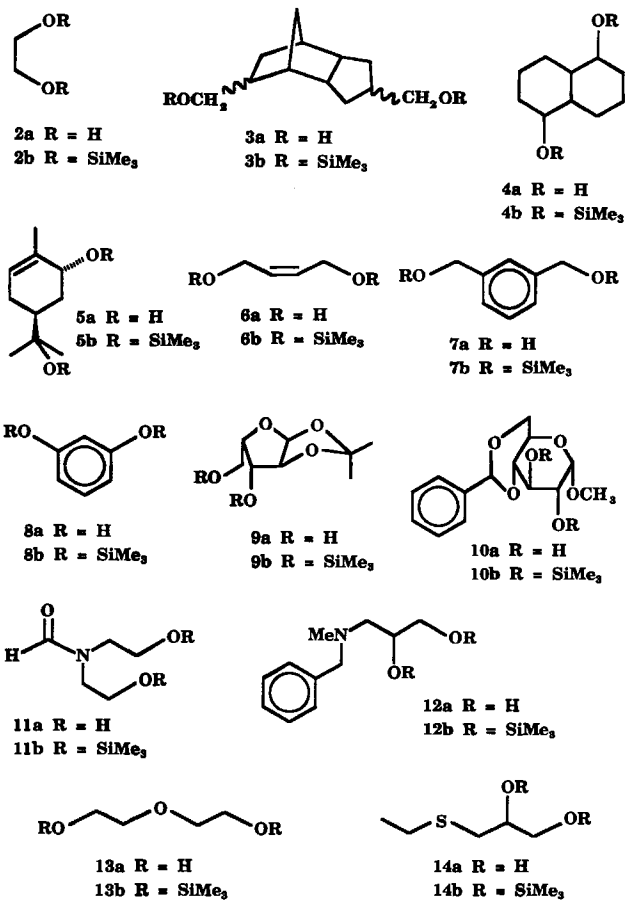
The reagent BSA can silylate amides, amino acids, carboxylic acids, enols, phenols, and ureas[7]. Lasocki[11] reported a method for the silylation of diols, in which an excess of BSA was used[12]. For the GC-MS analysis, Myerson et al. treated a high-molecular-weight diol with BSA in pyridine and obtained the corresponding disilyl ether[13]. Disilylation of 3-(1-hydroxypentadecyl)catechol with 2.2 equivalents of BSA was also reported[14]. Furthermore, BSA can silylate tertiary alcohols[4,8]. In all of these reactions, only one of the two Me_3Si groups of BSA is utilized.

In connection with our research in the development of counterattack reagents[15], we investigated the possibility of utilizing both Me_3Si groups of BSA in the disilylation of diols. We found that BSA acted as a counterattack reagent and disilylated diols efficiently under alkaline conditions.

Results

We treated various types of diols (**2a–14a**) with 0.3 or 1.1 equivalents of potassium hydride (KH) and 1.1 equivalents of BSA in tetrahydrofuran (THF) at room temperature. The corresponding disilylated ethers **2b–14b** were produced in good to excellent yields (60–95%, Table 1).



All the disilylated products were obtained pure by filtration of the crude products through silica gel. Starting materials and monosilylated byproducts were easily separated by column chromatography with nonpolar solvents as eluants, such as hexanes.

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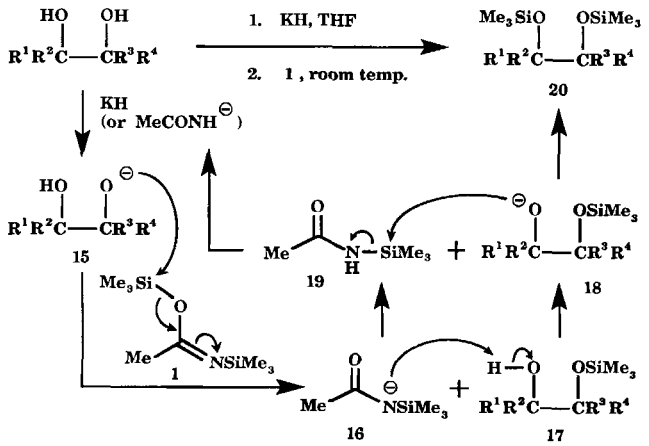
Table 1. Disilylation of diols with bis(trimethylsilyl)acetamide (BSA, **1**; 1.1 equiv.) and KH in THF at room temperature

