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Originally published:

March 2018

European Journal of Inorganic Chemistry (2018), 1302-1308

DOI: https://doi.org/10.1002/ejic.201701327

Perma-Link to Publication Repository of HZDR:

https://www.hzdr.de/publications/Publ-25909

EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201701327

Link to VoR: http://dx.doi.org/10.1002/ejic.201701327

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Facile Silylation of Cyclitols Using Silyl Bis(triflates)

Anke Topp,[a] Martin Köckerling,[a] Helmut Reinke,[a] Ralf Miethchen[a] and Constantin Mamat*[b,c]

Abstract: Novel silylated diols and polyols were prepared using a recently developed synthesis route with bifunctionalized silyl triflates. These silyl derivatives include two triflate functions which allow a selective protection of two hydroxy groups. Moreover, the conformation of the silyl chain in the silane backbone led to exceptional UV properties.

Introduction

Silyl ethers, especially bifunctional derivatives, have become important alcohol protecting groups,[1,2] which were used in the synthesis of natural products or pharmacologically active compounds.[3,4] Additionally, they are used to protect functional groups like primary amines,[5,6] amino acids,[7] diols[8,9] and hydroxy acids.[10] Furthermore, a regioselective protection via silylation is conceivable for bioactive molecules like carbohydrates as well as inositols.[11-13]

In general, natural products containing hydroxy functions or other alcohols are protected by treatment with a chlorinated silyl species in the presence of a base.[4,14] However, when bulky silylation reagents are applied or sterically hindered secondary or tertiary alcohols are employed, silylating agents like silyl triflates or iodides are favorable compared to the chlorides due to their higher reactivity.[15] However, silyl iodides were found to be less stable and, in some cases, other functional groups were not tolerated when silyl iodides were applied.[16]

Another important factor is the stability of the protected derivatives against hydrolysis or attack by other nucleophiles which can be controlled by the variation of the bulkiness of the introduced silyl group. Advantageously, a selective deprotection is possible depending on the steric demand of either the compound to be protected or the silyl moiety.[1-3,17]

Prominent bifunctional protecting groups like the tetraisopropyl-disiloxane-1,3-diyl (TIPDS) group are well known and widely used in carbohydrate chemistry as well as others.[17-21] Under kinetically controlled conditions the primary and the adjacent secondary hydroxy group of various carbohydrates were protected forming a 7-membered ring. In other cases, it is possible to connect two different carbohydrates.[22,23]

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Recently, novel bidentate silyl derivatives were prepared[9,24,25] by the treatment of phenyl silanes with triflic acid and applied as protecting groups for the protection of carbohydrates on the base of their oligosilyl triflates.[11]

In this paper we demonstrate a convenient silylation procedure for the protection of hydroxy groups on various cyclitols and carbohydrates leading to bicyclic silyl ethers using highly reactive silyl triflates. It is possible to fix the conformation of these cyclitols with the silyl backbone due to the formation of bridged (bicyclic) derivatives. In addition, a separation of a racemic 1,3-cyclohexanediol-mixture into stereoisomers was demonstrated.

Results and Discussion

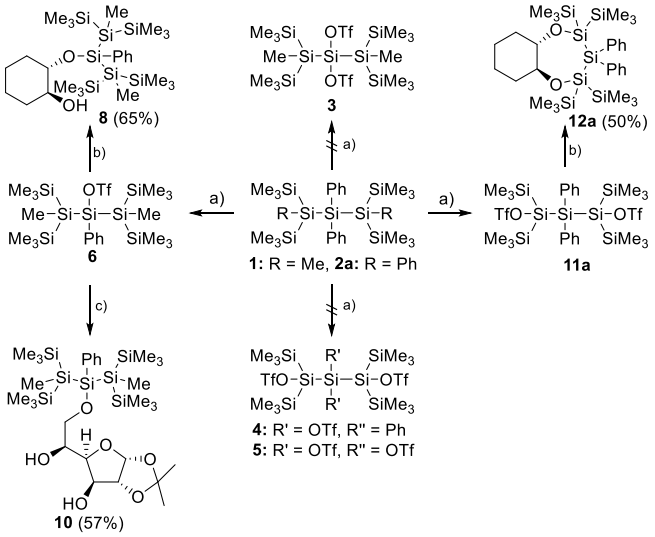
Several bidentate silylating agents mostly with halogens as leaving groups were prepared in the past.[26-28] To raise their reactivity, triflate was used instead of halogens.[9,11] These silyl triflates were prepared according to a facile, previously published method reacting phenyl silanes with triflic acid in nearly quantitative yield.[9,29] The silylation of diols was achieved in a one pot procedure by preparing the highly reactive silyl triflates from the respective phenyl compound followed by subsequent reaction with diols without further isolation of the triflate.[11]

Initial experiments were performed to determine the reactivity of phenyl groups placed on different positions of the silane backbone for a replacement with triflate (Scheme 1). For this purpose, the phenyl silanes **1** and **2a** were prepared and subsequently treated with different amounts of triflic acid in anhydrous *n*-pentane or dichloromethane at –20°C.

Silane derivative **1**, containing two interior phenyl groups, was treated with 2.2 to 4 equivalents of triflic acid. Interestingly, instead of the twofold triflated compound **3** solely silyl triflate **6** was obtained. This finding was confirmed by the subsequent reaction of triflate **6** with *trans*-cyclohexanediol **7a** which led exclusively to compound **8** in 65% yield. Due to the sterical demand of the silyl moiety just one of the OH groups of diol **7a** was silylated. Thus, a regioselective protection of polyols like carbohydrates using silyl compound **6** could be promising as it was demonstrated with the supersilyl moiety.[30,31] Therefore, triflate **6** was reacted with 1,2-*O*-isopropylidene-α-D-glucofuranose (**9**). It was successfully demonstrated that **6** was protecting the position 6 of the carbohydrate regioselectively to obtain the silylated glucose derivative **10** in 57% yield. NMR and MS analyses identified a phenyl group with the expected signals of the silyl residue and the carbohydrate moiety in **10**.

