Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
Tetrahedron 60 (2004) 11465–11475

Chemoselective deprotection of acid labile primary hydroxyl protecting groups under CBr_4-photoirradiation conditions

Ming-Yi Chen,[a,*] Laxmikant N. Patkar,[b] Kuo-Cheng Lu,[b] Adam Shih-Yuan Lee[c] and Chun-Cheng Lin[b,d,*]

[a]*Department of General Education, National Taipei College of Nursing, Taipei 112, Taiwan, ROC*
[b]*Institute of Chemistry, Academia Sinica, Nankang, Taipei 115, Taiwan, ROC*
[c]*Department of Chemistry, Tamkang University, Tamsui 251, Taiwan, ROC*
[d]*Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan, ROC*

Received 14 May 2004; revised 14 September 2004; accepted 17 September 2004

Abstract—The CBr_4-photoirradiation in methanol generates a controlled source of HBr, which can chemoselectively deprotect commonly used hydroxyl-protecting groups in saccharides and nucleosides, such as *tert*-butyldimethylsilyl, isopropylidene, benzylidene and triphenyl ethers in the presence of other acid-labile functional groups.

1. Introduction

A protective and deprotective strategy is a critical part of many synthetic scheme that involve carbohydrate and nucleoside chemistry. According, an impressive array of protective groups have been developed to protect the hydroxyl group, along with methods for removing them.[1] Additionally, the efficient synthesis of polyfunctional target molecules relies on the development of a protection–deprotection strategy with fewer steps than implemented at present. This, in principle, can be achieved using a single group to protect all functional groups and then chemoselectively deprotecting the desired functional group, rather than using different groups to protect each functional group and then deprotecting them individually.[2] The development of chemoselectively deprotecting reagents is critical to the success of this strategy. Our earlier results showed that a catalytic amount of carbon tetrabromide under photoirradiation in methanol can chemoselectively deprotect *tert*-butyldimethylsilyl (TBDMS), isopropylidenyl, benzylidenyl and triphenylmethyl groups on the primary hydroxyl groups of saccharides and nucleosides.[3] This study reports the scope of this mild and efficient protocol.

CBr_4 has been used as a catalyst and reagent to perform various interesting transformations.[4] It has also been successfully used to cleave acetals/ketals,[4b] tetrahydropyranyl ethers,[4a] trialkylsilyl ethers,[5] methoxymethyl ethers, methoxyethoxymethyl ethers,[6] trityl ethers,[7] *p*-methoxybenzyl (PMB)[8] and β-(trimethylsilyl)ethoxymethyl ethers[9] in only catalytic amounts, but heating in methanol to the reflux temperature is required. The success of this deprotection protocol depends on the in situ generation of HBr, which provides mild but sufficiently anhydrous and acidic reaction conditions.[4d,6] This fact motivated us to investigate the use of this protocol in carbohydrate and nucleoside chemistry, eventually leading to identifying the mild reaction conditions.[3]

Among the various protecting groups, commonly used groups, such as TBDMS, acetonide and trityl, were used in this deprotection study. Silyl ethers such as TBDMS are particularly useful because they are stable in the presence of various reagents and conditions.[10] TBDMS ethers can be deprotected under various conditions, including the prescence of fluoride ions, protic acids and Lewis acids.[11–13] In other cases the primary TBDMS group can be selectively removed under acidic conditions if the secondary silyl group is sterically hindered.[14,15] However, this procedure normally exhibits poor selectivity. Apart from silyl ethers, acetonide has been used widely in carbohydrate chemistry to selectively mask the hydroxyls of many sugars. Although normal acidic catalysts such as HCl, HBr, TFA and AcOH have been satisfactory reagents[1,4b,16] for selectively hydrolyzing primary–secondary hydroxyl groups in simple diacetonide derivatives, their strong acidity and free protons make them undesirable hydrolyzing derivatives with acid-sensitive groups.[17]

Keywords: CBr_4-photoirradiation; Deprotection.
* Corresponding authors. Address: National Taipei College of Nursing No. 365, Ming Road, Pei Tou, Taipei 112, Taiwan, ROC. Tel.: +886 2 28227101; fax: 886 2 28264238; e-mail addresses: mingyi@ntcn.edu.tw; cclin@chem.sinica.edu.tw

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.09.095

Triphenylmethyl (trityl) ethers are also extensively used as selective protecting groups for primary alcohols, particularly in carbohydrate and nucleoside chemistry, but few procedures exist for selectively cleaving them.[18] Trityl ethers are generally cleaved under strong protic or Lewis acid conditions, such as in formic acid, 80% acetic acid, mineral acids, zinc bromide, trifluoro acetic acid, iodine–methanol and BCl_3.[7,18] Some methods of detritylation under mild conditions have been reported to avoid the cleavage of glycosidic bond and the hydrolysis of acetate.[18] Numerous such methods suffer from the requirement of the use of strongly acidic conditions, incompatibility with other acid sensitive groups, unsatisfactory yields, corrosive/expensive reagents, longer reaction times and the need for anhydrous conditions.[18]

Here, the CBr_4/MeOH system was applied to cleave selectively *tert*-butyldimethylsilyl, isopropylidene acetals, benzylidine and trityl groups in carbohydrate and nucleoside chemistry.

