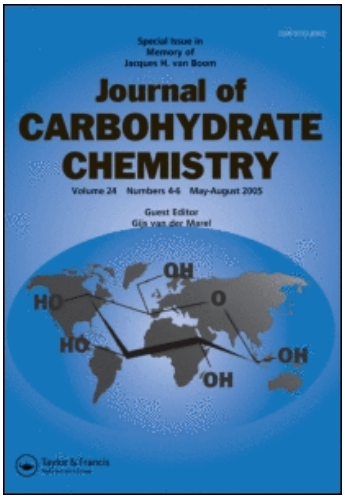

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STEREOSELECTIVE SYNTHESIS OF PSEUDOGLYCAL *C*-GLYCOSIDES VIA TRICHLOROACETIMIDATE ACTIVATION OF GLYCALS[a]

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STEREOSELECTIVE SYNTHESIS OF PSEUDOGLYCAL *C*-GLYCOSIDES VIA TRICHLOROACETIMIDATE ACTIVATION OF GLYCALS

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Dedicated to Prof. Joachim Thiem on the occasion of his 60th birthday.

ABSTRACT

A variety of functionalized pseudoglycal *C*-glycosides (*C*-pseudoglycals or *C*-hex-2-enopyranosides) have been obtained in excellent yield and stereoselectivity from the trimethylsilyl triflate (Me_3SiOTf) catalyzed reaction of trichloroacetimidate derivative **2** with silylated nucleophiles such as allyl and propargyl silanes and silyl enol ethers.

Key Words: Glycal; Pseudoglycal; *C*-glycosides; Trichloroacetimidates; Glycosidation

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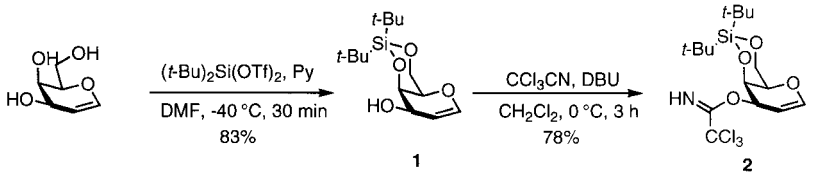
INTRODUCTION

The synthesis of *C*-glycosides has been the subject of intense study[1–4] for various reasons: (1) the discovery of naturally occurring *C*-nucleosides with important pharmacological properties[5] gave impetus to synthetic efforts for preparing active carbohydrate analogs; (2) the synthesis of biologically significant macromolecules such as palytoxin,[6] spongistatin[7] and halichondrin[8] requires *C*-glycosides as chiral building blocks; (3) *C*-glycosides are potential inhibitors of carbohydrate processing enzymes and they are stable analogues of glycans involved in important intra- and intercellular processes.[9,10] Among these *C*-glycosides, *C*-pseudoglycals, i.e., glycals possessing the double bond between C-2 and C-3, represent a very important class of compounds because the double bond can be easily modified, for instance by hydroxylation, hydrogenation, epoxidation and aminohydroxylation.

RESULTS AND DISCUSSION

For the *C*-glycosylation of galactal derivatives with carbon nucleophiles, as an activator a strong Lewis acid such as boron trifluoride etherate ($BF_3{\cdot}OEt_2$)[11,12] or titanium (IV) chloride ($TiCl_4$)[13] is generally required, thus furnishing via Ferrier rearrangement[14] *C*-pseudoglycals. A few examples with indium (III) chloride ($InCl_3$)[15] montmorillonite K-10,[16] 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)[17] and trimethylsilyl triflate (Me_3SiOTf)[18] have also been reported to promote *C*-glycosylation of galactal derivatives under different conditions. However, many of these procedures have limitations in terms of yields, stereoselectivities, reaction temperatures, compatibility with other functional groups present in the molecule, and amounts of catalyst or reagent used. Therefore, there is still a great demand to find a potentially general method for this transformation. Acid catalyzed trichloroacetimidate activation of *O*,*O*- and *N*,*O*-acetals has proven to be a highly attractive and powerful alternative to the classical glycosylation methods and it is currently one of the most frequently applied strategies for glycoside bond formation.[19–22] We reasoned that if one chooses the trichloroacetimidate moiety as the leaving group at the *C*-3 position of the galactal moiety and an efficient catalyst such as trimethylsilyl triflate to cause the desired transformation, the task could become practical. Thus, due to the presence of bulky substituents on the β-side, intermediate tight ion-pair formation, and stereoelectronic effects also favoring α-attack of nucleophiles, the desired α-glycosides of pseudoglycals should become readily accessible.