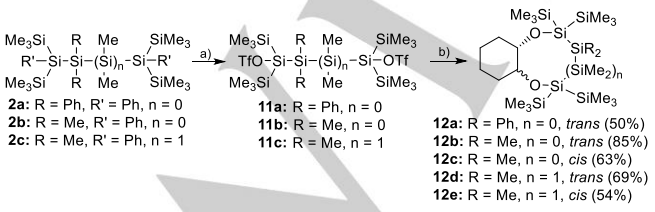
Next, phenylsilane **2a** with two interior and two exterior phenyl groups was treated in the same manner as **1**. It was found that only the exterior phenyl groups were replaced by triflate independent on the amount of triflic acid added. Solely compound **11a** was formed. The interior phenyl groups of **2a** remained unaffected when 1 to 3 equivalents of triflic acid were added. This result was confirmed by the subsequent reaction of

11a with **7a**, which led to silylated cyclitol **12a** in 50% yield. Unidentified by-products can occur, but they were not detectable using standard TLC analyses.



Scheme 1. Synthesis of the silyl-protected cyclitols. Reagents and conditions: a) TfOH, DCM, -20°C, b) *trans*-cyclohexane-1,2-diol (**7a**), Et_3N, dichloromethane, -20°C to rt, c) 1,2-*O*-isopropylidene-α-D-glucofuranose (**9**), Et_3N, dichloromethane, -20°C to rt.

The influence of the length of the silyl chain on the stability of the prepared silylated cyclitols was also investigated. Bis(phenyl) silanes **2a-c**, with variable silane backbones, were applied as starting materials. Using a similar preparation as for **11a**, phenylsilanes **2b,c** containing two exterior phenyl groups were treated with 2.2 equivalents triflic acid in *n*-pentane or dichloromethane at –20°C to prepare silyl bis(triflates) **11b,c** (Scheme 2). Afterwards, silyl triflates **11b,c** were reacted with 1,2-cyclohexanediols **7a,b** to obtain the desired sila-bicyclo derivatives **12b-e** in yields (54 – 85%). It was found, that the silyl backbone as well as the conformation (*cis* or *trans*) of the OH groups in 1,2-cyclitols **7a,b** did not affect the formation of the bicyclic products. Remarkably, no open-chained species were found.



Scheme 2. Preparation of the silyl-protected 1,2-cyclitols **12a-e**. Reagents and conditions: a) TfOH, DCM, -20°C, b) *trans*-cyclohexane-1,2-diol (**7a**) or *cis*-cyclohexane-1,2-diol (**7b**), Et_3N, dichloromethane, -20°C to rt.

Single crystals were obtained from compounds **12b**, **12c**, and **12d**, which were suitable for XRD analyses. Both *trans*-conformers **12b** and **12d** are found to be racemic mixtures and crystallize in centrosymmetric space groups $P2_1/c$ and $P2_1/n$, respectively (Figures 1 and 2).

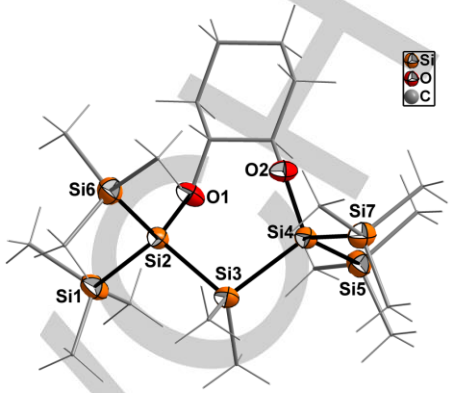


Figure 1. Molecular structure of the *trans*-1,2-derivative **12b** with pentasilyl backbone in the crystal (ORTEP, ellipsoids at the 50% probability level).

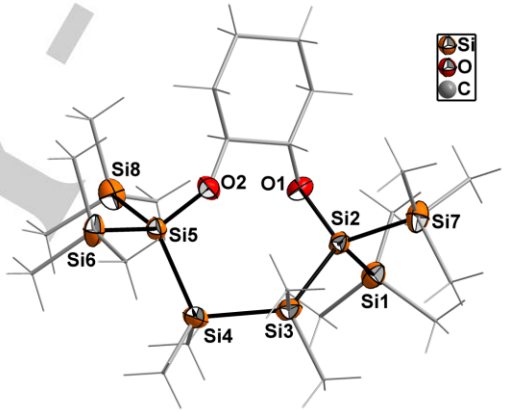


Figure 2. Molecular structure of the *trans*-1,2-derivative **12d** with hexasilyl backbone in the crystal (ORTEP, ellipsoids at the 50% probability level).

The *cis*-derivative **12c** with pentasilyl backbone crystallizes in the monoclinic space group $P2_1/c$. The structure is shown in Figure 3.