2. Results and discussion

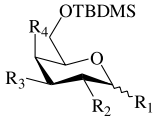
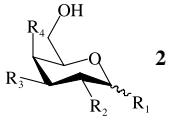
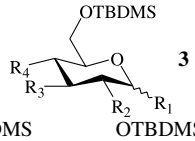
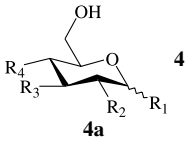
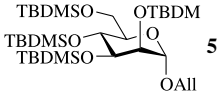
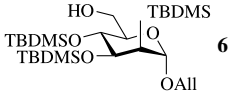
2.1. Deprotection of *tert*-butyldimethylsilyl ethers

Table 1 presents the results of our initial investigation of the regioselective deprotection of primary TBDMS ether in the presence of secondary TBDMS ethers. The primary TBDMS ethers of pyranose sugar,[19] **1**, **3** and **5**, are removed in excellent yields (71–94%) by treatment with a catalytic amount of CBr_4 in methanol under photochemical reaction conditions.[3] The results in Table 1 indicate that other protecting groups on saccharides affected the extent of deprotecting rates. When an anomeric hydroxyl group was protected as methyl ether, the rate of desilylation of the primary silyl ether normally exceeded faster than other types of protecting groups on anomeric center (Table 1, entries 3 and 7). Interestingly, the presence of the free hydroxyl group near the primary silyl ether accelerated the deprotection (Table 1, entry 2 and 11). Notably, no silyl group migration was observed in any cases.

Various substrates **7a–d** with primary and secondary TBDMS groups were prepared[20] and their cleavage investigated to elucidate the utility of the CBr_4/MeOH photoirradiation conditions for deprotecting TBDMS-protected nucleotides (Table 2, entries 1–4). In the presence of the amino group of adenosine **7c** and guanosine **7d**, only moderate yields were obtained after a reaction over 3 days (62 and 54%, respectively) even when the amount of CBr_4 was increased to 50% mole equivalent. In the presence of basic amine on the nucleoside base, the base is expected to trap the catalytic amount of HBr, making it unavailable for deprotection. Contrary to this expectation, however, the deprotection of primary TBDMS in nucleosides proceeded smoothly.

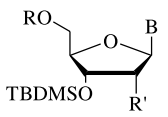
An interesting application of this method was demonstrated by the synthesis of sialic acid derivatives with a free primary

Table 1. Selective deprotection of TBDMS ethers with 5 mol% CBr_4/MeOH

Entry	Substrate[a]				Product	Time[b] (h)	Yield (%)[c]
	 **1**				 **2**		
	R_1	R_2	R_3	R_4			
1	β-SPh-*p*-Me	OTBDMS	OTBDMS	OTBDMS	**2a**	20	75
2	β-SPh-*p*-Me	OTBDMS	OTBDMS	OH	**2b**	1	87
3	α-Ome	OTBDMS	OTBDMS	OTBDMS	**2c**	4	94
4	α-All	OTBDMS	OTBDMS	OTBDMS	**2d**	28	90
5	β-SPh-*p*-Me	Obn	OBn	OTBDMS	**2e**	12	93
6	β-SPh-*p*-Me	OTol[b]	OTol	OTBDMS	**2f**	39	71
7	α-Ome	Obn	OBn	OTBDMS	**2g**	5	85
8	β-SPh-*p*-Me	N_3	OBz	OTBDMS	**2h**	12	89
9	α-SePh	N_3	OTBDMS	OTBDMS	**2i**	20	90
	 **3**				 **4**		
10	β-SPh-*p*-Me	OTBDMS	OTBDMS	OTBDMS	**4a**	28	83
11	β-SPh-*p*-Me	OTBDMS	OTBDMS	OH	**4b**	2	95
12	α-Ome	OTBDMS	OTBDMS	OTBDMS	**4c**	23	87
13	β-SPh-*p*-Me	Obn	OBn	OTBDMS	**4d**	19	90
14	β-SPh-*p*-Me	Otol	OTol	OTBDMS	**4e**	10	92
15	β-SPh-*p*-Me	NHTroc	OTBDMS	OTBDMS	**4f**	6	82
16	 **5**				 **6**	13	83

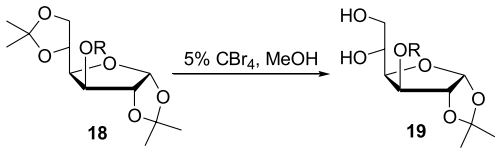
[a] TBDMS, *tert*-butyldimethylsilyl; Tol, *p*-methylbenzoyl; All, allyl; Troc, 2,2,2-trichloroethoxycarbonyl.
[b] Irradiated for 0.5 h then stirred at room temperature.
[c] The isolated yield after chromatographic purification.

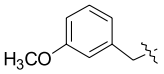
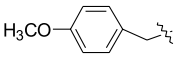
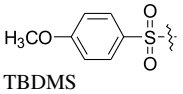
Table 2. Selective deprotection of TBDMS-protected nucleotides with 5 mol% CBr_4/MeOH

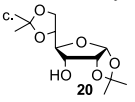
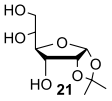
Entry	Substrate			Product	Time (h)[a]	Yield (%)[b]
						
	7 R=TBDMS			**8** R=H		
		B	R′			
1	**7a**	Thymine	H	**8a**	68	85
2	**7b**	Uracil	OTBDMS	**8b**	68	92
3	**7c**	Adenine	OTBDMS	**8c**	72	62 (33)[c]
4	**7d**	Guanosine	OTBDMS	**8d**	72	54 (43)[c]

[a] Irradiated for 0.5 h then stirred at room temperature.
[b] The isolated yield after chromatographic purification.
[c] The number in parenthesis indicates the yield of recovery of the starting material.

