General access to a novel class of silyl heterocycles

GENERAL ACCESS TO A NOVEL CLASS OF SILYL HETEROCYCLES

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Dedicated to Professor Edmunds Lukevics on his 70th birthday

2-Trimethylsilyl five membered heterocycles can be accessed through reaction of bromo (methoxy)methyl trimethylsilane with 1,2-dithiols, 1,2-mercaptoalcohols, 1,2-mercaptoamines and 1,2-hydroxyamines, leading to the formation of several 2-silylated 1,3-dithiolanes, -oxathiolanes, -thiazolidines and -oxazolidines.

Keywords: organosilanes; dithiolanes; oxathiolanes; thiazolidines; oxazolidines; silyl heterocycles.

Five membered ring heterocyclic derivatives are valuable intermediates in organic synthesis. Compounds containing either one heteroatom, as furans and pyrrolidines, or two or more heteroatoms have played an important role in different synthetic strategies. Among these last structures 1,3-dioxolanes, [1,2] 1,3-oxathiolanes, [3] 1,3-thiazolidines, 1,3-oxazolidines, imidazolines and benzotriazole derivatives [4-8] found large application as building blocks for the construction of more complex molecules. [9]

Furthermore, umpolung reactivity is a valuable synthetic strategy in organic synthesis providing unconventional access to molecules through the formation of

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bonds *via* the inversion of normal reactivity. [10] In this context, the development of synthetic equivalents of acyl anions has recently actracted a great deal of interest, for the synthetic potential that such reaction may disclose. In this connection suitably protected carbonyl derivatives, and in particular heterocyclic derivatives, represent a very interesting class of compounds being able to act as equivalents of acyl anions. In this context, for instance, lithiated chiral oxazolidinones, including compounds derived from camphor, [11] have been reported to react with aldehydes, ketones and imines leading to enantioselective formylation of the carbonyl compounds. [12, 13] Oxazolidines as well found application as chiral formyl anion equivalents, either for direct metalation in the presence of (-)-sparteine [14] or through transmetalation of tributylstannyl derivative with BuLi and condensation with benzaldehyde. [15, 16] Also thiazolidines upon treatment with BuLi and aldehydes or ketones in the presence of (-)-sparteine afforded products with high e.e. but moderate diastereoselectivity. [17, 18] Isopropyl N-Boc-thiazolidines have been used as chiral organolithium compounds in the addition to aldehydes, leading to products in good stereoselectivity. [19] Thiazolidines are also metalated with BuLi *via* their respective formamidines, but 40-50% fragmentation of the heterocyclic ring has been observed. [20] Also chiral dioxolanes [15] and dioxolanones [2] found application as acyl anion equivalents.

1,3-Dithianes have also been widely used in umpolung reactivity. They can be easily metalated with BuLi and reacted with a wide range of electrophiles, thus evidencing their behaviour as useful syntons and umpoled reagents [21-27] but although several methods for their unmasking have been reported, [28, 29] they still suffer from the

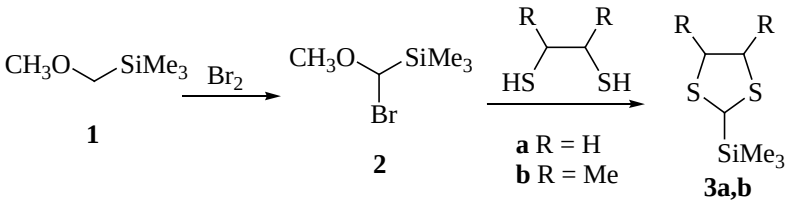
generally harsh condition of their unblocking. On the other hand, dioxolanes, oxathiolanes, dithiolanes, and thiazolidines have been reported to be unmasked under milder conditions, thus possibly giving a broader spectrum of application to such molecules in the generation of formyl and acyl anion equivalents. Unfortunately such heterocycles suffer generally of difficulties in their functionalizazion under strong basic conditions. For instance, 1,3-dithiolanes, upon treatment with bases, have been reported to undergo either deprotonation at C-2 with subsequent cycloelimination to dithiocarboxylate anions and ethylene derivatives [30] or at C-4 to afford products derived from thiocarbonyl derivatives and vinyl thiolate anion. [31, 32] A similar behaviour was evidenced in unsubstituted dioxolanes, whose anions undergo fragmentation. Thiazolidines also are reported to be metalated but only in the presence of specific nitrogen protecting groups. Only two examples of functionalization under basic conditions of dithiolanes bearing an electron withdrawing group are reported in the literature, thus evidencing the still present need for a general protocol for their functionalization. [33-36] Thus, taking advantage of the reactivity of organosilanes, which seems to occur *via* a pentacoordinated silicon species, and not a free carbanion, we envisaged that the functionalization of the C-Si bond in silyl heterocycles, could possibly lead to the solution of such problem, and to the development of a novel and general functionalization methodology for such labile heterocycles [37].