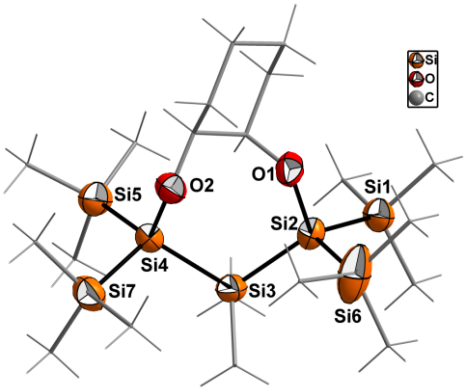
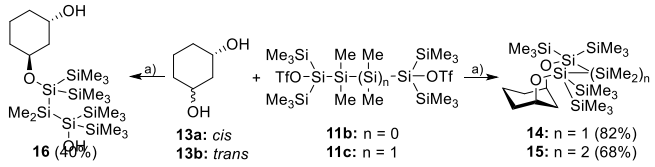


Figure 3. Molecular structure of the *cis*-1,2-derivative **12c** with pentasilyl backbone in the crystal (ORTEP, ellipsoids at the 50% probability level).

Cis- and *trans*-1,3-cyclohexanediols **13a** and **13b** were tested as starting materials for protection of the alcohol functions with silyl bis(triflates) **11b,c** to yield **14-16** using the above mentioned one-pot procedure.[11] It was found that *cis*-1,3-cyclohexanediol **13a** reacted with **11b,c** to produce *cis*-sila-bicyclo derivatives **14** (82%) and **15** (68%) in good yields. Interestingly, a bicyclic derivative was not formed when *trans*-1,3-cyclohexanediol **13b** was reacted with **11b**. Instead, the open-chained species **16** was formed in 80% yield after aqueous workup.



Scheme 3. Preparation of the silyl-protected 1,3-cyclitols **14-16**. Reagents and conditions: a) **13a** or **13b**, Et_3N, dichloromethane, -20°C to rt.

Either sila-bicyclo derivatives **14, 15** or open-chained derivatives like **16** were found depending on the conformation of the OH groups (*cis* or *trans*) in the 1,3-cyclitols **13a,b**. However, the length of the silicon backbone of the silyl triflates **11b,c** supposedly have no influence. The yields of the resulting bicyclic silyl ethers are comparable under the same reaction conditions.
Additionally, it was possible to obtain single crystals suitable for an X-ray analysis to prove the molecular structure of **15**. This compound crystalized in the monoclinic space group $P2_1/c$. Interestingly, two orientations for the cyclohexane residue relative to the silyl backbone are found in the crystal. The methylene group between the two oxygen atoms is either located in front or behind the silyl chain. This disorder has been refined as a split model with an approx. 80:20 ratio of the two isomers. A chair conformation of the cyclohexane scaffold is present in both orientations. The molecular structure of **15** is shown in Figure 4 with the major orientation of the cyclohexane ring.

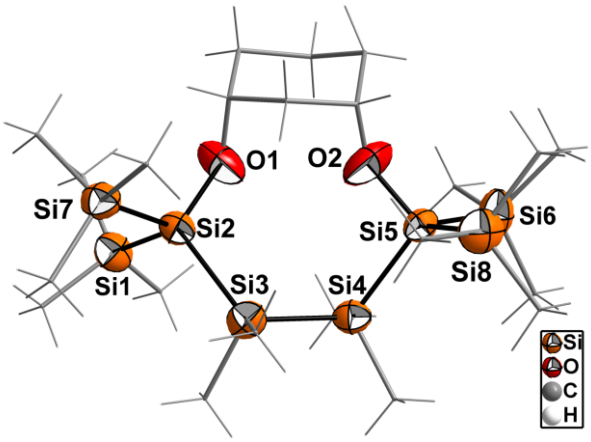


Figure 4. Molecular structure of the *cis*-1,3-derivative **15** in the crystal (ORTEP, ellipsoids at the 50% probability level). Only one of the two disordered orientations of the cyclohexane ring is shown.

In contrast to the previous findings with the 1,2-diols **7a,b**, only the open-chained compound **16** was found when *trans*-cyclitol **13b** was reacted with **11b**. NOESY measurements revealed that the silyl moiety from the open-chained compound **16** is located in the axial position to the cyclohexane ring. Correlations between proton H_1 and H_{2a}/H_{6a} and H_{2e}/H_{6e} of the cyclohexane scaffold were found and approve this result. This stereochemical specialty was also found in other silylated cyclitol derivatives published by Marzabadi and co-workers.[32]
As beneficial side effect, the separation of the *cis* from the *trans* isomer was possible when an isomeric mixture of cyclohexane-1,3-diol **13a,b** is used as starting material.

UV investigations

It was first reported in 1964 that oligosilanes show absorptions in the near UV (λ = 200 - 400 nm).[33,34] This promising photophysical property was explained due to extensive delocalization of σ-bonded electrons (σ-conjugation) along the silicon chain which is a result of strong electronic absorptions in the near UV due to a σ-σ* transition.[35-37] The conformation of the silicon chain, electronic and steric properties of the connected substituents[38-42] and length of the silicon chain[43] have a high influence on the intensity and energy of absorption.[44,45]
Furthermore, it has been demonstrated for peralkylated oligosilanes that σ-conjugation is effectively extended by an *anti* conformation (SiSiSiSi dihedral angle ω = 180° for a tetrasilane subunit) of the silicon chain.[36,44] Additional absorption maxima of silyl oligomers with the structural motif $(SiR_2)_n$ and R = alkyl were typically found at wave lengths between 300 and 325 nm .[35,46] In addition, oxygen-containing donor groups (e.g. OH, OR, $OSiR_3$) attached to the Si-chain lead to a strong electronic coupling, resulting in a substantial decrease of the optical band gaps.[37]