Diol	Disilyl ether	Equiv. of KH	Yield (%)	Yield (%) by other methods
2a	**2b**	1.1	90	65[24]
3a	**3b**	1.1	85	–
3a	**3b**	0.3	83	–
4a	**4b**	1.1	80	–
4a	**4b**	0.3	81	–
5a	**5b**	1.1	72	–
6a	**6b**	1.1	82	>80[21]
7a	**7b**	0.3	85	–
8a	**8b**	0.3	80	55[17]
9a	**9b**	1.1	79	–
9a	**9b**	0.3	81	–
10a	**10b**	1.1	60	41[2]
10a	**10b**	0.3	65	41[2]
11a	**11b**	1.1	81	88[18]
12a	**12b**	0.3	86	–
13a	**13b**	1.1	72	–
13a	**13b**	0.3	74	–
14a	**14b**	0.3	95	–

Discussion

Scheme 1 illustrates our design of the double trimethylsilylation of diols by use of BSA (**1**) and KH. In the entire transformation, BSA (**1**) provides two Me_3Si groups and is the source of amide ion **16** and $MeCONH^-$.

Scheme 1



In the first silylation, BSA (**1**) is attacked by alkoxide **15** to give amide **16** and alcohol **17**. Amide **16** then acts as a base to counterattack the stable intermediate **17** to produce alkoxide **18** and silyl amide **19**. Therefore, BSA (**1**) is regarded as a counterattack reagent.

In the reaction **16** + **17**→**18** + **19**, alcohol **17** was attacked by amide **16** to give alkoxide **18**. Then **18** counterattacks **19** to complete the second silylation and to give the desired product **20**. This double trimethylsilylation represents an example of a tandem double-counterattack process[15]. In the entire process, BSA (**1**) offers three reacting centers: two electrophilic silicon atoms and one nucleophilic nitrogen atom.

The proton transfer proceeded between **16** and **17**, because amides and alcohols have comparable pK_a values (ca. 18)[16]. Being an effective Me_3Si-donating agent[10], trimethylsilylacetamide (**19**) was able to silylate **18**. Furthermore, Klebe et al. reported that both of the Me_3Si groups of BSA (**1**) can be exchanged in cases where the position of equilibrium favors the transfer, as with alcoholic hydroxyl groups[7].

By using the counterattack method, we were able to obtain disilyl ethers from acyclic (**2a** and **3a**), alicyclic (**4a**), allylic (**5a** and **6a**), benzylic (**7a**), and aromatic (**8a**) diols, as well as carbohydrates (**9a** and **10a**). The diols may contain other functionalities, such as amide (**11a**), amine (**12a**), ether (**13a**), and thioether (**14a**).

Lebedev et al. prepared disiloxybenzene **8b** in 55% overall yield by stepwise silylations of resorcinol (**8a**) with hexamethyldisilathiane[17]; the counterattack method transformed **8a** into **8b** in 80% yield by a one-flask process. Hedgley and Overend used a traditional method for the preparation of **10b** from **10a** in 41% yield with chlorotrimethylsilane and pyridine[2]; the counterattack method provided a 65% yield. Sheludyakov et al. prepared **11b** in 88% yield by using bis(2-trimethylsiloxyethyl)amine and allyl formate[18]; the counterattack method gave **11b** from **11a** in 81% yield.

Some of disilyl ethers in Table 1 possess synthetic value: **2b** may selectively monoacetalize dicarbonyl compounds at the less sterically congested site[19, 20]; **6b** is a precursor for an allylsilane[21]; **8b** can be used for the synthesis of diglucosides[22].

