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Synthesis and NMR elucidation of four novel 2-(trimethylsilyl)ethyl glycosides

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Abstract Four novel 2-(trimethylsilyl)ethyl glycosides have been synthesized by a short and efficient route starting from D-glucose. Their structures were elucidated by applying high-resolution mass spectra, and one-dimensional and two-dimensional NMR techniques. These glycosides were prepared and used as intermediate building blocks in the scheme developed for oligosaccharide construction.

Keywords Total synthesis · Structure elucidation · Glycosides · NMR spectroscopy · Oligosaccharides

Introduction

Over the past three decades or so, carbohydrate chemistry has emerged from a fairly self-contained and specialized field to one that has been thrust into a position of center stage in chemical research. This shift in focus for the area, sometimes referred to as "glycoscience", has arisen through the impact of carbohydrates on many disciplines: biochemistry, immunology, medicinal chemistry, plant science, food science, and nanomaterials, to name a few [1]. In recent years, a steadily increasing research effort has been centered on the production of glycosides, and particularly of oligo- and polysaccharides. Crucial impetus has come from the increasing interest shown by biochemists in these substances [2].

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Since the first glycoside syntheses by Michael [3] and Fischer [4], followed by the seminal studies of Koenigs and Knorr [5], a very large number of glycosylation methods have been developed. Unlike proteins and nucleic acids, there is no general synthetic route for oligosaccharide syntheses [6]. The development of efficient and general synthetic routes for oligosaccharides remains a major challenge because of the complexity of their structures.

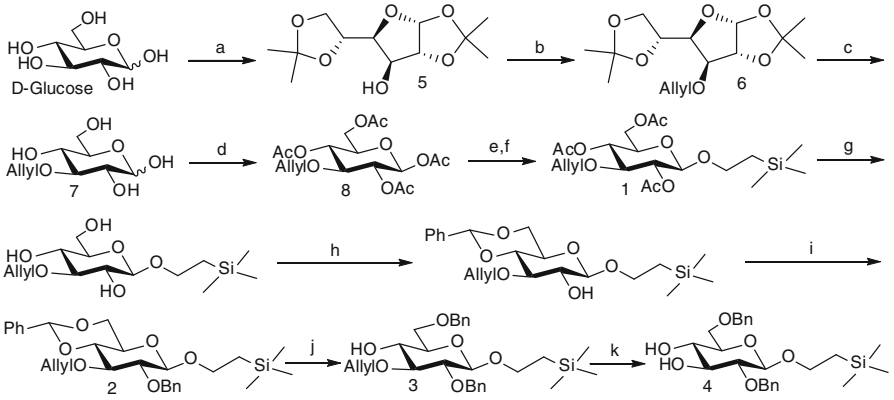
The chemical synthesis of glycosides usually involves the transformation of a sugar into a fully protected glycosyl donor with a leaving group at its anomeric center. Glycosylation of a suitably protected glycosyl acceptor, which generally contains only one free hydroxy group, then follows. Hence, the leaving group of the glycosyl donor and the protecting groups are the most fundamental parameters with respect to the yield and anomeric selectivity of glycosylation reaction [7]. Numerous novel glycosides have been synthesized in recent years to meet the demands of glycosylation reaction [8–10].

In this article, we present the synthesis of four novel 2-(trimethylsilyl)ethyl glycosides. High-resolution mass spectra (HRMS) as well as one-dimensional (1D) and two-dimensional (2D) NMR experiments were used to determine their structures and NMR spectral assignments. These new glycosides can be used as intermediate building blocks for oligosaccharide synthesis, which will be the subject of our further research.

Results and discussion

The total synthesis of new glycosides **1**, **2**, **3**, and **4** was carried as reported in Scheme 1, D-glucose was converted to its diacetonide **5** in high yields according to standard procedures [11, 12]. Subsequent allylation of the remaining free 3-OH group of diacetonide **5**, followed by removal of the isopropylidene protecting groups of allyl ether **6**, provided 3-*O*-allyl-glucose **7**. Acetylation of **7** with acetic anhydride and sodium acetate [13] gave 1,2,4,6-tetra-*O*-acetyl-3-*O*-allyl-β-D-glucopyranose **8**, as colorless crystals after recrystallization from ethanol, then subsequently, via a number of standard steps [14, 15], to a new 2-(trimethylsilyl)ethyl glycoside **1** in 95 % yield. Deacetylation, 4,6-*O*-benzylidenation, and 2-*O*-benzylidenation gave 2-(trimethylsilyl)ethyl 2-*O*-benzylidene-3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranoside **2**. Subsequent reductive benzylidene acetal opening with triethylsilane and trifluoroacetic acid [15, 16] gave the desired glycoside **3** in 81 % yield. Further, the allyl group of glycoside **3** was removed with palladium chloride in methanol [17] to afford glycoside **4** in 96 % yield. New compounds **1**, **2**, **3** and **4** obtained by these reactions were isolated by chromatography, were obtained in analytically pure state, and were fully characterized by HRMS, ^{1}H and ^{13}C NMR data, and physical constants.