In this context, direct access to silyl heterocycles being difficult or even prevented, an alternative access to such molecules had to be devised.

A general access to silyl dithiolanes, and, more generally, to five member ring silylated heterocycles could be envisaged through the simple reaction of bifunctional molecules, such as dithiols, amino alcohols, amino thiols, mercapto alcohols with formyl trimethylsilane. Difficulties anyway in the generation and handling of such labile molecule [38] led to search for a possible synthetic equivalent of such compound, and we envisaged in bromo (methoxy)methyl trimethylsilane **2** the reagent of choice. Such molecule in fact, can be obtained in quantitative yield by treatment of the commercially available methoxy methyl trimethylsilane **1** with bromine, [39-41] and subsequent one pot treatment with the required mercaptan (Scheme 1).

Thus, we reacted 1,2-ethanedithiol with bromo methoxy derivative **2**, and we were able to isolate in 72% yield the corresponding 2-trimethylsilyl-1,3-dithiolane **3a** (Scheme 1), which could be easily purified on tlc. Such reaction then evidenced the

Scheme 1

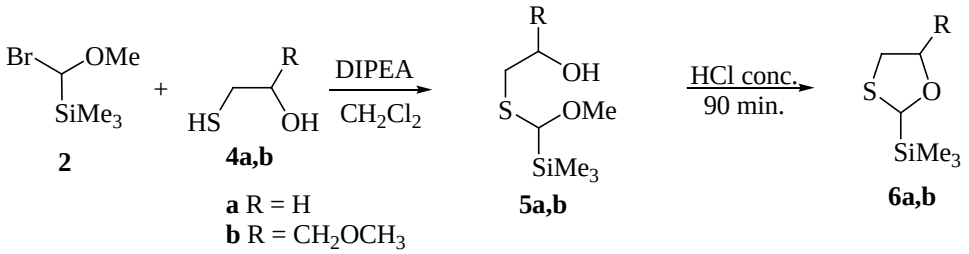


ability of **2** to act as a real synthetic equivalent of formyl silane, and opened the way to a possible general route to access a wide variety of silyl heterocycles.

In a similar way, by reacting *meso*-butane-2,3-dithiol both *cis* and *trans* diastereoisomers of *meso*-4,5-dimethyl-2-trimethylsilyl-1,3-dithiolane **3b** were isolated (Scheme 1).

Then, with the aim to seek for the generality of the present reaction, we decided to test different bifunctional molecules, and we took into consideration the possible access to silyl oxathiolanes, and thus freshly prepared methoxy bromo methyltrimethylsilane **2** was reacted *in situ* with β-mercaptoethanol **4a** at room

Scheme 2



temperature, in the presence of diisopropylethylamine (*i*-Pr_2NEt, DIPEA) and stirred overnight (Scheme 2), but this time the intermediate compound **5a**, arising from a nucleophilic substitution of the bromine by the thiol group, was obtained (Scheme 2). In order to achieve the cyclization to the desired oxathiolane we had to devise a slightly different synthetic approach with respect to that used for the synthesis of silyl-1,3-dithiolanes.