The mechanism shown in Scheme 1 indicates that BSA (**1**) is transformed into $MeCONH^-$ after the second silylation (i.e., **18**→**20**). Amide $MeCONH^-$ should be able to serve as a base to remove an OH proton from the starting diols. Therefore, only a catalytic amount of base would be required to initiate the reaction. A similar catalytic cycle has been established in the polysilylation of hydrazines[23].

To test this hypothesis, we treated diols **3a**, **4a**, **9a**, **10a**, and **13a** with BSA (**1**) and 0.3 equivalent of KH. The corresponding disilyl ethers **3b**, **4b**, **9b**, **10b**, and **13b** were obtained in yields comparable with those by use of 1.1 equivalents of KH (Table 1). This base-catalyzed disilylation was further utilized in the conversion of **7a**, **8a**, **12a**, and **14a** into the corresponding bis(trimethylsilyl) derivatives, which were obtained in 80–95% yields.

Conclusion

Reaction of diols with 1.1 equivalents of BSA (**1**) under alkaline conditions gave bis(trimethylsilyl) ethers in good to excellent yields. In the disilylation, BSA (**1**) acted as a counterattack reagent and exhibited multiple functions. Bis(trimethylsilyl)acetamide transferred both Me_3Si groups onto a diol and provided amide anions, which deprotonated the intermediates and the starting diol. Therefore, only a catalytic amount of base (i.e., KH) was needed in order to initiate the disilylation. This "one-flask" disilylation involved sequential silylation-proton abstraction-silylation.

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Experimental

General Procedure. All reactions were carried out in oven-dried glassware (120°C) under an atmosphere of nitrogen. – EtOAc and hexanes from Tilley Chemical Co. were dried with and distilled from CaH_2; THF and diethyl ether from J. T. Baker Chemical Co. were freshly distilled from Na and benzophenone. – BSA (**1**), KH (35%, dispersion in mineral oil), and all the diols were purchased from Aldrich Chemical Co. and used without further purification. – Melting points: Büchi 510 melting point apparatus. – TLC: precoated plates purchased from Analtech, Inc. (silica gel GHLF); visualization of spots on TLC plates by use of UV light or 2.5% phosphomolybdic acid in ethanol with heating or both; mixtures of EtOAc and hexanes as eluants. – GC: Hewlett-Packard 5794A instrument, equipped with a 12.5-m cross-linked methylsilicone gum capillary column (0.2-mm i.d.). – Purification of the products by gravity column chromatography by use of EM Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). – IR: Perkin-Elmer 599B or 710B spectrophotometer; wavenumbers referenced to the polystyrene 1601-cm^{-1} absorption. – ^1H NMR: Varian CFT-20 spectrometer with $CDCl_3$ as solvent and TMS as an internal standard; coupling constants J in Hz. – MS (high-resolution): VG Analytical 70-S mass spectrometer; 70 eV.

Standard Procedure for the Disilylation of Diols: In a one-necked, round-bottomed flask, euipped with a stirring bar and a rubber septum, KH (1.1 or 0.3 equiv.) was washed with hexanes (3 × 5 ml). Hexanes were removed to give KH as a white powder. A diol in THF was added to the flask at 0°C under an atmosphere of nitrogen. After 1 h of stirring, **1** was added to the solution, and stirring was continued at room temp. for 70 h. The reaction mixture was filtered through Celite and washed with diethyl ether. The filtrate was concentrated in vacuo and the residue chromatographed (10% EtOAc in hexanes as eluant) to give a pure disilyl ether.

1,2-Bis(trimethylsiloxy)ethane[24] (**2b**): The standard procedure was followed: KH (171 mg, 1.49 mmol, 1.1 equiv.), **2a** (84 mg, 1.35 mmol, 1.0 equiv.), **1** (303 mg, 1.49 mmol, 1.1 equiv.), THF (13 ml). After workup and purification, **2b** was obtained as a colorless oil in 90% yield (248 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 70°C, duration 2.00 min, increment rate 10°C/min, final temp. 250°C): t_R = 2.94 min. – ^1H NMR ($CDCl_3$): δ = 0.11 [s, 18H, 2 $OSi(CH_3)_3$], 3.64 (s, 4H, OCH_2CH_2O). – IR (neat): $\tilde{\nu}$ = 2960 (s), 1350 (s), 1300 (s, C–O), 1255 (s, Si–CH_3), 1110 (s, O–Si), 840 (m, Si–CH_3) cm^{-1}. – The physical and spectroscopic data of **2b** were consistent with those of an authentic sample.