The choice of the anomeric protecting group in the synthesis of oligosaccharides is important for several reasons. It should be compatible with a series of different reaction conditions that are to be utilized in the synthesis, it should be removable without affecting the remaining glycosidic bonds of the oligosaccharide, and, preferentially, it should be transformable into activated derivatives for further



Scheme 1 Reagents and conditions: *a* $ZnCl_2$, 85 % phosphoric acid, acetone, r.t., 30 h; 70 %; *b* DMF, NaH, AllBr, 0 °C - r.t., 1 h, 98 %; *c* 10 % AcOH, 80 °C, over night, quant.; *d* Ac_2O, NaOAc, 140 °C, 0.5 h, crystallization 87 %; *e* CH_2Cl_2, HBr/AcOH, 0 °C - r.t., 1.5 h; *f* TMSEtOH, HgO, $HgBr_2$, r.t., 18 h, 95 % (2 steps); *g* NaOMe, MeOH, r.t., over night, quant.; *h* $C_6H_5CH(OCH_3)_2$, CSA, dry CH_3CN, N_2, r.t., over night; *i* DMF, NaH, BnBr, 0 °C - r.t., 0.5 h, 92 % (2 steps); *j* CH_2Cl_2, TES, TFA, 0 °C - r.t., 0.5 h, 81 %; *k* MeOH, $PdCl_2$, r.t., 1 h, 96 %

glycoside synthesis [14, 18]. Here, we chose 2-(trimethylsilyl)ethyl as the anomeric protecting group which fulfills these criteria by being stable under the majority of reaction conditions used in oligosaccharide synthesis. At the same time, both allyl and benzyl are very common protecting groups which can be deprotected rapidly under mild conditions.

Conclusions

The synthesis and complete elucidation of four novel 2-(trimethylsilyl)ethyl glycosides were successfully carried out. The reactions allow the rapid construction of glycosides with high yields from simple and commercially available substrates and reagents. We believe the research will provide meaningful and useful references for oligosaccharide synthesis.

Experimental

All chemicals were purchased as reagent grade and used without further purification. Dichloromethane (CH_2Cl_2) was freshly distilled from P_2O_5. All reactions were carried out under anhydrous conditions with freshly distilled solvents, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on a precoated plate of silica gel 60 F_{254} (Merck), with detection by staining with sulfuric acid. Solvents were evaporated under reduced pressure and below 40 °C (bath). Flash column chromatography was performed on silica gel 60 (230–400 mesh; Merck). NMR spectra were recorded with a Bruker DRX 400 spectrometer (400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR). The chemical

shifts were referenced to the solvent peak, $\delta = 7.26$ ppm (^{1}H) and $\delta = 77.16$ ppm (^{13}C) for $CDCl_3$, at 25 °C, and coupling constants were given in Hz. High-resolution mass spectra (HRMS) were recorded with a Bruker micrOTOF spectrometer in electrospray ionization (ESI) mode, using Tuning-Mix as reference. Optical rotations were measured at 589 nm (Na line) at 20 °C with a Perkin–Elmer Model 343 digital polarimeter, using a 10-cm, 1-mL cell.

1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose **(5)**

To a well-stirred suspension of anhydrous D-glucose (5.0 g, 26.9 mmol) in anhydrous acetone (50 mL) was added pulverized anhydrous zinc chloride (4.0 g) followed by 0.15 mL of 85 % phosphoric acid. This mixture was stirred 30 h at room temperature, and the unreacted sugar was collected and washed with a little acetone. The filtrate and washings were cooled and made slightly alkaline with 2.5 N NaOH. The insoluble inorganic material was removed by filtration and washed with acetone. The almost colorless filtrate and washings were concentrated under reduced pressure and the residue was diluted with water (10 mL), extracted with CH_2Cl_2 (3 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Crystallization of the residue from hexane gave the desired compound as colorless needles (5.01 g, 70 %). $R_f = 0.44$ (Cy-EtOAc 1:1). The NMR data were identical to those reported in literatures [11, 19].