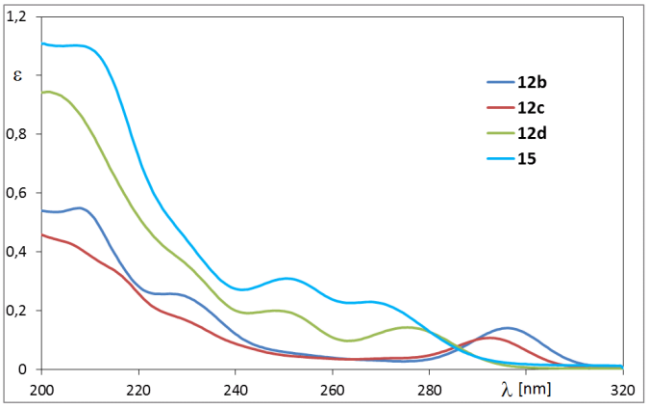


Figure 5. UV spectra of compounds **12b-d** and **15**.

To figure out the photophysical properties of the title compounds **12b-d** and **15**, UV measurements were performed (Figure 5). The UV spectra of **12b** and **12c** showed an additional absorption maximum between 290 and 300 nm, while the longer-chained derivatives **12d** and **15** absorbed on lower wave lengths.

This behavior has two reasons: 1) the oxo functionalization[9,46] of the silyl chain which leads to an interaction of the free electron pairs of the oxygen with the σ-bond electrons of the silyl chain; 2) the different conformation of the silyl chain in compounds **12b-d** and **15**.

A twisted conformation of the silane backbone was found for **12b** and **12c** in the solid state. The observed conformation is the result of ring formation between the silane moiety and the cyclohexane residue. Therefore, a fixation by covalent bonds occurred in the seven-membered ring system which leads to a remarkable red shift of the UV absorption maximum in contrast to silanes **12d** and **15**. This fact can be explained due to the dihedral angles of the silane backbone (Table 1).

Table 1. Dihedral angles of silanes **12b-d** and **15**.

Compound	UV [nm]	Dihedral Angles [°]				
12b	295	95.58	114.24	135.52	99.42	
12c	292	100.34	131.90	121.48	113.85	
12d	< 290	158.71	82.34	60.11	127.02	109.41
15	< 290	147.88	92.93	61.77	77.86	159.11

All dihedral angles of the silyl chain in compounds **12b,c** were found between 96 and 135°. This configuration of the silicon atoms in the chain led to the σ-conjugation and this conjugation is responsible for the resulting bathochromic shift in absorption. In contrast, the dihedral angles of approx. 60 and 62° found for **12d** and **15** disrupt the conjugation of the silyl chain. Thus, no maxima at wave lengths >285 nm were observed.

Conclusions

Silyl esters with one or two triflate functions were successfully used to conveniently and selectively protect diols and polyols. The bis-triflates were easily prepared from their respective phenylsilanes using triflic acid and allowed fast protection of two hydroxy groups in high yields in dependence of their conformation and the chain length of the silyl moiety. Two of the resulting silylated diols showed remarkable properties concerning UV absorptions due to the fixed silane backbone. The oxo functionalization of the silyl chain as well as the special conformation of the silicon atoms in the silyl chain enabled the σ-conjugation which led to a bathochromic shift of the absorption maximum of compounds **12b** and **12c** at wave lengths between 295 and 300 nm.

Experimental Section

All reactions involving organosilicon reagents were carried out using Schlenk techniques under an argon atmosphere. Triflic acid was distilled under argon prior to use. For the synthesis of the silyl ethers, the corresponding silyl triflates were conveniently generated without isolation. Melting points were obtained using a Leitz polarizing microscope (Laborlux 12 Pol) equipped with a hot stage (Mettler FP 90). Microanalyses were carried out with a CHNS-analyser Thermoquest Flash EA 1112 by addition of Pb_3O_4 for silicon containing compounds. Their results were found to be in good agreement (±0.5%) with the calculated values. ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on Bruker instruments: AC250 and ARX 300, internal standard TMS for ^1H and ^{13}C spectra. Optical rotations were measured on a polar LμP (IBZ Meßtechnik) instrument. Mass spectra were determined using an Intecta AMD 402 (EI with 70 eV or CI with isobutane). Chromatographic separations and TLC detections were carried out with Merck Silica Gel 60 (63–200 μm) and Merck Silica Gel 60 F_{254} sheets, respectively. TLCs were developed with 5% H_2SO_4 in methanol and heating (carbohydrates) or visualized under UV light (λ = 254 nm). Compounds **1, 2b, 2c** and **11a-c** were prepared as previously described.[9,11] Diffraction data were collected with a Bruker-Nonius Apex-X8 CCD-diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The unit cell dimension was recorded and refined by using the angular settings of reflections of 36 scans, recorded in three different directions of the reciprocal space. The structures were solved by Direct Methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[47,48] All non-hydrogen atoms were refined anisotropically; all hydrogen atoms bonded to carbon atoms were placed on geometrically calculated positions and refined using riding models. CCDC 1551252 (**12b**), CCDC 1539230 (**12c**), CCDC 1551253 (**12d**) and CDCC 1551254 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Syntheses and Characterizations

2,4-Bis(trimethylsilyl)-1,1,1,5,5,5-hexamethyl-2,3,3,4-tetraphenylpentasilane (**2a**)