$C_8H_{22}O_2Si_2$ Calcd. 191.09 [$M^+ - CH_3$] Found 191.14 (MS)

4,8-Bis[(trimethylsiloxy)methyl]tricyclo[5.2.1.0^{2,6}]decane (**3b**). – *Method 1:* The standard procedure was followed: KH (135 mg, 1.18 mmol, 1.1 equiv.), **3a** (mixture of diastereomers; 210 mg, 1.07 mmol, 1.0 equiv.), **1** (239 mg, 1.18 mmol, 1.1 equiv.), THF (11 ml). After workup and purification, **3b** was obtained as a colorless oil in 85% yield (301 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 80°C, duration 1.00 min, increment rate 20°C/min, final temp. 250°C): t_R = 7.75 and 7.95 min. – ^1H NMR ($CDCl_3$): δ = 0.10 [s, 18H, 2 $OSi(CH_3)_3$], 0.90–2.55 (m, 14H, 4 CH_2, 6 CH), 3.20–3.60 (m, 4H, 2 OCH_2). – IR (neat): $\tilde{\nu}$ = 2940 (s), 2860 (sh), 1460 (w), 1368 (w), 1240 (s, Si–CH_3), 1068 (s, O–Si), 860 (s, Si–CH_3), 811 (s), 726 (m) cm^{-1}.

$C_{18}H_{36}O_2Si_2$ (340.7) Calcd. C 63.47 H 10.65 Si 16.49
Found C 63.62 H 10.60 Si 16.55

Calcd. 325.2019 [$M^+ - CH_3$] Found 325.2022 (MS)

Method 2: The standard procedure was followed: KH (135 mg, 1.18 mmol, 0.3 equiv.), **3a** (mixture of diastereomers; 770 mg, 3.92 mmol, 1.0 equiv.), **1** (878 mg, 4.32 mmol, 1.1 equiv.), THF (39 ml). After workup and purification, **3b** was obtained as a colorless oil in 83% yield (1.08 g). Its physical properties were identical to those listed above.

1,5-Bis(trimethylsiloxy)bicyclo[4.4.0]decane (**4b**). – *Method 1:* The standard procedure was followed: KH (148 mg, 1.29 mmol, 1.1 equiv.), **4a** (mixture of diastereomers; 201 mg, 1.17 mmol, 1.0 equiv.), **1** (263 mg, 1.29 mmol, 1.1 equiv.), THF (12 ml). After workup and purification, **4b** was obtained as a colorless oil in 80% yield (295 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 50°C, duration 2.00 min, increment rate 15°C/min, final temp. 250°C): t_R = 10.60–11.29 min. – ^1H NMR ($CDCl_3$): δ = 0.09 [s, 18H, 2 $OSi(CH_3)_3$], 1.17–1.85 (m, 14H, 2 CH, 6 CH_2), 3.45–3.83 (m, 2H, 2 OCH). – IR (neat): $\tilde{\nu}$ = 2910 (s), 2830 (s), 1435 (m), 1361 (m, C–H), 1230 (s, Si–CH_3), 1112 (m, O–Si), 1080 (sh), 1058 (s, C–O), 943 (m), 919 (m), 861 (s), 843 (s), 808 (s, Si–CH_3) cm^{-1}.

$C_{16}H_{34}O_2Si_2$ (314.6) Calcd. C 61.08 H 10.89 Si 17.85
Found C 60.90 H 11.00 Si 17.79

Calcd. 314.2097 Found 314.2099 (MS)

Method 2: The standard procedure was followed: KH (40 mg, 0.35 mmol, 0.3 equiv.), **4a** (mixture of diastereomers; 201 mg, 1.17 mmol, 1.0 equiv.), **1** (264 mg, 1.29 mmol, 1.1 equiv.), THF (12 ml). After workup and purification, **4b** was obtained as a colorless oil in 81% yield (300 mg). Its physical properties were identical to those listed above.