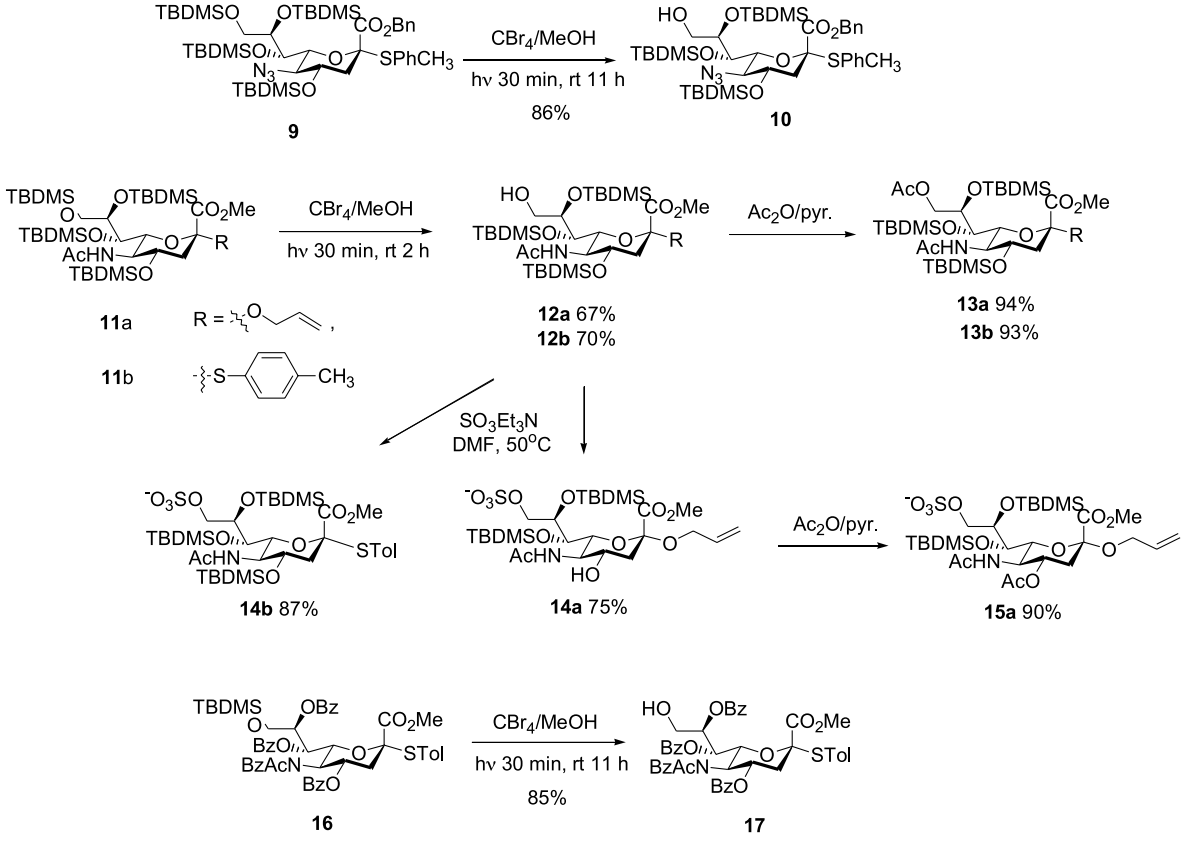
Table 3. Deprotection of isopropylidene from furanose substrates



	R	Reaction time (h)[a]	Yield (%)[b]
a	H[c]	19	95
b		36	86
c	Ac	24	89
d	Bz	24	82
e	Bn	48	84
f		42	85
g		35	83
h		48	88
i	TBDMS	45	81

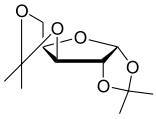
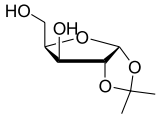
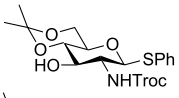
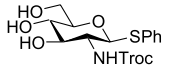
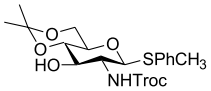
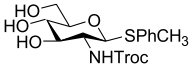
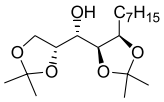
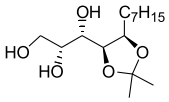
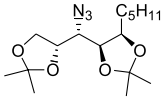
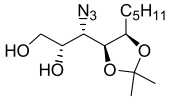
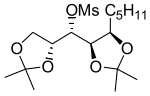
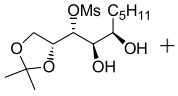
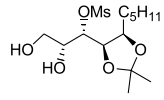
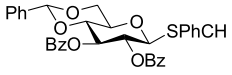
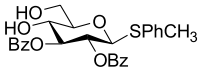
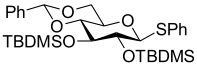
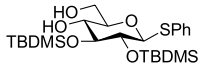
[a] Irradiated for 0.5 h then stirred at room temperature.
[b] The isolated yield after chromatographic purification.
[c]  was also deprotected to get  in 15 h (90%).

hydroxyl group in the C-9 position (Scheme 1). Sialic acids are the terminal sugars of various glycoproteins and glycolipids and participate in masking cell surface antigens, bacterial cell surface activity, cell-to-cell recognition and mitogenic–receptor activity with some lectins.[21] Therefore, the synthesis of analogs of sialic acids has attracted significant interest in studies of relationships between the structure and function and their inhibitory activity.[22] Access to these synthetic analogs depends primarily on the use of appropriate protection–deprotection schemes, since the sialic acid has many hydroxyl groups. As shown in Scheme 1, sialic acid derivative **9**, protected as silyl ether at positions C-4, 7, 8 and 9 underwent the optimized deprotection protocol, producing compound **10** in very high yield. Similarly, compounds **11a** and **11b** gave satisfactory yields of **12a** and **12b**. Compounds **12a** and **12b** were



Scheme 1.