Phenyltris(trimethylsilyl)silane (5.0 g, 15.4 mmol) and KO^{t}Bu (1.7 g, 15.4 mmol) were added into a flame dried and argon filled Schlenk tube with magnetic stirrer, anhydrous THF (70 mL) was added and the mixture was allowed to stand overnight. Afterwards, the solvent was removed, *n*-pentane was added to the residue and the suspension cooled to –78°C. Dichlorodiphenylsilane (2.0 g, 7.7 mmol) was added; the resulting mixture was stirred for 1 h and then allowed to warm to rt. An HCl-solution (0.1 M, 100 mL) was added, the organic layer separated, extracted with diethyl ether (3 x 50 mL), dried over $MgSO_4$ and the solvent was removed. Recrystallization from acetone afforded **2a** as colorless solid (1.32 g, 25%): m.p.: 293–294°C; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.70–7.63 (m, 5H, Ph), 7.48–7.41 (m, 5H, Ph), 7.33–7.22 (m, 10H, Ph), –0.14 (s, 36H, $SiMe_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 138.2, 137.2 (2 x CH_{Ph}), 128.8, 127.9, 127.8 (3 x C_{Ph}), 2.0 ($SiMe_3$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = –11.2 ($SiMe_3$), –29.1 ($SiPh_2$), –65.8 (SiPh) ppm; MS (CI–isobutane): *m/z* = 685 $[M+H]^+$, 669 $[M–Me]^+$, 611 $[M–SiMe_3]^+$; elemental analysis calcd (%) for $C_{36}H_{56}Si_7$ (685.4): C 63.08, H 8.23; found: C 63.21, H 8.26.

General procedure for the silylation of cyclitols

Under an argon atmosphere, triflic acid (2.2 eq.) was added to a stirred solution of the respective silanes **1** or **2a-c** (1 eq.) in anhydrous dichloromethane at –20°C and stirred for 1 h. Afterwards, hydroxy compound **7a,b**, **9** or **13a,b** (1 eq.) and Et_3N (2.2 eq.) were added at –20°C and the mixture was allowed to warm to rt. After completion of the reaction (TLC control) saturated hydrogen carbonate solution was added (15 mL), the mixture extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over $MgSO_4$, the solvent was

removed and the remaining residue was purified by column chromatography.

(1*RS*,2*RS*)-2-((1,1,1,2,4,5,5,5-octamethyl-3-phenyl-2,4-bis(trimethylsilyl)pentasilan-3-yl)oxy)cyclohexan-1-ol (**8**)

Silane **1** (500 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *trans*-cyclohexane-1,2-diol (**7a**, 100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane/toluene, 30/1) to yield **8** as a colorless solid (347 mg, 65%, racemate); R_f=0.8 (*n*-heptane/toluene 2:1); M.p.: 66–72°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.55–7.18 (m, 5H, Ph), 3.54–3.32 (m, 2H, H-1, H-2), 2.11–1.89 (m, 1H, H-3e/6e), 1.91–1.79 (m, 1H, H-3e/6e), 1.71–1.60 (m, 2H, H-3a, H-6a), 1.47–1.12 (m, 4H, H-4a, H-4e, H-5a, H-5e), 0.34 (s, 3H, SiMe), 0.30 (s, 3H, SiMe), 0.22–0.10 (br. s, 9H, $SiMe_3$), 0.09 (s, 9H, $SiMe_3$), -0.01 (s, 9H, $SiMe_3$), -0.15 (s, 9H, $SiMe_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 142.3 (C_{Ph}), 133.3, 128.5, 128.2, 127.6 (CH_{Ph}), 80.1 (C-2), 78.5 (C-1), 35.1 (C-6), 34.9 (C-6), 24.7 (C-4), 24.5 (C-5), 0.9, 0.8, –0.1 ($SiMe_3$), –10.3, –10.9 (SiMe); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 22.1 (SiO), –12.6, –11.9 ($SiMe_3$), –79.5 (*Si*($SiMe_3$)$_2$Me) ppm; MS (CI–isobutane): *m/z* = 583 [M-Me]$^+$, 568 [M–Me_2]$^+$, 409 [M–Si($SiMe_3$)$_2$Me]$^+$, 73 [$SiMe_3$]; elemental analysis calcd (%) for $C_{26}H_{58}O_2Si_7$ (599.3): C 52.10, H 9.75; found: C 51.86, H 9.45.

6-*O*-(2,6-Bis(trimethylsilyl)-1,1,1,2,4,5,5,5-octamethyl-3-phenyl-pentasilan-3-yl)-1,2-*O*-isopropylidene-α-D-glucofuranose (**10**)