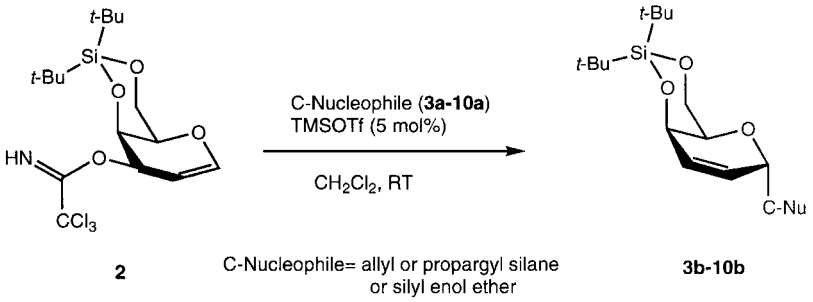


Scheme 1.

The required galactal trichloroacetimidate **2**[23] was synthesized as shown in Scheme 1. Trichloroacetimidate donor **2** was then subjected to *C*-glycosylation using various silylated species as acceptors in the presence of 5 mol% of trimethylsilyl triflate at room temperature (Scheme 2). In a test case, glycosyl donor **2** (1 equiv) was treated with allyltrimethylsilane **3a** (1.1 equiv) as acceptor in the presence of trimethylsilyl triflate (0.05 equiv) in dichloromethane at ambient temperature for 2 h (entry 1, Table 1). This reaction led regio-and stereoselectively to the desired pseudogalactal *C*-allyl α-glycoside **3b** in 93% yield (S_N' reaction) and no trace of 2-deoxyglycoside product nor any attack of the nucleophile at C-3 was detected. Thus, to our utmost satisfaction we were successful in proving our hypothesis concerning the reactivity of galactal trichloroacetimidate **2**. The protons in the ^{1}H NMR spectrum of **3b** and all other products were assigned by ^{1}H–^{1}H homonuclear shift correlated (COSY) 2D NMR spectroscopy. The α-configuration of the allyl *C*-glycoside **3b** was confirmed by the appearance of the anomeric proton at δ 4.19 with a coupling constant value of $J_{1,2}=3.5$ Hz.

Encouraged by these findings, a cross section of silylated nucleophiles was chosen to react with trichloroacetimidate **2**. Substituted allylsilanes such as 2-bromoallylsilane **4a** (entry 2, Table 1) and 2-acetoxymethylallylsilane **5a** (entry 3, Table 1) smoothly afforded the corresponding *C*-α-glycosides **4b** and **5b** in 92% and 93% yield, respectively. The α-configurations of **4b** and **5b** were confirmed by the appearance of the anomeric protons at δ 4.47 and 4.32 with coupling constant values of $J_{1,2}=3.4$ and 3.3 Hz, respectively. The ^{1}H NMR spectrum of **5b** showed a singlet at δ 2.08 corresponding to the acetyl group, while the ^{13}C NMR spectrum showed signals at δ 170.59 (C═O) and 20.90 (Me) of the acetyl group. The reaction of propargylsilane **6a** (entry 4, Table 1) with **1** at 0 °C for 3 h provided allenyl *C*-α-glycoside **6b**, which is a useful precursor for our ongoing programme of enzyme inhibitor synthesis.[24] The ^{1}H NMR spectrum of 6b showed the anomeric proton at δ 4.34 with a coupling constant value of $J_{1,2}=3.5$ Hz, in addition to the presence of multiplets at δ 4.90 and 5.25, which correspond to CH_2 and CH groups. The ^{13}C NMR spectrum of **6b** showed signals at δ 77.22 (CH_2), 89.58 (CH) and 290.15 (═C═) of the allenyl group.