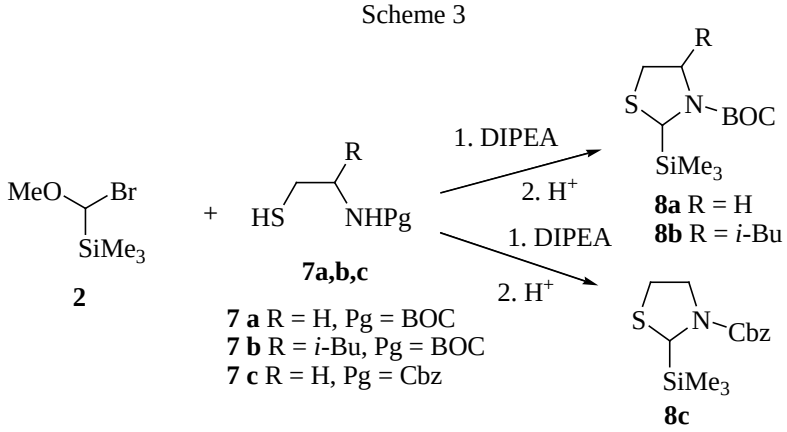
The reaction was repeated under the same conditions and, after stirring overnight in the presence of DIPEA, HCl conc. was added in the same flask and the mixture was stirred for 1 h and 30 min, to obtain the wanted 2-trimethylsilyl-1,3-oxathiolane **6a** (Scheme 2).

Due to the instability of these heterocycles under acidic conditions, it is convenient to underline that the treatment with HCl must not be longer than 1h 30min. In fact if the intermediate product is treated under acidic conditions for longer times, fragmentation of the oxathiolane ring was observed.

2-Trimethylsilyl-5-(methoxymethyl)-1,3-oxathiolane **6b** was obtained similarly, as a mixture of diastereoisomers (6:1), by reacting **2** with 1-mercapto-3-methoxypropan-2-ol **4b**.

As a further step we wanted to try the possible generalization to another interesting heterocyclic system, thiazolidines, and we reacted **2** *in situ* with N-protected aminoethanethiols **7a,c** to afford smoothly 2-silyl-N-protected 1,3-thiazolidines **8a** and **8c** (Scheme 3).

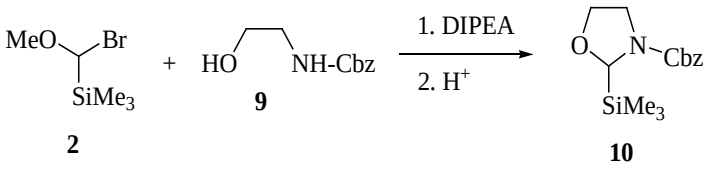
Scheme 3



Moreover, when N-Boc protected 2-amino-4-methylpentane-1-thiol **7b** was reacted, the substituted 4-isobutyl N-Boc-2-silyl thiazolidine **8b** was obtained as equimolar mixture of *cis* and *trans* isomers (Scheme 3).

Finally, we took into consideration the possibility to device a simple access to silylated oxazolidines. Thus, performing the reaction following the described procedure, treatment of bromo (methoxy)methyl trimethylsilane **2** with a suitably N-protected 2-aminoethanol **9** led to the isolation of the N-Cbz 2-silyl-1,3-oxazolidine **10** (Scheme 4).

Scheme 4



In conclusion we have reported a novel and general protocol for the synthesis of a variety of silyl heterocycles through simple and high yielding procedures, thus opening the way to a thorough investigation of their chemistry.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 (200 MHz and 50 MHz respectively) and a Varian Mercury 400 (400 MHz and 100 MHz respectively) in $CDCl_3$ solutions. Chemical shifts are given relative to the residue signals of the solvents (^{1}H: 7.26 ppm; ^{13}C: 77.0 ppm). Mass spectra were obtained on a MFC500/QMD 1000 Carlo Erba instrument and a Shimadzu GCMS-QP5050/GC 17A apparatus with electron impact ionization (70 or 30 eV).

Synthesis of 2-trimethylsilyl-1,3-dithiolanes (General procedure). A solution of bromine (2.57 mmol) in dry CCl_4 (4 mL) was added dropwise with stirring under N_2 to a solution of methoxymethyl trimethylsilane (2.57 mmol) in dry CCl_4 (5 mL). The mixture was stirred until. A solution of the suitable dithiol (2.57 mmol) in CH_2Cl_2 (5 mL) was then added and the mixture was stirred overnight. After washing with water, the organic layer was dried (Na_2SO_4) and evaporation of the solvent gave the crude product, which was purified by chromatography (column or TLC).