Silane **1** (1.0 g, 1.78 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.34 mL, 3.92 mmol) were reacted with 1,2-*O*-isopropylidene-α-D-glucofuranose (**9**, 310 mg, 1.41 mmol) and Et_3N (0.69 mL, 5.0 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane/EtOAc, 20/1 → 10/1) to yield **10** as a colorless syrup (580 mg, 57%): R_f=0.6 (*n*-heptane/EtOAc 1:1); $[\alpha]_D^{22}$ = –9.41 (*c* = 0.97 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.27–7.46 (m, 5H, Ph), 5.96 (d, 1H, $^3J_{1,2}$ = 3.4 Hz, H-1), 4.54 (d, 1H, $^3J_{1,2}$ = 3.4 Hz, H-2), 4.35 (d, 1H, $^3J_{3,4}$ = 2.7 Hz, H-3), 4.14 (d, 1H, $^3J_{3,4}$ = 2.7 Hz, H-4), 4.10–4.22 (m, 1H, $^3J_{5,6a}$ = 6.7 Hz, $^3J_{5,6b}$ = 3.4 Hz, H-5), 3.86 (dd, 1H, $^2J_{6a,6b}$ = 9.5 Hz, $^3J_{5,6b}$ = 3.4 Hz, H-6b), 3.76 (dd, 1H, $^2J_{6a,6b}$ = 9.5 Hz, $^3J_{5,6a}$ = 6.7 Hz, H-6a), 1.47, 1.32 (s, 3H, ^{i}Pr-CH_3), 0.29 (s, 6H, SiMe), 0.14 (s, 18H, 2 x $SiMe_3$), –0.03, –0.04 (2s, 9H, 2 x $SiMe_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 140.5 (C_{Ph}), 133.1, 128.8, 128.2 (3 x CH_{Ph}), 111.8 (^{i}Pr-C), 105.2 (C-1), 85.3 (C-2), 79.4 (C-4), 75.9 (C-3), 71.2 (C-5), 67.9 (C-6), 27.0, 26.4 (2 x ^{i}Pr-CH_3), 1.1, 0.6 ($SiMe_3$), –10.5 (SiMe); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 21.6 (PhSiO), –11.6 ($SiMe_3$), –82.6, –82.7 (SiMe) ppm; MS (EI, 70 eV): *m/z* = 703 [M$^+$+H]$^+$, 513 [M–SiMe(SiMe_3)$_2$]$^+$; elemental analysis calcd (%) for $C_{29}H_{62}O_6Si_7$ (703.4): C 49.52, H 8.88; found: C 49.63, H 8.94.

(5a*RS*,9a*RS*)-3,3-diphenyl-2,2,4,4-tetrakis(trimethylsilyl)octahydro-2*H*-benzo[*f*][1,5,2,3,4]dioxatrisilepine (**12a**)

Silane **2a** (610 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *trans*-cyclohexane-1,2-diol (**7a**, 100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane) to yield **12a** as a colorless solid (287 mg, 50%, racemate): R_f=0.7 (*n*-heptane); m.p.: 201–204°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.54–7.24 (m, 10H, CH_{Ph}), 3.33–3.20 (m, 2H, H-1, H-2), 1.94–1.79 (m, 2H, H-3e, H-6e), 1.70–1.59 (m, 2H, H-3a, H-6a), 1.36–1.09 (m, 4H, H-4a, H-4e, H-5a, H-5e), 1.36–1.09 (m, 4H, H-4a, H-4e, H-5a, H-5e), 0.09 (s, 18H, $SiMe_3$), 0.01 (s, 18H, $SiMe_3$); ^{13}C NMR (76 MHz, $CDCl_3$): δ = 137.2 (C_{Ph}), 136.9, 128.5, 127.8 (CH_{Ph}), 83.6 (C-1, C-2), 35.2 (C-3, C-6), 24.7 (C-4, C-5), 1.4 ($SiMe_3$), 0.3 ($SiMe_3$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 8.2 (SiO), –14.0, –15.6 ($SiMe_3$), –22.2 ($SiPh_2$) ppm; MS (CI–isobutane): *m/z* = 645 [M+H]$^+$, 571 [M–$SiMe_3$]$^+$, 567 [M–Ph]$^+$, 73 [$SiMe_3$]; elemental analysis calcd (%) for $C_{30}H_{56}O_2Si_7$ (645.4): C 55.83, H 8.75; found: C 54.82, H 8.64.

(5a*RS*,9a*RS*)-3,3-dimethyl-2,2,4,4-tetrakis(trimethylsilyl)octahydro-2*H*-benzo[*f*][1,5,2,3,4]dioxatrisilepine (**12b**)

Silane **2b** (500 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *trans*-cyclohexane-1,2-diol (**7a**, 100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane) to yield **12b** as a colorless solid (395 mg, 85%, racemate): R_f=0.6 (*n*-heptane); m.p.: 135–136°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.02–2.92 (m, 2H, H-1, H-2), 1.81–1.69 (m, 2H, H-3e, H-6e), 1.63–1.53 (m, 2H, H-3a, H-6a), 1.19–1.04 (m, 4H, H-4a, H-4e, H-5a, H-5e), 0.34 (s, 6H, $SiMe_2$), 0.22 (s, 18H, $SiMe_3$), 0.17 (s, 18H, $SiMe_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 84.2 (C-1, C-2), 35.0 (C-3, C-6), 24.8 (C-4, C-5), 0.1, –1.1 ($SiMe_3$), –1.8 ($SiMe_2$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 9.5 (SiO), –14.5, –16.2 ($SiMe_3$), –29.0 ($SiMe_2$) ppm; MS (CI–isobutane): *m/z* = 521 [M+H]$^+$, 506 [M–Me]$^+$, 447 [M–$SiMe_3$]$^+$, 73 [$SiMe_3$]; elemental analysis calcd (%) for $C_{20}H_{52}O_2Si_7$ (521.2): C 46.09, H 10.06; found: C 46.23, H 10.12.

(5a*R*,9a*S*)-3,3-dimethyl-2,2,4,4-tetrakis(trimethylsilyl)octahydro-2*H*-benzo[*f*][1,5,2,3,4]dioxatrisilepine (**12c**)

Silane **2b** (500 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *cis*-cyclohexane-1,2-diol (**7b**, 100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane) to yield **12c** as a colorless solid (293 mg, 63%): R_f = 0.6 (*n*-heptane); m.p.: 84–86°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.61–3.51 (m, 2H, H-1, H-2), 1.67–1.46 (m, 4H, H-3a, H-3e, H-6a, H-6e), 1.42–1.13 (m, 4H, H-4a, H-4e, H-5a, H-5e), 0.44 (s, 3H, Me), 0.33 (s, 3H, Me), 0.20 (s, 18H, $SiMe_3$), 0.19 (s, 18H, $SiMe_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 69.8 (C-1, C-2), 30.1 (C-3, C-6), 21.6 (C-4, C-5), 1.4, 1.3 ($SiMe_2$), 0.0, –2.8 ($SiMe_3$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 4.5 (SiO), –13.7, –16.1 ($SiMe_3$), –35.2 ($SiMe_2$) ppm; MS (CI–isobutane): *m/z* = 521 [M+H]$^+$, 506 [M–Me]$^+$, 447 [M–$SiMe_3$]$^+$, 73 [$SiMe_3$]; elemental analysis calcd (%) for $C_{20}H_{52}O_2Si_7$ (521.2): C 46.09, H 10.06; found: C 46.64, H 9.90.