Table 4. Deprotection of isopropylidene and benzylidene groups from saccharides with 5 mol% CBr_4

Entry	Substrate[a]		Time (h)[b]	Product		Yield (%)[c]
1		**22**	8		**23**	86
2		**24**	5		**25**	93
3		**26**	3		**27**	92
4		**28**	43		**29**	72
5		**30**	36		**31**	62
6		**32**	36		**33a**	70 (4:1)
					**33b**	
7[d]		**34**	41		**35**	83
8		**36**	32		**37**	86

[a] Troc, 2,2,2-trichloroethoxycarbonyl; Ms, methanesulfonyl; TBDMS, *tert*-butyldimethylsilyl.
[b] Irradiated for 0.5 h then stirred at room temperature.
[c] The isolated yield after chromatographic purification.
[d] Cosolvent was used to dissolve the substrate ($CH_3OH/CH_2Cl_2=1:1$).

subjected to the standard acetylation protocol to yield compound **13a** and **13b**, confirming that the C-9 hydroxy group had indeed undergone deprotection. The sulfation of **12a** and **12b** in DMF at 50 °C with SO_3/Et_3N gave the sulfated derivatives **14a** (75%) and **14b** (87%). Notably, the TBDMS protecting group at C-4 position of **12a** was cleaved under sulfation conditions. The deprotection of C-4 TBDMS was further verified by acetlyation of **14a** to give **15a**. Consistent with the above results, compound **17** was obtained from **16**. Interestingly, the substituent of amine function group in position C-5 in sialic acid affected the rate of deprotection of C-9 TBDMS. In the presence of the proton at the nitrogen atom, the cleavage of C-9 TBDMS of compounds **11a** and **11b** proceeded more quickly than that of compounds **9** and **16**.

2.2. Deprotection of isopropylidene and benzylidene

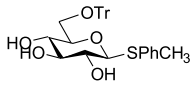
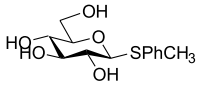
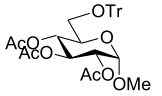
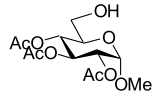
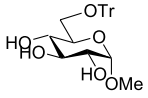
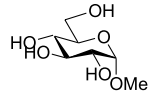
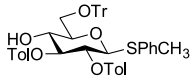
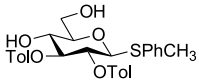
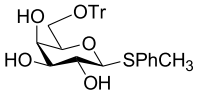
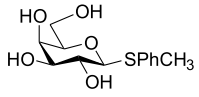
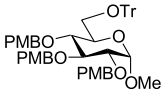
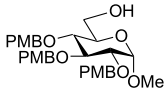
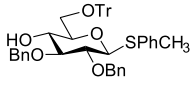
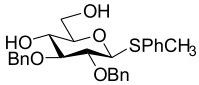
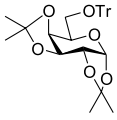
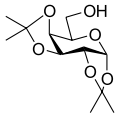
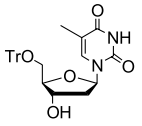
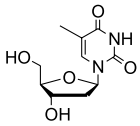
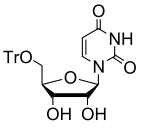
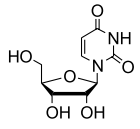
Following the success of the selective cleavage of TBDMS ethers, whether the protocol could be effective in selectively cleaving the isoproylidene group in sugar derivatives was examined (Table 3). Selectively deprotecting of the five-membered 5,6-O-isopropylidene group in **18** using a catalytic amount of CBr_4 in MeOH formed **19**[23] in good yields (81–95%). As shown in Table 3, Ac, Bz, Bn and acid-sensitive protecting groups, such as PMB, MMB, Ts, TBDMS, and allyl ethers, were unaffected under the reaction conditions. The PMB group, which undergoes cleavage in the presence of CBr_4 under methanol reflux conditions, survived under photoirradiation (Entry 7).

According to Table 4, many acid labile acetonide protecting groups were selectively hydrolyzed by the CBr_4-photo-irradiation protocol (Entries 1–6).[24] Notably, in the deprotection of isopropylidene of compound **32**, the internal isopropylidene was more easily cleaved than the terminal isopropylidene. The difference in reactivity may follow from electron withdrawal properties of the Ms group. As expected, the benzylidene group was deprotected with this protocol, yielding **35** (83%) and **37** (86%) from **34** and **36**.

2.3. Deprotection of trityl protecting group

The cleavage of trityl-protected saccharides **38–56**[25] and nucleotides **39–52** by the same method also proceeded smoothly with high yields (Table 5). Other protecting

Table 5. Deprotection of trityl group from saccharides and nucleotides with 5 mol% CBr_4/MeOH

Entry	Substrate[a]		Time (h)[b]	Product[26]		Yield (%)[c]
1		**38**	8		**39**	90
2		**40**	6		**41**	86
3		**42**	5		**43**	93
4		**44**	9		**45**	88
5		**46**	8		**47**	95
6		**48**	38		**49**	91
7		**50**	12		**51**	91
8		**52**	9		**53**	90
9		**54**	13		**55**	97
10		**56**	12		**57**	94

[a] Tr, triphenylmethyl; Tol , *p*-methylbenzoyl; PMB, *p*-methoxybenzyl.
[b] Irradiated for 0.5 h then stirred at room temperature.
[c] The isolated yield after chromatographic purification.

groups present on the substrates were unaffected and no protecting group migrated during the reaction.