We focused our attention further on the reactivity of silyl enol ethers with **2** under the same conditions. In order to check this, commercially available silyl enol ether **7a** (entry 5, Table 1) was reacted with **2** to produce the corresponding *C*-α-glycoside **7b** as the major product. The ^{1}H NMR spectrum of **7b** showed the anomeric proton at δ 4.49 with a coupling constant value of $J_{1,2}=3.4$ Hz, and the appearance of multiplets at δ 3.10



Scheme 2.

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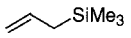
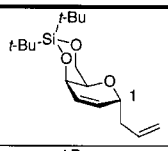
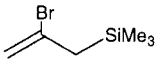
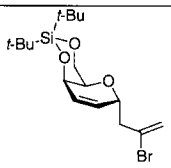
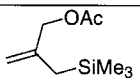
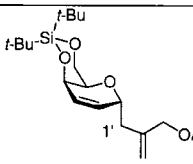
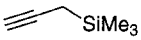
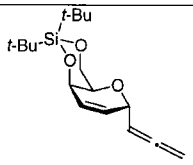
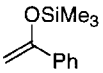
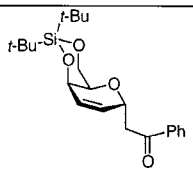
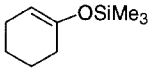
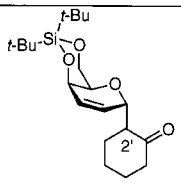
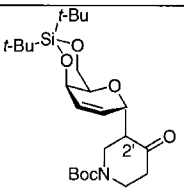
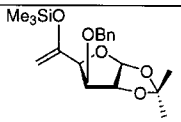
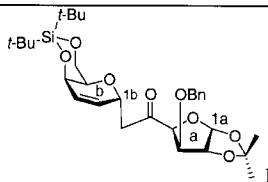
Table 1. Glycosidation of **2** with Silylated Nucleophiles in the Presence of 5 mol% of TMSOTf

Entry	Acceptor	Glycoside	Time (h)	Yield (%)[a]
1	 **3a**	 **3b**	2	93
2	 **4a**	 **4b**	0.5	92
3	 **5a**	 **5b**	3	93
4	 **6a**	 **6b**	0.5	87
5	 **7a**	 **7b**	0.5	92
6	 **8a**	 **8b**	1	89
7	 **9a**	 **9b**	1	89
8	 **10a**	 **10b**	0.5	90

and 3.32, which correspond to the CH_2 group, in addition to the presence of the aromatic protons at δ 7.26–7.92. The ^{13}C NMR spectrum of **7b** showed signals at δ 42.70 (CH_2) and 197.55 (C═O), in addition to the aromatic carbons at δ 128.12, 128.60, 130.01 and 136.91. Silyl enol ether **8a** (entry 6, Table 1) also behaved identically to give *C*-glycoside **8b** in 89% yield. The success of *C*-glycosylation of **2** with silyl enol ether **9a**[25] furnishing **9b** (entry 7, Table 1) is notable, since this indicates that similar Boc-protected amino acid derivatives will be suitable substrates for these reaction conditions, thereby allowing access to *C*-glycosyl amino acids, which have become objects of synthetic interest.[26–32] The α-configurations of compounds **8b** and **9b** were confirmed by the appearance of the anomeric protons as a doublet of doublet at δ 4.33 with a coupling constant value of $J_{1,2} = 3.3$, 6.1 Hz for **8b** and a multiplet at δ 4.39 for **9b**, respectively. The ^1H NMR spectrum of **8b** showed three multiplets at δ 1.57–1.68, 1.97 and 2.39–2.52 corresponding to cyclohexanone, while the ^{13}C NMR spectrum showed signals at δ 210.89 (C═O), 24.64, 27.91, 30.27, 42.71 and 53.45 of the cyclohexanone residue. The ^1H NMR spectrum of **9b** showed two singlets at δ 1.81 and 2.10 corresponding to the *tert*-Bu group of two diastereoismeric forms, while the three multiplets at δ 1.88, 2.19 and 4.39 corresponded to CH and three CH_2 groups. The general applicability of this protocol was further exemplified by the synthesis of a (1→6)-linked *C*-disaccharide derivative **10b** from **10a**[33] (entry 8, Table 1) in 86% yield. The ^1H NMR spectrum of **10b** showed two singlets at δ 1.31 and 1.48 corresponding to two methyl groups, while the multiplets at δ 2.94–3.35 corresponded to two CH_2 groups, in addition to the presence of the aromatic protons at δ 7.20–7.41. The ^{13}C NMR spectrum showed signals at δ 205.70 (C═O), 45.81 and 72.40 (two CH_2), in addition to the aromatic carbons at δ 127.74, 128.16, 128.50 and 132.25. The α-configuration at C-1 in the reaction products was established by careful ^1H NMR analysis and comparison with the spectroscopic data recorded in literature.[13,14,34]