(6a*RS*,10a*RS*)-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)decahydrobenzo[*g*][1,6,2,3,4,5]dioxatetrasilocine (**12d**)

Silane **2c** (420 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *trans*-cyclohexane-1,2-diol (**7a**, 100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane) to yield **12d** as a colorless solid (359 mg, 69%, racemate): R_f=0.4 (*n*-heptane); m.p.: 111–127°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.03–2.92 (m, 2H, H-1, H-2), 1.81–1.68 (m, 2H, H-3e, H-6e), 1.61–1.53 (m, 2H, H-3a, H-6a), 1.17–1.02 (m, 4H, H-4a, H-4e, H-5a, H-5e), 0.26 (s, 12H, $SiMe_2$), 0.22 (s, 18H, $SiMe_3$), 0.17 (s, 18H, $SiMe_3$); ^{13}C NMR (76 MHz, $CDCl_3$): δ = 82.1 (C-1, C-2), 34.2 (C-3, C-6), 24.4 (C-4, C-5), 0,4,–1.6 ($SiMe_3$), –3.0, -3.7 ($SiMe_2$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 5.5 (Si-O), –15.6, –16.3 ($SiMe_3$), –37.4 ($SiMe_2$) ppm; MS (CI–isobutane): *m/z* = 579 [M+H]$^+$, 563 [M–Me]$^+$, 505 [M–$SiMe_3$]$^+$, 73 [$SiMe_3$]; elemental analysis calcd (%) for $C_{22}H_{58}O_2Si_8$ (579.4): C 45.61, H 10.09; found: C 45.29, H 10.16.

(6a*R*,10a*S*)-3,3,4,4-tetramethyl-2,2,5,5-tetrakis(trimethylsilyl)decahydrobenzo[*g*][1,6,2,3,4,5]dioxatetrasilocine (**12e**)

Silane **2c** (420 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *cis*-cyclohexane-1,2-diol (**7b**, 100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane) to yield **12e** as a colorless solid. (281 mg, 54%): R_f=0.6 (*n*-heptane); m.p.: 123–126°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.36–3.27 (m, 2H, H-1, H-2), 1.74–1.45 (m, 4H, H-3e, H-3a, H-6e, H-6a), 1.37–1.09 (m, 4H, H-4a, H-4e, H-5a, H-5e), 0.27 (s, 6H, $SiMe_2$), 0.26 (s, 6H, $SiMe_2$), 0.19 (s, 18H, $SiMe_3$), 0.18 (s, 18H, $SiMe_3$); ^{13}C NMR (76 MHz, $CDCl_3$): δ = 76.9 (C-1, C-2), 30.9 (C-3, C-6), 22.0 (C-4, C-5), –1.3, 0.4 ($SiMe_3$), –3.1, –3.3 ($SiMe_2$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 1.7 (SiO), –14.0, –16.5 ($SiMe_3$), –37.1 ($SiMe_2$) ppm; MS (CI–isobutane): *m/z* = 579 $[M+H]^+$, 563 $[M–Me]^+$, 505 $[M–SiMe_3]^+$, 73 $[SiMe_3]$; elemental analysis calcd (%) for $C_{22}H_{58}O_2Si_8$ (579.4): C 45.61, H 10.09; found: C 45.73, H 10.02.

(1*R*,7*S*)-4,4-dimethyl-3,3,5,5-tetrakis(trimethylsilyl)-2,6-dioxa-3,4,5-trisilabicyclo[5.3.1]undecane (**14**)

Silane **11b** (500 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *cis*-cyclohexane-1,3-diol **13a** (100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane) to yield **14** as a colorless solid (380 mg, 82%): R_f=0.6 (*n*-heptane); m.p.: 147–150°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.80–3.73 (m, 2H, H-1, H-3), 2.23–2.10 (m, 1H, H-2e), 2.08–1.87 (m, 1H, H-5a), 1.77–1.64 (m, 2H, H-4e, H-6e), 1.41–1.29 (m, 2H, H-4a, H-6a), 1.28–1.23 (m, 1H, H-2a), 1.17–1.08 (m, 1H, H-5e), 0.46 (s, 3H, Me), 0.29 (s, 3H, Me), 0.20 (s, 18H, $SiMe_3$), 0.19 (s, 18H, $SiMe_3$); ^{13}C NMR (76 MHz, $CDCl_3$): δ = 70.8 (C-1, C-3), 34.9 (C-2), 34.3 (C-4, C-6), 14.4 (C-5), 1.4 ($SiMe_3$), 0.4, 0.1 ($SiMe_2$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = –0.3 (SiO), –13.3, –16.1 ($SiMe_3$), –38.5 ($SiMe_2$) ppm; MS (CI–isobutane): *m/z* = 521 $[M+H]^+$, 506 $[M–Me]^+$, 447 $[M–SiMe_3]^+$, 73 $[SiMe_3]$; elemental analysis calcd (%) for $C_{20}H_{52}O_2Si_7$ (521.2): C 46.09, H 10.06; found: C 46.23, H 10.10.