3-*O*-Allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofura-nose **(6)**

To a solution of **5** (3.26 g, 12.5 mmol) in dry DMF (70 mL) were added NaH (60 % in oil, 1.00 g, approximately 25.0 mmol) and allyl bromide (2.2 mL, 25.0 mmol) at 0 °C. The mixture was stirred for 1 h at 23 °C, quenched by careful addition of MeOH, and diluted with diethyl ether and water [20]. The aqueous layer was extracted four times with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (Cy-EtOAc 6:1). Compound **6** was obtained (3.68 mg, 98 %) as a white amorphous solid. $R_f = 0.35$ (Cy-EtOAc 5:1). The NMR spectral data were in good agreement with those reported in literature [21].

3-*O*-Allyl-D-glucofuranose **(7)**

Compound **6** (3.39 g, 11.3 mmol) was dissolved in acetic acid solution (10 %) and stirred at 80 °C overnight. Solvent was evaporated and the resulting sugar **7** was rendered free of water and acetic acid by repeated coevaporation with dry toluene. Yield 2.44 g (yellow syrup, quant.). $R_f = 0.33$ (CH_2Cl_2-MeOH 6:1). The NMR data were identical to those reported in the literature [22].

1,2,4,6-Tetra-*O*-acetyl-3-*O*-allyl-β-D-glucopyranose **(8)**

Compound **7** (2.44 g) was acetylated with acetic anhydride (50 mL) and sodium acetate (2.46 g, 30.0 mmol) under reflux for 30 min. Most of the solvent was

evaporated, and the residue was poured into ice-water, and extracted with chloroform (3 × 30 mL). The extracts were combined, washed successively with water, sat. $NaHCO_3$ solution, and water, dried, and evaporated. Crystallization from ethanol gave **8** (3.74 g, 87 %) as colorless crystals. $R_f = 0.49$ (Cy-EtOAc 1:1). The NMR data were identical to those reported in literature [13].

2-(Trimethylsilyl)ethyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranoside (**1**, $C_{20}H_{34}O_9Si$)

To a stirred, ice-cold solution of **8** (2.55 g, 6.6 mmol) in CH_2Cl_2 (30 mL) was added dropwise HBr in acetic acid (10 mL). The mixture was allowed to gradually warm to room temperature and was stirred 1.5 h. The reaction mixture was neutralized by careful addition of $NaHCO_3$ and iced-water, and the aqueous solution was extracted three times with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was dissolved in dry CH_2Cl_2 (40 mL), and (2-trimethylsilyl)ethanol (2.7 mL, 18.9 mmol), mercury(II) oxide (1.50 g, 6.9 mmol) and mercury(II) bromide (377 mg, 1.0 mmol) were added. The resulting suspension was stirred for 18 h at room temperature. The reaction mixture was then diluted with CH_2Cl_2, stirred with KI and $NaHCO_3$ solution for 2 h at room temperature, and filtered through a pad of Celite. The aqueous eluate was extracted three times with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (Cy-EtOAc 3:1). Compound **1** was obtained (2.82 g, 95 %) as a white amorphous solid. $R_f = 0.32$ (Cy-EtOAc 3:1); mp 65–66 °C; $[\alpha]_D^{20} = -23.4$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.81$–5.70 (m, 1H, =CH), 5.23–5.15 (m, 1H, =CH_2), 5.14–5.09 (m, 1H, =CH_2), 5.02 (d, $J = 9.5$ Hz, 1H, H-4), 4.98–4.92 (m, 1H, H-2), 4.40 (d, $J = 7.9$ Hz, 1H, H-1), 4.23–4.16 (dd, $J = 12.2$, 5.2 Hz, 1H, H-6a), 4.10 (dd, $J = 12.2$, 2.6 Hz, 1H, H-6b), 4.04 (dd, $J = 5.6$, 1.0 Hz, 2H, OCH_2-CH=CH_2), 3.93 (ddt, $J = 13.7$, 9.3, 4.6 Hz, 1H, O$CH_a$$CH_2$Si), 3.61–3.50 (m, 3H, H-3, H-5, O$CH_b$$CH_2$Si), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.06 (s, 3H, OAc), 0.97–0.84 (m, 2H, OCH$_2$$CH_2$Si),−0.01 (s, 9H, Si$(CH_3)_3$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 170.90$ (C=O, Ac), 169.41 (C=O, Ac), 169.20 (C=O, Ac), 134.41 (=CH), 117.06 (=CH_2), 100.57 (C-1), 80.05, 72.70 (OCH_2-CH=CH_2), 72.59 (C-2), 72.09, 69.81 (C-4), 67.32 (O$CH_2$$CH_2$Si), 62.56 (C-6), 21.09 (CH_3, Ac), 20.97 (CH_3, Ac), 20.88 (CH_3, Ac), 18.04 (OCH$_2$$CH_2$Si),−1.32 (3C, Si$(CH_3)_3$) ppm; ESI-HRMS *(m/z)* $C_{20}H_{34}O_9SiNa$ $[M + Na]^+$: calcd. 469.1870, found: 469.1887.