(±)-trans-1-Methyl-4-[1-methyl-1-(trimethylsiloxy)ethyl]-6-(trimethylsiloxy)cyclohexene (**5b**): The standard procedure was followed: KH (153 mg, 1.33 mmol, 1.1 equiv.), **5a** (206 mg, 1.21 mmol, 1.0 equiv.), **1** (271 mg, 1.33 mmol, 1.1 equiv.), THF (12 ml). After workup and purification, **5b** was obtained as a colorless oil in 72% yield (336 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 70°C, duration 2.00 min, increment rate 10°C/min, final temp. 250°C): t_R = 11.23 min. – ^1H NMR ($CDCl_3$): δ = 0.09 and 0.15 [2 s, 18H, 2 $OSi(CH_3)_3$], 1.11–1.36 [br., 6H, $C(CH_3)_2OSi$], 1.65–2.27 (m, 8H, C=CCH_3, 2 CH_2, $CHCMe_2OSi$), 3.95–4.11 (br. m, 1H, C=CCHOSi), 5.45–5.66 (m, 1H, C=CH). – IR (neat): $\tilde{\nu}$ = 2955 (s), 2905 (m), 1665 (br., w, C=C), 1440 (w), 1383 (m), 1367 (m), 1252 (s, Si–CH_3), 1162 (m), 1148 (m), 1040 (s, O–Si), 992 (m), 911 (m), 842 (s, Si–CH_3), 755 (m) cm^{-1}.

$C_{16}H_{34}O_2Si_2$ (314.6) Calcd. C 61.08 H 10.89 Si 17.85
Found C 61.21 H 11.80 Si 17.77

Calcd. 314.2097 Found 314.2106 (MS)
$C_{13}H_{26}O_2Si$ (monosilylated diol)
Calcd. 242.1702 Found 242.1708 (MS)

1,4-Bis(trimethylsiloxy)-2-butene[21] (**6b**): The standard procedure was followed: KH (292 mg, 2.55 mmol, 1.1 equiv.), **6a** (204 mg, 2.32 mmol, 1.0 equiv.), **1** (518 mg, 2.55 mmol, 1.1 equiv.), THF (23 ml). After workup and purification, **6b** was obtained as a colorless oil in 82% yield (441 mg). – GC (injector temp. 260°C; column temp.

program: initial temp. 70°C, duration 2.00 min, increment rate 10°C/min, final temp. 250°C): t_R = 5.91 min. – ^{1}H NMR ($CDCl_3$): δ = 0.12 [s, 18H, 2 $OSi(CH_3)_3$], 4.18 (br., 4H, 2 $SiOCH_2$), 5.39–5.61 (m, 2H, CH=CH). – IR (neat): $\tilde{\nu}$ = 3020 (w, C=C–H), 2945 (s), 2890 (m), 1395 (br., w), 1250 (s, Si–CH_3), 1071 (s, O–Si), 866 (s), 832 (s, Si–CH_3) cm^{-1}.

$C_{10}H_{24}O_2Si_2$ Calcd. 217.1080 [$M^+ - CH_3$]
Found 217.1082 (MS)

1,3-Bis[(trimethylsiloxy)methyl]benzene (**7b**): The standard procedure was followed: KH (84 mg, 0.73 mmol, 0.3 equiv.), **7a** (338 mg, 2.45 mmol, 1.0 equiv.), **1** (547 mg, 2.69 mmol, 1.1 equiv.), THF (25 ml). After workup and purification, **7b** was obtained as a colorless oil in 85% yield (587 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 70°C, duration 2.00 min, increment rate 10°C/min, final temp. 250°C): t_R = 11.27 min. – ^{1}H NMR ($CDCl_3$): δ = 0.07 [s, 18H, 2 $OSi(CH_3)_3$], 4.61 (s, 4H, 2 $SiOCH_2$), 7.00–7.25 (m, 4H, C_6H_4). – IR (neat): $\tilde{\nu}$ = 3020 (w, =C–H), 2950 (s), 1610 (m, C=C), 1460 (m), 1375 (m), 1155 (s, C–O), 1060 (s, Si–O), 860 (s, Si–CH_3), 750 (s) cm^{-1}.