2-Trimethylsilyl-1,3-dithiolane (3a). TLC petroleum ether/ diethyl ether 20:1 (72%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.18 (9H, s, $SiMe_3$); 3.06-3.29 (4H, m); 3.53 (1H, s, *H*$CSiMe_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -2.3 ($Si(\underline{C}H_3)_3$); 37.6; 39.4. Mass spectrum, *m/z* (I_{rel}, %): 178 (41) $[M]^+$, 135 (97), 105

(72), 91 (25), 75 (63), 73 (100) 59 (81). Found, %: C 40.16; H 8.12. $C_6H_{14}S_2Si$. Calculated, %: C 40.40; H 7.91.

meso-**4,5-Dimethyl-2-trimethylsilyl-1,3-dithiolane (3b).** TLC hexanes/ethyl acetate 200:1 (82%). Mixture 1:3 of the two isomers. ***Cis*-isomer**: ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.14 (9H, s, $SiMe_3$); 1.25-1.28 (6H, m); 3.50-3.64 (2H, m); 3.69 (1H, s, *H*CSiMe$_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -2.5 (Si($\underline{C}H_3)_3$); 16.5; 36.9; 53.2. Mass spectrum, *m/z* (I_{rel}, %): 206 (5) $[M]^+$, 150 (11); 135 (32), 73 (100) 59 (16). Found, %: C 46.20; H 8.90. $C_8H_{18}S_2Si$. Calculated, %: C 46.54; H 8.79. ***Trans*-isomer**: ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.16 (9H, s, $SiMe_3$); 1.31 (6H, d, *J* = 6.6, CH_3); 3.62-3.75 (2H, m); 3.81 (1H, s, *H*CSiMe$_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -2.6 (Si($\underline{C}H_3)_3$); 15.5; 33.7; 53.4. Mass spectrum, *m/z* (I_{rel}, %): 206 (30) $[M]^+$, 163 (25); 150 (71); 135 (100), 73 (89) 59 (56). Found, %: C 46.32; H 9.06. $C_8H_{18}S_2Si$. Calculated, %: C 46.54; H 8.79.

Synthesis of 2-trimethylsilyl-1,3-oxathiolanes (General procedure). A solution of freshly prepared bromo(methoxy)methyl trimethylsilane (4.24 mmol) (obtained from methoxymethyl trimethylsilane and bromine in CCl_4) was slowly added at room temperature with a solution of the appropiate β-mercaptoalcohol (4.24 mmol) and DIPEA (5.08 mmol) in 23 mL of anhydrous CH_2Cl_2. The mixture was stirred overnight and then treated with HCl 12M (5 mL) for 1.5 h. After dilution with CH_2Cl_2 and addition with water, the mixture was stirred for 5-10 min. and then transferred in a separatory funnel. Solid $NaHCO_3$ is slowly added to neutralize the solution. The organic phase was washed with water (2 x 15 mL) and dried over

Na_2SO_4. Evaporation of the solvent afforded crude compounds, which were chromatographically purified.

2-Trimethylsilyl-1,3-oxathiolane (6a). TLC petroleum ether/ethyl acetate 4:1 (70%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.13 (9H, s, $SiMe_3$); 2.79-2.93 (1 H, m, *H*CHS); 3.03-3.12 (1 H, m, *H*CHS); 3.49-3.62 (1 H, m, *H*CHO); 4,37-4.47 (1 H, m, *H*CHO); 4.50 (1 H, s, *H*C$SiMe_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -3.7 (Si($\underline{C}H_3)_3$); 32.8 (CH_2S); 73.7 (CH_2O); 78.7 (H$\underline{C}SiMe_3$). Mass spectrum, *m/z* (I_{rel}, %): 163 (2) $[M+1]^+$, 162 (1) $[M]^+$, 134 (25), 119 (100), 89 (15), 73 (74). Found, %: C 44.22; H 8.74. $C_6H_{14}OSSi$. Calculated, %: C 44.39; H 8.69.