In conclusion, we have developed an efficient and highly regio- and stereoselective protocol for the *C*-glycosylation of galactal derivatives by using trichloroacetimidate as a leaving group at the C-3 position and trimethylsilyl triflate as catalyst. The present method permits the synthesis of a variety of differently functionalized *C*-α-pseudoglycals which are useful intermediates for various applications.

EXPERIMENTAL

General Methods. Allyltrimethylsilane (**3a**), 2-bromoallyltrimethylsilane (**4a**), 2-acetoxymethylallyltrimethylsilane (**5a**), propargyltrimethylsilane (**6a**), 1-phenyl-1-trimethylsiloxyethylene (**7a**) and 1-trimethylsiloxycyclohexene (**8a**) were purchased from Aldrich Chemical and used as received. 1-*tert*-Butoxycarbonyl-1,2,3,6-tetrahydro-4-(trimethylsilyloxy)pyridine (**9a**)[25] and [1-(3-benzyloxy-4,5-dimethyltetrahydrofuran-2-yl)-vinyloxy]trimethylsilane (**3a**)[33] were prepared according to the literature procedures. *N*,*N*-Dimethylformamide (DMF), dichloromethane (CH_2Cl_2), and pyridine were distilled from CaH_2 and stored over molecular sieves. Tetrahydrofuran (THF) was distilled from sodium/benzophenone before use. Other solvents were purified according to the standard procedures. Standard syringe techniques were employed for handling air-sensitive reagents, and all reactions were carried out under argon. TLC was performed on plastic plates Silica Gel 60 F_{254} (E. Merck, layer thickness 0.2 mm). The detection was

achieved by treatment with a solution of 20 g ammonium molybdate and 0.4 g cerium (IV) sulfate in 400 mL 10% H_2SO_4 or with 15% H_2SO_4, and heating at 150°C. Flash chromatography was carried out on silica gel (Baker, 30–60 μm). Optical rotations were determined at rt with a Perkin–Elmer 241/MC polarimeter (1 dm cell). NMR spectra were recorded with Bruker AC 600 DRX instruments, using tetramethylsilane as internal standard. EI and FAB mass spectra were recorded on a Finnigan MAT 312/AMD 5000 spectrometer, using a 1:1 (3-nitrobenzyl)alcohol/glycerol matrix.

Glycosidation of 2 with Allylsilanes and Silyl Enol Ethers (3a–10a) to Give Glycosides (3b–10b): General Procedure. To a stirred mixture of trichloroacetimidate **2** (1 mmol) and acceptor (1.1 mmol) in dry dichloromethane was added TMSOTf (0.05 mmol) at ambient temperature under an argon atmosphere and the contents were stirred for the required time (Table 1). Reactions were monitored by TLC and quenched by the addition of solid sodium bicarbonate (90 mg), diluted with dichloromethane, filtered and concentrated. The crude residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluent to furnish the products.

3-[4,6-*O*-(Di-*tert*-butyl)silanediyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl]-1-propene (3b). TLC (petroleum ether/ethyl acetate, 5:1) $R_f = 0.71$. $[\alpha]_D = -7.5$ (*c* 0.80, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.92 (s, 9 H, C_4H_9), 1.03 (s, 9 H, C_4H_9), 2.27–2.35 (m, 2 H, CH_2), 3.88 (d, 1 H, $J_{5,6} = 6.0$ Hz, H-5), 4.17 (m, 2 H, H-6), 4.19 (m, 1 H, $J_{1,2} = 3.5$ Hz, H-1), 4.48 (m, 1 H, H-4), 5.08 (t, 2 H, $J = 18$ Hz, CH_2), 5.82 (m, 2 H, CH, H-2), 5.96 (m, 1 H, H-3′). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 20.98 (*C*Me_3), 22.24 (*C*Me_3), 27.17 (C*Me*$_3$), 27.34 (C*Me*$_3$), 38.51 (CH_2) 65.06 (C-6), 66.01 (C-4), 68.90 (C-5), 71.22 (C-1), 117.36 (CH_2), 126.70 (C-3), 130.23 (C-2), 134.24 (CH). Mass spectrum, EI (positive mode): $m/z = 310$ (M^+).