3. Conclusion

This work described a novel and efficient method for chemoselectively removing TBDMS, isopropylidene, benzylidine, trityl groups using CBr_4 in MeOH. The method provides several advantages, including operational simplicity, mild reaction conditions, compatibility with other acid sensitive functional groups, low cost of the reagents and high yields of the deprotected products. This method should, therefore, have broad applications in carbohydrate chemistry, in which the selective deprotection of acid labile ethers is an important requirement. The authors believe that this elegant method of deprotection method will also have many applications in natural product synthesis.

4. Experimental

4.1. General

The ^{1}H NMR (proton nuclear magnetic resonance) spectra were recorded at 300 MHz (Bruker-AC300P) with deuteriochloroform ($CDCl_3$, Aldrich 99.8 atom% D) as the solvent and the internal standard. The ^{13}C NMR (carbon nuclear magnetic resonance) spectra were recorded at 75.5 MHz (Bruker-AC300P) with $CDCl_3$ as the solvent and the internal standard. Chemical shifts are reported in parts per million and resonance patterns are reported with the notations of either s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constant (*J*) are reported in hertz (Hz). MeOH was distilled from magnesium and recirculated prior to use. Hexane and ethyl acetate were distilled from calcium hydride. Thin-layer-chromatography

(TLC) analysis was performed on a plastic plate (or glass plate) precoated with silica gel (Merck, 5554 Silica gel 60 F_{254}). Visualization was accomplished by UV light or developed by spraying with a 10% phosphomolybdic acid ethanol solution. Column chromatography was performed using silica gel (Merck, 230–400 mesh) and ethyl/hexane mixture as the eluent.

4.2. General deprotection procedure using CBr_4/MeOH photoirradiation conditions

A solution of protected saccharide (1.0 equiv), CBr_4 (0.05 equiv) and anhydrous MeOH (10 mL/1.0 equiv saccharide) in a pyrex round bottom was irradiated by a TLC-lamp (Uvltec Limited, 245 nm, 8 W) for 0.5 h, followed by stirring without irradiation at room temperature. After the reaction was complete (by TLC), the organic solvent was removed directly under reduced pressure. Further purification was achieved on a flash chromatograph with silica gel and ethyl acetate/hexane.

4.2.1. *p*-Methylphenylsulfinyl 2,3,4-tri-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (2a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.10 (s, 3H), 0.11 (s, 3H), 0.14 (s, 3H), 0.15 (s, 3H), 0.16 (s, 3H), 0.91 (s, 9H), 0.93 (s, 9H), 0.98 (s, 9H), 2.02 (br s, 1H), 2.32 (s, 3H), 3.78–3.83 (m, 2H), 3.85–3.88 (m, 1H), 4.02–4.05 (m, 1H), 4.13 (dd, J=9.0, 2.8 Hz, 1H), 4.54 (d, J=2.8 Hz, 1H), 5.01 (d, J=9.0 Hz, 1H), 7.11 (d, J=7.9 Hz, 2H), 7.39 (d, J=7.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9 (2C), −4.6 (2C), −4.4 (2C), 17.9, 18.3, 18.4, 21.0, 25.8, 25.9, 26.0, 61.9, 68.1, 74.4, 74.9, 78.3, 87.2, 129.9, 130.4, 133.6, 136.8. HRMS (EI) Calcd for $C_{31}H_{61}O_5SSi_3$ $[M+H]^+$: 629.3548. Found: 629.3567.

4.2.2. *p*-Methylphenylsulfinyl 2,3-di-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (2b). ^{1}H NMR (300 MHz, $CDCl_3$) δ0.09 (s, 3H), 0.10 (s, 3H), 0.13 (s, 3H), 0.16 (s, 3H), 0.92 (s, 9H), 0.94 (s, 9H), 0.98 (s, 9H), 1.90 (br s, 2H), 2.31 (s, 3H), 3.46 (dd, J=8.8, 2.8 Hz, 1H, H-3), 3.50–3.54 (m, 1H, H-5), 3.57 (dd, J=11.0, 4.1 Hz, 1H, H-6), 3.77 (dd, J=9.0, 8.8 Hz, 1H, H-2), 3.88 (dd, J=11.0, 7.8 Hz, 1H, H-6), 3.97 (d, J=2.8 Hz, 1H, H-4), 4.47 (d, J=9.0 Hz, 1H, H-1), 7.08 (d, J=7.9 Hz, 2H), 7.38 (d, J=7.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.7, −4.2 (2C), −4.0, 18.3, 18.4, 21.0, 25.9, 26.0, 62.9, 70.4, 71.6, 76.5, 79.7, 88.9, 129.6, 130.5, 131.4, 137.0. HRMS (EI) Calcd for $C_{25}H_{47}O_5SSi_2$ $[M+H]^+$: 515.2683. Found: 515.2696.

4.2.3. *O*-Methyl 2,3,4-tri-*O*-*tert*-butyldimethylsilyl-α-D-galactopyranoside (2c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.08 (s, 3H), 0.09 (s, 3H), 0.11 (s, 6H), 0.87 (s, 9H), 0.88 (s, 9H), 0.89 (s, 9H), 2.00 (br s, 1H), 3.39 (s, 3H), 3.58–3.62 (m, 2H), 3.76–3.82 (m, 3H), 4.12–4.16 (m, 1H), 4.65 (d, J=2.9 Hz, 1H, H-1). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.7, −4.6, −4.5, −3.9, −3.7, −3.2, 17.9, 18.0, 18.4, 25.9, 26.0, 26.1, 55.0, 62.8, 72.1, 73.0, 73.6, 75.9, 98.0. HRMS (EI) Calcd for $C_{25}H_{57}O_6Si_3$ $[M+H]^+$: 537.3463. Found: 537.3478.