$C_{14}H_{26}O_2Si_2$ (282.5) Calcd. C 59.52 H 9.28 Si 19.88
Found C 59.45 H 9.37 Si 19.69
Calcd. 267.1237 [$M^+ - CH_3$] Found 267.1237 (MS)

1,3-Bis(trimethylsiloxy)benzene[17, 22, 25] (**8b**): The standard procedure was followed: KH (190 mg, 1.63 mmol, 0.3 equiv.), **8a** (601 mg, 5.45 mmol, 1.0 equiv.), **1** (1.22 g, 5.99 mmol, 1.1 equiv.), THF (55 ml). After workup and purification, **8b** was obtained as a colorless oil in 80% yield (1.11 g). – GC (injector temp. 260°C; column temp. program: initial temp. 50°C, duration 2.00 min, increment rate 15°C/min, final temp. 250°C): t_R = 8.61 min. – ^{1}H NMR ($CDCl_3$): δ = 0.25 [s, 18H, 2 $OSi(CH_3)_3$], 6.25–7.16 (m, 4H, C_6H_4). – IR (neat): $\tilde{\nu}$ = 3080 (w), 3045 (w), 2965 (s), 2910 (w), 1602 (s, C=C), 1482 (s), 1298 (s, C–O), 1254 (s, Si–CH_3), 1179 (s), 1146 (s, O–Si), 993 (s), 907 (m), 843 (s, Si–CH_3), 773 (m), 748 (m) cm^{-1}.

$C_{12}H_{22}O_2Si_2$ Calcd. 254.1158 [$M^+ - CH_3$]
Found 254.1156 (MS)

1,2-O-Isopropylidene-3,5-bis-O-trimethylsilyl-xylofuranose (**9b**). – *Method 1:* The standard procedure was followed: KH (166 mg, 1.45 mmol, 1.1 equiv.), **9a** (250 mg, 1.31 mmol, 1.0 equiv.; Aldrich 29,636-8), **1** (294 mg, 1.45 mmol, 1.1 equiv.), THF (13 ml). After workup and purification, **9b** was obtained as a colorless oil in 79% yield (348 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 50°C, duration 2.00 min, increment rate 15°C/min, final temp. 250°C): t_R = 10.22 min. – ^{1}H NMR ($CDCl_3$): δ = 0.11 and 0.15 [2 s, 18H, 2 $OSi(CH_3)_3$], 1.31 and 1.49 [2 s, 6H, $OC(CH_3)_2O$], 3.64–3.82 (m, 2H, CH_2OSi), 4.04–4.41 (m, 3H, 3 OCH), 5.90 (d, *J* = 3.8, 1H, OCHO). – IR (neat): $\tilde{\nu}$ = 2945 (s), 2920 (s), 1445 (w), 1362 (m), 1241 (s, Si–CH_3), 1210 (m), 1118 (s), 1070 (s, O–Si), 1005 (s), 859 (s), 820 (s, Si–CH_3), 745 (m) cm^{-1}.

$C_{14}H_{30}O_5Si_2$ (334.6) Calcd. C 50.26 H 9.04 Si 16.79
Found C 50.20 H 9.11 Si 16.68
Calcd. 319.1397 [$M^+ - CH_3$] Found 319.1401 (MS)

Method 2: The standard procedure was followed: KH (108 mg, 0.95 mmol, 0.3 equiv.), **9a** (598 mg, 3.15 mmol, 1.0 equiv.), **1** (706 mg, 3.47 mmol, 1.1 equiv.), THF (32 ml). After workup and purification, **9b** was obtained as a colorless oil in 81% yield (855 mg). Its physical properties were identical to those listed above.