Anal. Calcd for $C_{17}H_{30}O_3Si$ (310.51): C, 65.76, H, 9.73. Found: C, 65.49, H, 9.54.

3-[4,6-*O*-(Di-*tert*-butyl)silanediyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl]-2-bromo-1-propene (4b). TLC (petroleum ether/ethyl acetate, 5:1) $R_f = 0.70$. $[\alpha]_D = -211.0$ (*c* 1.0, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.97 (s, 9 H, C_4H_9), 1.05 (s, 9 H, C_4H_9), 2.54 (dd, 1 H, $J = 6.0$, 14.0 Hz, CH_2), 2.69 (dd, 1 H, $J = 8.0$, 14.0 Hz, CH_2), 3.83 (dd, 1 H, $J_{5,6} = 6.1$ Hz, $J_{5,4} = 8.1$ Hz, H-5), 4.18 (m, 2 H, H-6), 4.47 (m, 1 H, $J_{1,2} = 3.4$ Hz, H-1), 4.49 (m, 1 H, H-4), 5.50 (s, 1 H, CH_2), 5.65 (s, 1 H, CH_2), 5.83 (dd, 1 H, $J_{1,2} = 3.4$ Hz, $J_{2,3} = 9.9$ Hz, H-2), 5.98 (m, 1 H, H-3). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 20.92 (*C*Me_3), 22.28 (*C*Me_3), 27.11 (C*Me*$_3$), 27.30 (C*Me*$_3$), 45.11 (CH_2) 65.03 (C-6), 65.72 (C-4), 68.90 (C-5), 69.57 (C-1), 117.24 (CH_2), 127.25 (C-3), 129.28 (C-2), 129.48 (C═). Mass spectrum, EI (positive mode): $m/z = 388/390$ (M^+).

Anal. Calcd for $C_{17}H_{29}BrO_3Si$ (289.40): C, 52.43, H, 7.50. Found: C, 52.58, H, 7.69.

3-[4,6-*O*-(Di-*tert*-butyl)silanediyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl]-2-acetoxymethyl-1-propene (5b). TLC (petroleum ether/ethyl acetate, 5:1) $R_f = 0.73$. $[\alpha]_D = -121.1$ (*c* 1.10, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.96 (s, 9 H, C_4H_9), 1.05 (s, 9 H, C_4H_9), 2.08 (s, 3 H, COC*H*$_3$), 2.24 (m, 1 H, CH_2), 2.35 (m, 1 H, CH_2), 3.85 (d, 1 H, $J_{5,6} = 6.0$ Hz, H-5), 4.17 (m, 2 H, H-6), 4.32 (ddd, 1 H, $J_{1,2} = 3.3$, $J_{1,1'a} = 5.9$, $J_{1,1'b} = 8.3$

Hz, H-1), 4.46 (m, 1 H, H-4), 4.57 (m, 2 H, CH_2), 5.03 (s, 1 H, CH_2), 5.15 (s, 1 H, CH_2), 5.82 (dd, 1 H, $J_{1,2}=3.0$ Hz, $J_{2,3}=10.0$ Hz, H-2), 5.97 (dd, 1 H, $J_{2,3}=10.0$ Hz, $J_{3,4}=5.6$ Hz, H-3). ^{13}C NMR (150.8 MHz, $CDCl_3$): $\delta=20.90$ (*C*Me_3, CO*C*H_3), 22.29 (*C*Me_3), 27.13 (C*Me*$_3$), 27.31 (C*Me*$_3$), 37.36 (CH_2), 65.13 (C-6), 65.82 (C-4), 66.83 (CH_2) 68.62 (C-5), 70.50 (C-1), 115.36 (CH_2), 126.80 (C-3), 130.23 (C-2), 140.32 (=C=), 170.59 (*C*OCH_3). Mass spectrum, EI (positive mode): $m/z=382$ (M^+).