(1*R*,8*S*)-4,4,5,5-tetramethyl-3,3,6,6-tetrakis(trimethylsilyl)-2,7-dioxa-3,4,5,6-tetrasilabicyclo[6.3.1]dodecane (**15**) $C_{22}H_{58}O_2Si_8$)

Silane **11c** (420 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *cis*-cyclohexane-1,3-diol **13a** (100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane/EtOAc 100/1) to yield **15** as colorless solid (354 mg, 68%): R_f = 0.2 (*n*-heptane); m.p.: 146–152°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.73–2.66 (m, 2H, H-1, H-3), 2.09–1.90 (m, 1H, H-5a), 1.85–1.73 (m, 1H, H-2e), 1.68–1.56 (m, 2H, H-4e, H-6e), 1.56–1.29 (m, 3H, H-2a, H-4a, H-6a), 1.21–1.07 (m, 1H, H-5e), 0.28 (s, 6H, Me), 0.24 (s, 6H, Me), 0.21 (s, 18H, $SiMe_3$), 0.17 (s, 18H, $SiMe_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 74.5, 71.5 (C-1, C-3), 34.4 (C-2), 34.0, 33.9 (C-4, C-6), 14.0 (C-5), 1.2, –0.1 ($SiMe_3$), –2.3, –2.6 ($SiMe_2$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 5.8, –4.9 (SiO), –10.8, –15.7 ($SiMe_3$), –32.1, –37.5 ($SiMe_2$) ppm; MS (CI–isobutane): *m/z* = 579 $[M+H]^+$, 563 $[M–Me]^+$, 505 $[M–SiMe_3]^+$, 73 $[SiMe_3]$; elemental analysis calcd (%) for $C_{22}H_{58}O_2Si_8$ (579.4): C 45.61, H 10.09; found: C 45.55, H 10.21.

4-(((1*RS*,3*RS*)-3-hydroxycyclohexyl)oxy)-1,1,1,3,3,5,5,5-octamethyl-2,4-bis(trimethylsilyl)pentasilan-2-ol (**16**) $C_{20}H_{54}O_3Si_7$)

Silane **11b** (500 mg, 0.89 mmol) dissolved in anhydrous dichloromethane (30 mL) and triflic acid (0.17 mL, 1.96 mmol) were reacted with *trans*-cyclohexane-1,3-diol **13b** (100 mg, 0.89 mmol) and Et_3N (0.28 mL, 2 mmol) according to the general procedure. The crude product was purified by column chromatography (*n*-heptane) to yield **14** as a colorless solid (384 mg, 40%,racemate): R_f=0.5 (*n*-heptane/EtOAc 50:1); m.p.: 60–75°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.98–3.92 (m, 1H, H-1), 3.57 (tt, 1H, $^3J_{2a,3}$ = $^3J_{3,4a}$ = 11.5 Hz, $^3J_{2e,3}$ = $^3J_{3,4e}$ = 3.0 Hz, H-3), 2.34–2.23 (m, 1H, $^2J_{2e,2a}$ = 13.5 Hz, H-2e), 1.93–1.83 (m, 1H, H-4e), 1.71–1.53 (m, 3H, H-5e, H-6e, H-5a), 1.39–1.22 (m, 3H, $^2J_{6a,6e}$ = 14.8 Hz, $^3J_{4e,4a}$ = 11.5 Hz, $^3J_{5a,6a}$ = 5.2 Hz, H-4a, H-2a, H-6a), 0.46 (s, 3H, Me), 0.29 (s, 3H, Me), 0.20 (s, 18H, $SiMe_3$), 0.19 (s, 18H, $SiMe_3$); ^{13}C NMR (76 MHz, $CDCl_3$): δ = 75.7 (C-3), 70.8 (C-1), 40.9 (C-2), 35.4 (C-4), 32.3 (C-5), 21.2 (C-6), 1.8 ($SiMe_3$), 0.6, 0.5 ($SiMe_2$); ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 16.1, –4.4 (SiO), –12.8, –14.9 ($SiMe_3$), –36.4 ($SiMe_2$) ppm; MS (CI–isobutane): *m/z* = 522 $[M–Me]^+$, 73 $[SiMe_3]$; elemental analysis calcd (%) for $C_{20}H_{54}O_3Si_7$ (539.2): C 44.55, H 10.09; found: C 44.94, H 10.10.

Acknowledgements

Prof. Dr. Clemens Krempner (Texas Tech University) is gratefully acknowledged for his helpful discussions during the experiments and on the manuscript.

Keywords: silyl triflates • hydrodesilylation • diol protecting group • oligosilanes • σ-conjugation

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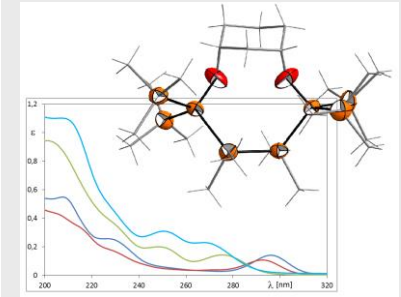
Oligosilanes protecting cyclitols: Oligosilyl triflates were used to protect cyclitols. Depending on the conformation of the OH groups a regioselective protection of the cyclitols was possible. Additionally, several oligosilyl derivatives show a remarkable behavior in the UV due to their σ-conformation.



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Facile Silylation of Cyclitols Using Silyl Bis(triflates)

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