2-(Trimethylsilyl)ethyl 2-*O*-benzylidene-3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**2**, $C_{28}H_{38}O_6Si$)

To a solution of **1** (2.82 g, 6.3 mmol) in MeOH (40 mL) was added sodium methoxide (cat.) and the mixture was stirred overnight at room temperature. The reaction mixture was neutralized with Amberlite IR-120 (H^+) ion-exchange resin, filtered, and concentrated in vacuo. The residue (2.02 g) was dissolved in dry CH_3CN (50 mL), benzaldehyde dimethyl acetal (1.57 mL, 10.4 mmol), and

camphorsulfonic acid (300 mg, 1.29 mmol) were added, and the mixture was stirred overnight at room temperature. The reaction mixture was neutralized with sat. $NaHCO_3$ solution and the resulting aqueous solution was extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue (2.57 g) was dissolved in dry DMF (50 ml), and benzyl bromide (0.9 mL, 7.6 mmol) and NaH (60 % in oil, 504 mg, approximately 21.0 mmol) at 0 °C. The mixture was stirred for 0.5 h, quenched by careful addition of MeOH, and diluted with diethyl ether and water. The aqueous layer was extracted four times with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (Cy-EtOAc 10:1). Compound **2** was obtained (2.89 g, 92 %) as a white amorphous solid. $R_f = 0.35$ (Cy-EtOAc 10:1); mp 78–79 °C; $[\alpha]_D^{20} = -11.5$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.43$–7.30 (m, 10H, Ar–H), 6.05–5.89 (m, 1H, =CH), 5.56 (s, 1H, *CH*-Ph), 5.30 (dd, $J = 17.2$, 1.6 Hz, 1H, =CH_2), 5.17 (dd, $J = 10.4$, 1.4 Hz, 1H, =CH_2), 4.91 (d, $J = 11.0$ Hz, 1H, OCH_2-Ph), 4.80 (d, $J = 11.0$ Hz, 1H, OCH_2-Ph), 4.51 (d, $J = 7.8$ Hz, 1H, H-1), 4.45–4.34 (m, 2H, OCH_2-CH=CH_2, H-6a), 4.33–4.25 (m, 1H, OCH_2-CH=CH_2), 4.01 (dd, $J = 13.5$, 5.4 Hz, 1H, O$CH_a$$CH_2$Si), 3.79 (t, $J = 10.3$ Hz, 1H, H-6b), 3.71–3.60 (m, 3H, O$CH_b$$CH_2$Si, H-4, H-3), 3.41 (dd, $J = 9.8$, 6.4 Hz, 2H, H-2, H-5), 1.09–1.04 (m, 2H, OCH_2CH_2Si), 0.05 (s, 9H, Si$(CH_3)_3$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 138.66$ (C aromatic), 138.21 (C aromatic), 135.33 (=CH), 128.53 (2C, CH aromatic), 128.43 (2C, CH aromatic), 128.22 (2C, CH aromatic), 127.91 (2C, CH aromatic), 127.88 (C, CH aromatic), 127.75 (C, CH aromatic), 116.93 (=CH_2), 103.77 (C-1), 101.23 (*C*H-Ph), 82.34 (C-2), 81.57, 80.81, 75.51 (OCH_2-Ph), 74.15 (OCH_2-CH=CH_2), 68.97 (C-6), 68.14 (OCH_2CH_2Si), 66.14 (C-5), 18.74 (OCH_2CH_2Si),−1.28 (3C, Si$(CH_3)_3$) ppm; ESI-HRMS *(m/z)* $C_{28}H_{38}O_6SiNa$ $[M + Na]^+$: calcd. 521.2335, found: 521.2330.