2-Trimethylsilyl-5-(methoxymethyl)-1,3-oxathiolane (6b). Mixture 6:1 of diastereoisomers purified on TLC (petroleum ether/ethyl acetate 100:1). (52%). **Major isomer:** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.12 (9H, s, $SiMe_3$); 2.65 (1H, dd, *J* = 8.2, *J* = 10, *H*CHS); 3.09 (1H, dd, *J* = 6.0, *J* = 10, *H*CHS); 3.40 (3H, s, CH_3O); 3.44-3.61 (2H, m, CH_2O); 3.96-4.08 (1H, m, CHO); 4.65 (1 H, s, *H*C$SiMe_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -3.6 (Si($\underline{C}H_3)_3$); 35.1 (CH_2S); 59.4 (CH_3O); 73.5 (CH_2O); 77.2 (H$\underline{C}SiMe_3$); 84.5 (CHO). Mass spectrum, *m/z* (I_{rel}, %): 206 (2) $[M]^+$, 146 (55), 135 (60), 119 (100), 91 (49), 73 (57), 59 (38). Found, %: C 46.38; H 8.84. $C_8H_{18}O_2SSi$. Calculated, %: C 46.56; H 8.79. **Minor isomer:** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.12 (9H, s, $SiMe_3$); 2.82-2.88 (2H, m, CH_2S); 3.33-3.40 (2H, m, CH_2O, partially overlapped with signal at 3.38); 3.38 (3H, s, CH_3O); 4.38-4.51 (1H, m, CHO); 4.68 (1 H, s, *H*C$SiMe_3$).). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -3.5 (Si($\underline{C}H_3)_3$); 39.9 (CH_2S); 59.3 (CH_3O); 72.7 (CH_2O);

77.2 (H<u>C</u>SiMe$_3$); 82.1 (CHO). Mass spectrum, *m/z* (I_{rel}, %): 206 (1) $[M]^+$, 146 (21), 135 (32), 119 (100), 91 (23), 73 (63), 59 (24).

Synthesis of 2-trimethylsilyl-1,3-thiazolidines (General procedure). To a freshly prepared solution of bromo(methoxy)methyl trimethylsilane (5 mmol) (obtained from methoxymethyl trimethylsilane and bromine in CCl_4) were added at r. t. anhydrous CH_2Cl_2 (10 mL), the appropriate N-protected 2-mercaptoamine (5 mmol) dissolved in 5 mL of CH_2Cl_2 and DIPEA (1.2 eq). The mixture was stirred overnight, then treated with *p*-toluensulfonic acid (0.1 eq) for 1.5 h. The resulting mixture was washed with water and brine, and the organic phase dried over Na_2SO_4. Evaporation of the solvent afforded the crude N-protected thiazolidines, which were purified by flash chromatography.

***tert*-Butyl 2-(trimethylsilyl)thiazolidine-3-carboxylate (8a).** Petroleum ether/ethyl acetate 8:1 (81%). R_f 0.8. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.10 (9H, s, SiMe$_3$); 1.46 (9H, s, $(CH_3)_3$); 2.81-2.92 (m, 2H, CH_2S); 3.10-3.30 (1H, m, *H*CHN); 4.10-4.35 (1H, m, *H*CHN); 4.60 (1H, s, *H*CSiMe$_3$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -2.6 (Si(<u>C</u>H$_3$)$_3$); 28.3; 30.5; 49.4; 50.9; 80.1; 154.0. Mass spectrum, *m/z* (I_{rel}, %): 263 (0.5) $[M+2]^+$, 204 (89), 188 (10), 160 (100), 132 (56), 100 (63), 88 (94), 73 (98). Found, %: C 50.30; H 9.05; N 5.08. $C_{11}H_{23}NO_2SSi$. Calculated, %: C 50.53; H 8.87; N 5.36.

***tert*-Butyl 4-isobutyl-2-(trimethylsilyl)thiazolidine-3-carboxylate (8b).** Mixture 1:1 of diastereoisomers purified on TLC (petroleum ether/ethyl acetate 10:1 (53%). R_f 0.9 and 0.7. ***Trans*-isomer:** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.12 (9H, s, SiMe$_3$); 0.95 (6H, d, *J* = 5.8, CH(C*H*$_3$)$_2$); 1.38-1.61 (3H, m, C*H*$_2$C*H*(CH$_3$)$_2$); 1.47