Methyl 4,6-O-Benzylidene-2,3-bis-O-trimethylsilyl-α-D-glucopyranoside[2, 3] (**10b**). – *Method 1:* The standard procedure was followed: KH (89 mg, 0.78 mmol, 1.1 equiv.), **10a** (199 mg, 0.71 mmol, 1.0 equiv.), **1** (159 mg, 0.78 mmol, 1.1 equiv.), THF (7.0 ml). After workup, purification, and recrystallization (hexanes), **10b** was obtained as a colorless solid in 60% yield (181 mg), mp 74.5–75.5°C (ref.[2]) oil, bp 148–150°C/0.15 Torr). – GC (injector temp. 260°C; column temp. program: initial temp. 80°C, duration 1.00 min, increment rate 20°C/min, final temp. 250°C): t_R = 9.86 min. – ^{1}H NMR ($CDCl_3$): δ = 0.09 and 0.16 [2 s, 18H, 2 $OSi(CH_3)_3$], 3.41 (s, 3H, OCH_3), 3.57–3.99 (m, 6H, 4 OCH, OCH_2), 4.61 (d, *J* = 3.6, 1H, MeOCHO), 5.49 (s, 1H, OCHPh), 7.23–7.58 (m, 5H, C_6H_5). – IR (neat): $\tilde{\nu}$ = 2940 (m), 2880 (m), 1445 (br., w), 1365 (m), 1239 (s, Si–CH_3), 1163 (m), 1137 (m), 1098 (m), 1078 (s, O–Si), 1040 (s), 980 (m), 869 (s), 830 (s, Si–CH_3), 738 (m) cm^{-1}.

$C_{20}H_{34}O_6Si_2$ Calcd. 411.1659 [$M^+ - CH_3$]
Found 411.1667 (MS)

Method 2: The standard procedure was followed: KH (24 mg, 0.21 mmol, 0.3 equiv.), **10a** (199 mg, 0.71 mmol, 1.0 equiv.), **1** (158 mg, 0.78 mmol, 1.1 equiv.), THF (7.0 ml). After workup, purification, and recrystallization (hexanes), **10b** was obtained as a colorless solid in 65% yield (197 mg). Its physical properties were identical to those listed above.

N,N-Bis[2-(trimethylsiloxy)ethyl]formamide[18] (**11b**). The standard procedure was followed: KH (189 mg, 1.65 mmol, 1.1 equiv.), **11a** (202 mg, 1.50 mmol, 1.0 equiv.), **1** (336 mg, 1.65 mmol, 1.1 equiv.), THF (15 ml). After workup and purification, **11b** was obtained as a colorless oil in 81% yield (338 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 50°C, duration 2.00 min, increment rate 15°C/min, final temp. 250°C): t_R = 10.19 min. – ^{1}H NMR ($CDCl_3$): δ = 0.10 [s, 18H, 2 $OSi(CH_3)_3$], 3.23–3.92 (m, 8H, 2 OCH_2CH_2N), 8.06 (s, 1H, NCHO). – IR (neat) $\tilde{\nu}$ = 2955 (s), 2865 (s), 1678 (s, C=O), 1430 (br., m), 1397 (m), 1298 (w, C–O), 1249 (s, Si–CH_3), 1106 (s, O–Si), 1081 (s), 934 (s), 841 (s, Si–CH_3), 823 (s), 748 (m) cm^{-1}.

$C_{11}H_{27}NO_3Si_2$ Calcd. 262.1295 [$M^+ - CH_3$]
Found 262.1297 (MS)

3-(N-Benzyl-N-methylamino)-1,2-bis(trimethylsiloxy)propane (**12b**): The standard procedure was followed: KH (114 mg, 1.00 mmol, 0.3 equiv.), **12a** (650 mg, 3.33 mmol, 1.0 equiv.), **1** (745 mg, 3.66 mmol, 1.1 equiv.), THF (33 ml). After workup and purification, **12b** was obtained as a colorless oil in 86% yield (972 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 50°C, duration 2.00 min, increment rate 15°C/min, final temp. 250°C): t_R = 11.68 min. – ^{1}H NMR ($CDCl_3$): δ = 0.09 and 0.12 [2 s, 18H, 2 $OSi(CH_3)_3$], 2.21 (m, 3H, NCH_3), 2.31–2.52 (m, 2H, NCH_2). 3.52 (s, 2H, NCH_2Ph), 3.38–3.85 (m, 3H, $SiOCH_2CHOSi$), 7.28 (s, 5H, C_6H_5). – IR (neat): $\tilde{\nu}$ = 3055 (w), 3020 (m, Ar–H), 2940 (s), 2890 (m), 2765 (m), 1484 (w), 1441 (m), 1353 (w), 1237 (s, Si–CH_3), 1104 (s, O–Si), 1071 (s), 1018 (m), 973 (m), 830 (s, Si–CH_3), 737 (m) cm^{-1}.