2-(Trimethylsilyl)ethyl 3-*O*-allyl-2,6-di-*O*-benzyl-β-D-glucopyranoside (**3**, $C_{28}H_{40}O_6Si$)

To a stirred, ice-cold solution of **2** (1.00 g, 2.0 mmol) and triethylsilane (1.9 mL, 11.9 mmol) in CH_2Cl_2 (25 mL) was added dropwise trifluoroacetic acid (1.2 mL, 15.6 mmol). The mixture was stirred for 0.5 h. The reaction mixture was then diluted with CH_2Cl_2 and neutralized with sat. $NaHCO_3$ solution. The aqueous layer was extracted three times with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by flash column chromatography (Cy-EtOAc 5:1). Compound **3** was obtained (0.81 g, 81 %) as a white amorphous solid. $R_f = 0.28$ (Cy-EtOAc 5:1); mp 103–106 °C; $[\alpha]_D^{20} = -25.2$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$–7.27 (m, 10H, Ar–H), 6.02–5.88 (m, 1H,=CH), 5.27 (ddd, $J = 17.2$, 3.3, 1.6 Hz, 1H,=CH_2), 5.21–5.15 (m, 1H, =CH_2), 4.94 (d, $J = 11.1$ Hz, 1H, OCH_2-Ph), 4.71 (d, $J = 11.1$ Hz, 1H, OCH_2-Ph), 4.60 (d, $J = 3.1$ Hz, 2H, OCH_2-Ph), 4.44–4.37 (m, 2H, H-1, OCH_2-CH=CH_2), 4.25 (ddt, $J = 12.6$, 6.0, 1.3 Hz, 1H, OCH_2-CH=CH_2), 4.01 (ddd, $J = 9.6$, 8.2, 6.0 Hz, 1H, O$CH_a$$CH_2$Si), 3.80 (dd, $J = 10.4$, 4.0 Hz, 1H, H-6a), 3.73 (dd, $J = 10.4$, 5.3 Hz, 1H, H-6b),

3.65–3.53 (m, 2H, O$CH_b$$CH_2$Si, H-4), 3.46 (ddd, J = 9.5, 5.3, 4.1 Hz, 1H, H-5), 3.38–3.32 (m, 2H, H-3, H-2), 2.82–2.68 (m, 1H, OH), 1.09–1.00 (m, 2H, O$CH_2$$CH_2$Si), 0.04 (s, 9H, Si($CH_3$)$_3$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.72 (C aromatic), 138.08 (C aromatic), 135.27 (=CH), 128.55 (2C, CH aromatic), 128.45 (2C, CH aromatic), 128.20 (2C, CH aromatic), 127.85 (C, CH aromatic), 127.81 (2C, CH aromatic), 127.76 (C, CH aromatic), 117.20 (=CH_2), 103.29 (C-1), 83.95 (C-3), 81.91 (C-2), 74.81 (OCH_2-Ph), 74.28 (OCH_2-CH=CH_2), 74.06 (C-5), 73.80 (OCH_2-Ph), 71.90 (C-4), 70.66 (C-6), 67.66 (O$CH_2$$CH_2$Si), 18.69 (O$CH_2$$CH_2$Si),−1.29 (3C, Si($CH_3$)$_3$) ppm; ESI-HRMS *(m/z)* $C_{28}H_{40}O_6SiNa$ $[M + Na]^+$: calcd. 523.2492, found: 523.2487.

2-(Trimethylsilyl)ethyl 2,6-di-*O*-benzyl-β-D-glucopyranoside (**4**, $C_{25}H_{36}O_6Si$)