4.2.4. *O*-Allyl 2,3,4-tri-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (2d). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.07 (s, 3H), 0.10 (s, 3H), 0.12 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 0.91 (s, 9H), 0.94 (s, 9H), 1.94 (br s, OH, 1H), 3.62 (dd, J=6.3, 2.0 Hz, 1H), 3.86–3.91 (m, 2H), 3.94–3.99 (m, 4H), 4.22 (dd, J=13.2, 4.9 Hz, 1H), 4.85 (d, J=4.9 Hz, 1H), 5.15 (dd, J=10.4, 1.3 Hz, 1H), 5.31 (dd, J=14.0, 1.3 Hz, 1H), 5.87–6.00 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −4.6, −4.3, −4.1, −4.0, −3.7, 18.3, 18.4, 18.6, 26.0, 26.1, 26.4, 62.3, 68.8, 70.6, 72.3, 73.8, 83.2, 90.8, 116.4, 134.4. HRMS (EI) Calcd for $C_{27}H_{59}O_6Si_3$ $[M+H]^+$: 563.3619. Found: 563.3633.

4.2.5. *p*-Methylphenylsulfinyl 2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (2e). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.90 (s, 9H), 2.19 (br s, 1H, OH), 2.33 (s, 3H), 3.45 (dd, J=9.4, 2.5 Hz, 1H, H-3), 3.48 (dd, J=7.8, 4.3 Hz, 1H, H-5), 3.60 (dd, J=11.1, 4.3 Hz, 1H, H-6), 3.80 (t, J=9.4 Hz, 1H, H-2), 3.91 (dd, J=11.1, 7.8 Hz, 1H, H-6), 4.04 (d, J=2.5 Hz, 1H, H-4), 4.55 (d, J=9.4 Hz, 1H, H-1), 4.71 (s, 2H), 4.72 (d, J=10.3 Hz, 1H), 4.76 (d, J=10.3 Hz, 1H), 7.09 (d, J=8.0 Hz, 2H), 7.26–7.40 (m, 10H), 7.48(d, J=8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.0, −3.9, 18.5, 21.1, 26.0, 62.9, 69.2, 73.4, 75.2, 76.6, 80.0, 83.6, 87.3, 127.5, 127.6, 127.8, 128.1, 128.2, 128.3, 129.6, 129.7, 132.3, 137.3, 138.0, 138.3. HRMS (EI) Calcd for $C_{33}H_{45}O_5SSi$ $[M+H]^+$: 581.2757. Found: 581.2774.

4.2.6. *p*-Methylphenylsulfinyl 2,3-di-*O*-*p*-methylbenzyl-4-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (2f). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.20 (s, 3H), −0.07 (s, 3H), 0.83 (s, 9H), 2.32 (s, 3H), 2.33 (s, 3H), 2.34 (s, 3H), 3.62–3.65 (m, 1H), 3.82 (dd, J=7.8, 4.0 Hz, 1H), 3.92 (dd, J=10.7, 7.8 Hz, 1H), 4.33 (d, J=2.5 Hz, 1H, H-4), 4.83 (d, J=10.1 Hz, 1H, H-1), 5.16 (dd, J=10.0 Hz, 2.5, 1H, H-3), 5.66 (dd, J=10.1, 10.0 Hz, 1H), 7.09–7.18 (m, 6H), 7.41 (d, J=8.0 Hz, 2H), 7.80 (d, J=8.2 Hz, 2H), 7.87 (d, J=8.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −4.6, 18.0, 21.2, 21.5, 21.6, 25.6, 62.6, 67.3, 68.6, 76.5, 79.9, 85.4, 126.6, 126.8, 127.0, 129.0, 129.1, 129.5, 129.7, 129.9, 134.4, 138.4, 143.7, 144.0, 165.2, 166.4. HRMS (EI) Calcd for $C_{35}H_{45}O_7SSi$ $[M+H]^+$: 637.2655. Found: 637.2676.

4.2.7. *O*-Methyl 2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (2g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.11 (s, 3H), 0.92 (s, 9H), 2.66 (br d, 1H, OH), 3.40 (s, 3H), 3.72–3.89 (m, 5H), 4.04–4.07 (m, 1H), 4.67–4.86 (m, 5H), 7.28–7.42 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −3.9, 18.5, 26.0, 55.2, 62.9, 70.5, 71.7, 73.4, 73.8, 75.6, 78.0, 98.9, 127.5(2C), 127.8, 128.0, 128.2, 128.4, 138.4, 138.5. HRMS (EI) Calcd for $C_{27}H_{41}O_6Si$ $[M+H]^+$: 489.2672. Found: 489.2690.