$C_{17}H_{33}NO_2Si_2$ (339.6) Calcd. C 60.12 H 9.79 Si 16.54
Found C 60.30 H 9.94 Si 16.38
Calcd. 339.2050 Found 339.2054 (MS)

Bis(2-trimethylsiloxyethyl) Ether (**13b**). – *Method 1:* The standard procedure was followed: KH (131 mg, 1.14 mmol, 1.1 equiv.), **13a** (110 mg, 1.04 mmol, 1.0 equiv.), **1** (232 mg, 1.14 mmol, 1.1 equiv.), THF (10 ml). After workup and purification, **13b** was obtained as a colorless oil in 72% yield (187 mg). – GC (injector temp. 260°C; column temp. program: initial temp. 70°C, duration 2.00 min, increment rate 10°C/min, final temp. 250°C): t_R = 6.95 min. – ^{1}H NMR ($CDCl_3$): δ = 0.12 [s, 18H, 2 $OSi(CH_3)_3$], 3.64 (m, 8H, 2 $SiOCH_2CH_2$). – IR (neat): $\tilde{\nu}$ = 2960 (s), 1460 (m), 1357 (m), 1295

(s, C–O), 1250 (s, Si–CH_3), 1110 (s, O–Si), 840 (s, Si–CH_3), 755 (m) cm^{-1}.

$C_{10}H_{26}O_3Si_2$ (250.5) Calcd. C 47.95 H 10.46 Si 22.43
Found C 47.81 H 10.55 Si 22.39

Calcd. 235.1186 [$M^+ - CH_3$] Found 235.1191 (MS)

Method 2: The standard procedure was followed: KH (36 mg, 0.31 mmol, 0.3 equiv.), **13a** (109 mg, 1.04 mmol, 1.0 equiv.), **1** (233 mg, 1.14 mmol, 1.1 equiv.), THF (10 ml). After workup and purification, **13b** was obtained as a colorless oil in 74% yield (192 mg). Its physical properties were identical to those listed above.

3-Ethylthio-1,2-bis(trimethylsiloxy)propane (**14b**). The standard procedure was followed: KH (166 mg, 1.45 mmol, 0.3 equiv.), **14a** (657 mg, 4.82 mmol, 1.0 equiv.), **1** (1.08 g, 5.31 mmol, 1.1 equiv.), THF (48 ml). After workup and purification, **14b** was obtained as a colorless oil in 95% yield (1.29 g). – GC (injector temp. 260°C; column temp. program: initial temp. 50°C, duration 2.00 min, increment rate 15°C/min, final temp. 250°C): t_R = 8.71 min. – ^1H NMR ($CDCl_3$): δ = 0.12 and 0.14 [2 s, 18H, 2 OSi(CH_3)$_3$], 1.25 (t, *J* = 7.2, 3H, CH_3), 2.35–2.86 (m, 2 CH_2S), 3.47–3.90 (m, 3H, CHOSi, CH_2OSi). – IR (neat): $\tilde{\nu}$ = 2940 (s), 2910 (m), 2860 (w), 1400 (br., w), 1237 (s, Si–CH_3), 1106 (s, O–Si), 1061 (s) 855 (sh), 830 (s, Si–CH_3) cm^{-1}.

$C_{11}H_{28}O_2SSi_2$ (280.6) Calcd. C 47.09 H 10.06 S 11.43 Si 20.02
Found C 47.21 H 10.05 S 11.36 Si 20.15

Calcd. 265.1114 [$M^+ - CH_3$] Found 265.1116

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[405/89]