To a mixture of **3** (0.70 g, 1.4 mmol) in MeOH (35 mL), $PdCl_2$ (124 mg, 0.7 mmol) was added and the solution was stirred at room temperature for 1 h, and filtered through a pad of Celite. The solvent was removed and the crude product was immediately charged into a column of silica gel and eluted with Cy-EtOAc 3:2. Compound **4** was obtained (0.62 g, 96 %) as a white amorphous solid. R_f = 0.30 (Cy-EtOAc 3:2); mp 111–114 °C; $[\alpha]_D^{20} = -8.8$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 10H, Ar–H), 4.98 (d, J = 11.5 Hz, 1H, OCH_2-Ph), 4.69 (d, J = 11.5 Hz, 1H, OCH_2-Ph), 4.60 (d, J = 3.3 Hz, 2H, OCH_2-Ph), 4.41 (d, J = 7.8 Hz, 1H, H-1), 4.06–3.96 (m, 1H, O$CH_a$$CH_2$Si), 3.77 (dd, J = 10.4, 3.6 Hz, 1H, H-6a), 3.70 (dd, J = 10.4, 5.1 Hz, 1H, H-6b), 3.64–3.43 (m, 4H, O$CH_b$$CH_2$Si, H-3, H-4, H-5), 3.23 (dd, J = 8.7, 8.0 Hz, 1H, H-2), 3.16 (d, J = 2.1 Hz, 1H, OH), 2.94 (d, J = 2.2 Hz, 1H, OH), 1.11–0.97 (m, 2H, O$CH_2$$CH_2$Si), 0.04 (s, 9H, Si($CH_3$)$_3$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.59 (C aromatic), 138.06 (C aromatic), 128.58 (2C, CH aromatic), 128.53 (2C, CH aromatic), 128.19 (2C, CH aromatic), 127.94 (C, CH aromatic), 127.84 (C, CH aromatic), 127.79 (2C, CH aromatic), 102.93 (C-1), 81.04 (C-2), 76.21 (C-3), 74.45 (OCH_2-Ph), 74.25 (C-5), 73.72 (OCH_2-Ph), 71.60 (C-4), 70.38 (C-6), 67.56 (O$CH_2$$CH_2$Si), 18.63 (O$CH_2$$CH_2$Si),−1.30 (3C, Si($CH_3$)$_3$) ppm; ESI-HRMS (*m/z*) $C_{50}H_{72}O_{12}Si_2Na$ $[2 M + Na]^+$: calcd. 943.4460, found: 943.4464.

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References

1. H. Pellissier, Tetrahedron **61**, 2947 (2005)
2. G. Wulff, G. Röhle, Angew. Chem. Int. Ed. Engl. **13**, 157 (1974)
3. A. Michael, Am. Chem. J. **1**, 305 (1879)
4. E. Fischer, Ber. Dtsch. Chem. Ges. **26**, 24002 (1893)
5. W. Koenig, E. Knorr, Ber. Dtsch. Chem. Ges. **34**, 957 (1901)
6. H. Paulsen, Angew. Chem. Int. Ed. Engl. **21**, 155 (1982)
7. D.P. Galonic, D.Y. Gin, Nature **446**, 1000 (2007)
8. K. Larsen, K. Worm-Leonhard, P. Olsen, A. Hoel, K.J. Jensen, Org. Biomol. Chem. **3**, 3966 (2005)
9. M. Takatani, J. Nakano, M.A. Arai, A. Ishiwata, H. Ohta, Y. Ito, Tetrahedron Lett. **45**, 3929 (2004)
10. A.V. Demchenko, Lett. Org. Chem. **2**, 580 (2005)

11. Y. Saito, T.A. Zevaco, L.A. Agrofoglio, Tetrahedron **58**, 9593 (2002)
12. J. Milecki, E. Zamaratski, T.V. Maltseva, A. Foldesi, R.W. Adamiak, J. Chattopadhyaya, Tetrahedron **55**, 6603 (1999)
13. K. Takeo, T. Nakaji, K. Shinmitsu, Carbohydr. Res. **133**, 275 (1984)
14. K. Jansson, S. Ahlfors, T. Frejd, J. Kihlberg, G. Magnusson, J. Org. Chem. **53**, 5629 (1988)
15. H. Shimizu, J.M. Brown, S.W. Homans, R.A. Field, Tetrahedron **54**, 9489 (1998)
16. M.P. DeNinno, J.B. Etienne, K.C. Duplantie, Tetrahedron Lett. **36**, 669 (1995)
17. B. Mukhopadhyay, N. Roy, Carbohydr. Res. **338**, 589 (2003)
18. K. Jansson, G. Noori, G. Magnusson, J. Org. Chem. **55**, 3181 (1990)
19. C. Adelwohrer, T. Takano, F. Nakatsubo, T. Rosenau, Biomacromolecules **10**, 2817 (2009)
20. V. Pozsgay, E.P. Dubois, L. Pannell, J. Org. Chem. **62**, 2832 (1997)
21. A.B. Smith III, R.A. Rivero, K.J. Hale, H.A. Vaccaro, J. Am. Chem. Soc. **113**, 2092 (1991)
22. H. Ito, R. Eby, S. Kramer, C. Schuerch, Carbohydr. Res. **86**, 193 (1980)