4.2.8. *O*-*tert*-Butyldiphenylsilyl-2-azido-3-*O*-benzoyl-4-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (2h). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.18 (s, 3H), −0.08 (s, 3H), 0.91 (s, 9H), 1.14 (s, 9H), 2.20 (br d, 1H, OH), 3.20 (dd, J=7.6, 6.1 Hz, 1H, H-5), 3.27 (dd, J=10.9, 6.1 Hz, 1H, H-6), 3.50 (dd, J=10.8, 7.6 Hz, 1H, H-2), 3.99 (dd, J=10.9, 7.6 Hz, 1H, H-2), 4.06 (d, J=2.7 Hz, 1H, H-4), 4.68 (d, J=7.6 Hz, 1H, H-1), 4.75 (dd, J=10.8, 2.7 Hz, 1H, H-3), 7.36–7.50 (m, 8H), 7.57–7.60 (m, 1H), 7.70–7.80 (m, 4H), 8.05–8.08 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.8, −5.7,

18.1, 19.2, 22.6, 25.7, 63.2, 63.8, 67.6, 73.0, 74.6, 97.2, 127.4, 128.2, 128.4, 129.4, 129.6, 129.7, 129.9, 132.7, 133.2, 133.3, 135.8, 135.9, 165.7. HRMS (EI) Calcd for $C_{35}H_{48}N_3O_6Si_2$ $[M+H]^+$: 662.3082. Found: 662.3100.

4.2.9. Phenylselenyl 2-azido-3,4-di-*O*-*tert*-butyldimethylsilyl-α-D-galactopyranoside (2i). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.17 (s, 3H), 0.19 (s, 3H), 0.22 (s, 3H), 0.90 (s, 9H), 0.98 (s, 9H), 1.56 (br s, 1H), 3.53 (dd, J=11.3, 4.2 Hz, 1H, H-6), 3.73 (dd, J=11.3, 7.9 Hz, 1H, H-6), 3.86 (dd, J=9.8, 2.1 Hz, 1H, H-3), 3.94 (d, J=2.1 Hz, 1H, H-4), 4.12–4.18 (m, 2H), 6.01 (d, J=4.8 Hz, 1H, H-1), 7.24–7.29 (m, 3H), 7.61–7.64 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −4.5, −3.9, −3.6, 18.4, 18.5, 26.0, 26.3, 62.4, 62.7, 71.7, 73.4, 75.2, 84.8, 128.0, 129.1, 131.5, 135.2. HRMS (EI) Calcd for $C_{24}H_{44}N_3O_4SeSi_2$ $[M+H]^+$: 574.2036. Found: 574.2051.

4.2.10. *p*-Methylphenylsulfinyl 2,3,4-tri-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (4a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.08 (s, 3H), 0.10 (s, 3H), 0.11 (s, 3H), 0.13 (s, 6H), 0.88 (s, 9H), 0.89 (s, 9H), 0.91 (s, 9H), 2.04 (br s, 1H), 2.32 (s, 3H), 3.68–3.79 (m, 3H), 3.80–3.89 (m, 3H), 4.90 (d, J=6.7 Hz, 1H), 7.09 (d, J=8.1 Hz, 2H), 7.37 (d, J=8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −4.4, −4.3, −4.2, −4.1, −4.0, 17.9, 18.0, 18.1, 21.0, 25.8, 25.9, 26.0, 64.0, 71.2, 75.4, 77.2, 82.8, 87.5, 129.6, 131.0, 131.7, 136.8. HRMS (EI) Calcd for $C_{31}H_{61}O_5SSi_3$ $[M+H]^+$: 629.3547. Found: 629.3564.

4.2.11. *p*-Methylphenylsulfinyl 2,3-di-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (4b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.10 (s, 3H), 0.13 (s, 3H), 0.19 (s, 3H), 0.84 (s, 9H), 0.90 (s, 9H), 1.80 (br s, 2H), 2.28 (s, 3H), 3.38–3.46 (m, 4H), 3.59 (dd, J=11.8, 6.0 Hz, 1H), 3.87 (dd, J=11.8, 2.7 Hz, 1H), 4.51 (d, J=9.0 Hz, 1H), 7.06 (d, J=7.9 Hz, 2H), 7.31 (d, J=7.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −4.0, −3.8, −3.6, 18.2, 18.4, 21.1, 25.9, 26.1, 62.5, 71.2, 74.5, 79.9, 80.1, 89.1, 129.7, 130.6, 131.7, 137.6. HRMS (EI) Calcd for $C_{25}H_{47}O_5SSi_2$ $[M+H]^+$: 515.2682. Found: 515.2701.

4.2.12. *O*-Methyl 2,3,4-tri-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (4c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.07 (s, 3H), 0.08 (s, 3H), 0.09 (s, 3H), 0.11 (s, 3H), 0.14 (s, 3H), 0.88 (s, 9H), 0.89 (s, 9H), 0.91 (s, 9H), 3.38 (s, 3H), 3.56–3.64 (m, 2H), 3.77–3.84 (m, 3H), 3.92 (m, 1H), 4.65 (d, J=3.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.7, −4.6, −4.5, −3.9, −3.7, −3.2, 18.0, 18.1, 18.4, 25.9, 26.0, 26.1, 55.0, 62.9, 72.1, 73.0, 73.5, 75.2, 98.0. HRMS (EI) Calcd for $C_{25}H_{57}O_6Si_3$ $[M+H]^+$: 537.3463. Found: 537.3478.