Anal. Calcd for $C_{20}H_{34}O_5Si$ (382.57): C, 62.79, H, 8.95. Found: C, 62.51, H, 8.89.

1-[4,6-*O*-(Di-*tert*-butyl)silanediyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl]-1,2-propadiene (6b). TLC (petroleum ether/ethyl acetate, 5:1) $R_f=0.69$. $[\alpha]_D=+70.1$ (*c* 1.0, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=0.94$ (s, 9 H, C_4H_9), 1.05 (s, 9 H, C_4H_9), 3.86 (d, 1 H, $J_{5,6}=6.1$ Hz, H-5), 4.18–4.30 (m, 2 H, H-6), 4.34 (m, 1 H, $J_{1,2}=3.5$ Hz, H-1), 4.50 (m, 1 H, H-4), 4.90 (m, 2 H, CH_2), 5.25 (m, 1 H, CH), 5.80 (dd, 1 H, $J_{1,2}=3.3$ Hz, $J_{2,3}=10.1$ Hz, H-2), 5.90 (m, 1 H, H-3). ^{13}C NMR (150.8 MHz, $CDCl_3$): $\delta=20.99$ (*C*Me_3), 22.22 (*C*Me_3), 27.19 (C*Me*$_3$), 27.37 (C*Me*$_3$), 65.00 (C-6), 66.07 (C-4), 68.70 (C-5), 71.25 (C-1), 77.22 (CH_2), 89.58 (CH), 126.61 (C-3), 130.21 (C-2), 290.15 (=C=). Mass spectrum EI (positive mode): $m/z=308$ (M^+).

Anal. Calcd for $C_{17}H_{28}O_3Si$ (308.49): C, 66.18, H, 9.14. Found: C, 66.00, H, 9.03.

2-[4,6-*O*-(Di-*tert*-butyl)silanediyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl]-acetophenone (7b). TLC (petroleum ether/ethyl acetate, 5:1) $R_f=0.75$. $[\alpha]_D=-34.7$ (*c* 1.0, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=0.95$ (s, 9 H, C_4H_9), 1.06 (s, 9 H, C_4H_9), 3.10 (m, 1 H, CH_2), 3.32 (m, 1 H, CH_2), 3.86 (dd, 1 H, $J_{5,6}=6.1$ Hz, $J_{5,4}=8.2$ Hz, H-5), 4.14 (m, 2 H, H-6), 4.49 (m, 1 H, $J_{1,2}=3.4$ Hz, H-1), 4.83 (m, 1 H, H-4), 5.94–6.00 (m, 2 H, H-2, H-3), 7.26–7.44 (m, 2 H, arom. H), 7.54–7.57 (m, 1 H, arom. H), 7.92 (m, 2 H, arom. H). ^{13}C NMR (150.8 MHz, $CDCl_3$): $\delta=20.91$ (*C*Me_3), 22.21 (*C*Me_3), 27.10 (C*Me*$_3$), 27.27 (C*Me*$_3$), 42.70 (CH_2), 64.90 (C-6), 65.79 (C-4), 68.60 (C-5), 69.16 (C-1), 126.94 (C-3), 128.12, 128.60, 130.01, 136.91 (arom. C), 133.24 (C-2), 197.55 (C=O). Mass spectrum EI (positive mode): $m/z=388$ (M^+).

Anal. Calcd for $C_{22}H_{32}O_4Si$ (388.58): C, 68.00, H, 8.30. Found: C, 67.79, H, 8.12.