(9H, s, $(CH_3)_3$); 2.63 (1H, dd, *J* = 3.8, *J* = 11.6, *H*CHS); 3.02 (1H, dd, *J* = 6.4, *J* = 11.6, *H*CHS); 4.22-4.37 (1H, m, *H*CHN); 4.7 (1H, s, *H*CSiMe_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -1.9 (Si($\underline{C}H_3)_3$); 21.9; 23.8; 25.8; 28.6; 36.1; 43.8; 52.3; 60.0; 80.0; 157.1. Mass spectrum, *m/z* (I_{rel}, %): 260 (07) $[M-57]^+$, 188 (5), 144 (7), 73 (56), 57 (100). Found, %: C 56.48; H 10.08; N 4.60. $C_{15}H_{31}NO_2SSi$. Calculated, %: C 56.73; H 9.84; N 4.41. ***Cis*-isomer:** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.15 (9H, s, SiMe_3); 0.94 (6H, d, *J* = 5.8, CH(C$H_3)_2$); 1.40-1.59 (3H, m, CH_2C*H*$(CH_3)_2$); 1.46 (9H, s, $(CH_3)_3$); 2.65 (1H, dd, *J* = 2.0, *J* = 11.2, *H*CHS); 3.03 (1H, dd, *J* = 6.8, *J* = 11.2, *H*CHS); 4.10 (1H, s, *H*CSiMe_3); 4.26-4.36 (1H, m, *H*CHN). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -0.6 (Si($\underline{C}H_3)_3$); 22.1; 23.5; 25.7; 28.5; 36.0; 42.4; 52.1; 59.5; 80.1; 157.1. Mass spectrum, *m/z* (I_{rel}, %): 260 (07) $[M-57]^+$, 188 (5), 144 (7), 73 (56), 57 (100). Found, %: C 56.60; H 9.98; N 4.39. $C_{15}H_{31}NO_2SSi$. Calculated, %: C 56.73; H 9.84; N 4.41.

Benzyl 2-(trimethylsilyl)thiazolidine-3-carboxylate (8c). Petroleum ether/ethyl acetate 4:1 (56%). R_f 0.8. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.09 (9H, s, SiMe_3); 2.85-2.92 (2H, m, CH_2S); 3.23-3.42 (1H, m, *H*CHN); 4.11-4.37 (1H, m, *H*CHN); 4.61 (1H, s, *H*CSiMe_3), 5.09 (1H, d, *J* = 14, *H*CHPh), 5.18 (1H, d, *J* = 14, *H*CHPh), 7.33-7.37 (5H, m, H-C_{Ph}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -2.5 (Si($\underline{C}H_3)_3$); 30.6; 50.0; 51.8; 67.5; 128.1; 128.4; 128.6; 139.8; 154.6. Mass spectrum, *m/z* (I_{rel}, %): 204 (8) $[M-91]^+$, 160 (22), 91 (100), 73 (44). Found, %: C 56.66; H 7.44; N 4.45. $C_{14}H_{21}NO_2SSi$. Calculated, %: C 56.91; H 7.16; N 4.74.

Synthesis of 2-trimethylsilyl-1,3-oxazolidines (General procedure). A freshly prepared solution of bromo(methoxy)methyl trimethylsilane (8.7 mmol) (obtained

from methoxymethyl trimethylsilane and bromine in CCl_4) was added at r. t. with anhydrous CH_2Cl_2 (10 mL), the appropriate N-protected β-aminoalcohol (8.7 mmol) dissolved in 5 mL of CH_2Cl_2 and DIPEA (1.2 eq). The mixture was stirred overnight, then was treated with *p*-toluensulfonic acid (0.1 eq) for 1.5 h. The resulting mixture was washed with water and brine, and the organic phase was dried over Na_2SO_4. Evaporation of the solvent afforded the crude N-protected oxazolidines, which were purified by flash chromatography.

Benzyl 2-(trimethylsilyl)oxazolidine-3-carboxylate (10). Petroleum ether/ethyl acetate 5:1 (52%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.07 (9H, s, $SiMe_3$); 3.19-3.34 (1H, m, *H*CHN); 3.63-3.81 (2H, m, *H*CHN+*H*CHO); 4.01-4.12 (1H, m, *H*CHO); 4.77 (1H, s, *H*CSiMe$_3$), 5.10-5.16 (2H, m, CH_2Ph), 7.35-7.37 (5H, m, H-C_{Ph}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: -3.1 (Si(CH_3)$_3$); 45.7; 67.0; 67.9; 85.7; 127.9; 128.3; 138.6; 156.5. Mass spectrum, *m/z* (I_{rel}, %): 264 (0.5) $[M-15]^+$, 188 (7), 144(26); 91 (100), 73 (43). Found, %: C 59.96; H 7.72; N 5.17. $C_{14}H_{21}NO_3Si$. Calculated, %: C 60.18; H 7.58; N 5.01.

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