2-[4,6-*O*-(Di-*tert*-butyl)silanediyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl]-cyclohexanone (8b). TLC (petroleum ether/ethyl acetate, 5:1) $R_f=0.72$. $[\alpha]_D=+28.1$ (*c* 0.60, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=0.95$ (s, 9 H, C_4H_9), 1.03 (s, 9 H, C_4H_9), 1.57–1.68 (m, 4 H, 2 CH_2), 1.97 (m, 1 H, CH), 2.39–2.52 (m, 4 H, 2 CH_2), 3.88 (m, 1 H, H-5), 4.19 (m, 2 H, H-6), 4.33 (d, 1 H, $J_{1,2}=3.3$ Hz, $J_{1,2'}=6.1$, H-1), 4.41 (m, 1 H, H-4), 5.85 (m, 1 H, H-2), 5.91 (m, 1 H, H-3). ^{13}C NMR (150.8 MHz, $CDCl_3$): $\delta=20.91$ (*C*Me_3), 22.21 (*C*Me_3), 27.20 (C*Me*$_3$), 27.35 (C*Me*$_3$), 24.64, 27.91, 30.27, 42.71, 53.45 (cyclohexanone), 65.11 (C-6), 65.99 (C-4), 68.75 (C-5), 71.29 (C-1), 126.77 (C-3), 130.27 (C-2), 210.89 (C=O). Mass spectrum EI (positive mode): $m/z=366$ (M^+).

Anal. Calcd for $C_{20}H_{34}O_4Si$ (366.57): C, 65.53, H, 9.35. Found: C, 65.33, H, 9.17.

2-[4,6-*O*-(Di-*tert*-butyl)silanediyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl]-*tert*-butoxycarbonyl-4-piperidone (9b). TLC (petroleum ether/ethyl acetate, 5:1) $R_f=0.69$. $[\alpha]_D=+17.9$ (*c* 0.90, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=0.94$ (s, 9 H, C_4H_9), 1.08 (s, 9 H, C_4H_9), 1.81 (s, 6 H, Boc), 1.88 (m, 2 H, CH_2), 2.10 (s, 3 H, Boc), 2.29 (m, 1 H, CH), 3.80 (d, 1 H, $J_{5,6}=6.0$ Hz, H-5), 4.19 (m, 2 H, H-6),

4.32–4.39 (m, 5 H, H-1, 2 CH_2), 4.40 (m, 1 H, H-4), 5.80 (m, 1 H, H-2), 5.90 (m, 1 H, H-3). Mass spectrum FAB (positive mode, NBOH/NaI-matrix): $m/z = 468$ (MH^+), 490 (MNa^+).

6-[4,6-*O*-(Di-*tert*-butyl)silanediyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl]-3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (10b). TLC (petroleum ether/ethyl acetate, 5:1) $R_f = 0.74$. $[\alpha]_D = -23.5$ (*c* 0.80, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.96$ (s, 9 H, C_4H_9), 1.08 (s, 9 H, C_4H_9), 1.31 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 2.94–3.02 (m, 2 H, CH_2), 3.13 (m, 1 H, CH_2), 3.35 (m, 1 H, CH_2), 3.90 (m, 1 H, H-5b), 4.15 (m, 2 H, H-6b), 4.30 (m, 1 H, H-3a), 4.49–4.54 (m, 3 H, CH_2, H-1b), 4.61 (m, 1 H, H-2a), 4.70 (m, 1 H, H-4a), 4.81 (m, 1 H, H-4b), 6.01–6.03 (m, 2 H, H-2b, H-3b), 6.08 (m, 1 H, H-1a), 7.20–7.41 (m, 5 H, arom. H). ^{13}C NMR (150.8 MHz, $CDCl_3$): $\delta = 20.90$ (*C*Me_3, CO*C*H_3), 22.22 (*C*Me_3), 26.30 (CH_3), 26.92 (CH_3), 27.11 (C*Me*$_3$), 27.25 (C*Me*$_3$), 45.81 (CH_2), 64.85 (C-6b), 65.69 (C-4b), 68.50 (C-5b), 69.15 (C-1b), 72.40 (CH_2), 81.60 (C-2a), 84.01 (C-3a), 85.40 (C-4a), 105.94 (C-1a), 111.15 (*C*Me_2), 126.80 (C-3b), 127.74, 128.16, 128.50, 132.25 (arom. C), 133.20 (C-2b), 205.70 (C═O). Mass spectrum FAB (positive mode, NBOH/NaI-matrix): $m/z =$ 561 (MH^+), 583 (MNa^+).

Anal. Calcd for $C_{30}H_{44}O_8Si$ (560.76): C, 64.25, H, 7.90. Found: C, 64.09, H, 7.67.

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