4.2.13. *p*-Methylphenylsulfinyl 2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (4d). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (s, 3H), 0.10 (s, 3H), 0.89 (s, 9H), 1.96 (br s, 1H), 2.36 (s, 3H), 3.33–3.37 (m, 1H), 3.46–3.56 (m, 2H), 3.62 (dd, J=6.2, 3.2 Hz, 1H), 3.69 (dd, J=5.9, 5.9 Hz, 1H), 3.88 (dd, J=11.6, 2.7 Hz, 1H), 4.66 (d, J=10.1 Hz, 1H), 4.69–4.72 (m, 1H), 4.81 (d, J=11.6, 1H), 4.93 (d, J=10.1, 1H), 5.00 (d, J=11.6, 1H), 7.14 (d, J=8.2 Hz, 2H), 7.26–7.34 (m, 10H), 7.54 (d, J=8.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.8, −3.9, 17.9, 21.0, 25.8, 62.3, 68.1, 70.6, 75.2, 80.7, 81.5, 86.6, 87.8, 126.7, 127.1, 127.8, 128.1, 128.3, 128.8, 129.2, 129.8, 130.8, 132.3, 137.8, 138.7. HRMS (EI) Calcd for $C_{33}H_{45}O_5SSi$ $[M+H]^+$: 581.2757. Found: 581.2776.

4.2.14. *p*-Methylphenylsulfinyl 2,3-di-*O*-*p*-methylbenzyl-4-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (4e). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.20 (s, 3H), 0.05 (s, 3H), 0.75 (s, 9H), 2.33 (s, 3H), 2.34 (s, 6H), 3.52–3.58 (m, 1H), 3.73–3.79 (m, 1H), 3.93–3.99 (m, 2H), 4.90 (d, J=9.8, 1H), 5.26 (dd, J=9.7, 9.7 Hz, 1H), 5.58 (dd, J=9.8, 9.7 Hz, 1H), 7.09–7.13 (m, 6H), 7.32–7.35 (m, 2H), 7.76–7.81 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.8, −4.3, 17.8, 21.1, 21.6, 22.6, 25.5, 61.7, 68.8, 70.9, 76.7, 80.9, 86.3, 126.6, 127.0, 128.4, 129.0(2C), 129.7(2C), 129.8, 133.2, 138.4, 143.6, 143.8, 165.3, 165.8. HRMS (EI) Calcd for $C_{35}H_{45}O_7SSi$ $[M+H]^+$: 637.2655. Found: 637.2676.

4.2.15. *p*-Methylphenylsulfinyl 3,4-tri-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-(2,2,2-trichloro ethoxycarbonylamino)-β-D-glucopyranoside (4f). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.10 (s, 3H), 0.12 (s, 3H), 0.87 (s, 9H), 0.89 (s, 9H), 1.99 (br s, 1H), 2.34 (s, 3H), 3.35–3.48 (m, 2H), 3.51 (dd, J=9.2, 9.2 Hz, 1H), 3.63–3.67 (m, 1H), 3.67–3.71 (m, 1H), 4.74–4.78 (m, 3H), 4.85 (dd, J=9.2, 2.6 Hz, 1H), 5.23 (br d, J=12.5 Hz, NH, 1H), 7.11 (d, J=8.1 Hz, 2H), 7.36 (d, J=8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −3.9, −2.7, −1.8, 18.2, 21.0, 21.1, 22.6, 25.8, 53.4, 60.4, 62.2, 71.8, 74.8, 76.8, 80.6, 95.3, 129.9, 130.6, 133.0, 137.3, 156.0. HRMS (EI) Calcd for $C_{28}H_{49}Cl_3NO_6SSi_2$ $[M+H]^+$: 688.1885. Found: 688.1902.

4.2.16. *O*-Allyl 2,3,4-tri-*O*-*tert*-butyldimethylsilyl-β-D-mannoside (6). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.07 (s, 3H), 0.09 (s, 3H), 0.10 (s, 3H), 0.13 (s, 3H), 0.14 (s, 3H), 0.88 (s, 9H), 0.90 (s, 9H), 0.94 (s, 9H), 1.82 (br s, 1H, OH), 3.61–3.80 (m, 5H), 3.89 (dd, J=4.2, 1.8 Hz, 1H), 3.99–4.02 (m, 1H), 4.20 (dd, J=12.8, 5.0 Hz, 1H), 4.66 (d, J=5.0 Hz, 1H), 5.15 (dd, J=10.4, 1.5 Hz, 1H), 5.27 (dd, J=15.3, 1.5 Hz, 1H), 5.90 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.3, −4.8, −4.5, −4.2, −3.8, −3.7, 17.9, 18.1, 18.2, 25.7, 25.8, 26.0, 62.7, 68.6, 72.0, 73.0, 75.3, 83.2, 100.0, 116.4, 134.5. HRMS (EI) Calcd for $C_{27}H_{59}O_6Si_3$ $[M+H]^+$: 563.3619. Found: 563.3632.

4.2.17. 3-*O*-*tert*-Butyldimethylsilyl-2-deoxy-β-D-thymidine (8a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.86 (s, 9H), 2.01 (s, 3H), 2.19–2.30 (m, 2H), 3.02 (br s, 1H, OH), 3.72 (dd, J=12.6, 3.6 Hz, 1H), 3.86–3.91 (m, 2H), 4.46 (dd, J=6.5, 2.6 Hz, 1H), 6.15 (dd, J=6.7, 6.5 Hz, 1H), 7.42 (d, J=1.0 Hz, 1H), 9.62 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, −4.8, 12.4, 17.9, 25.7, 40.5, 61.8, 71.5, 86.4, 87.6, 110.8, 137.0, 150.5, 164.2. HRMS (EI) Calcd for $C_{16}H_{29}N_2O_5Si$ $[M+H]^+$: 357.1845. Found: 357.1868.

4.2.18. 2,3-di-*O*-*tert*-Butyldimethylsilyl-β-D-uridine (8b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.06 (s, 3H), 0.08 (s, 3H), 0.09 (s, 3H), 0.87 (s, 9H), 0.90 (s, 9H), 2.93 (br s, 1H, OH), 3.72 (d, J=11.0 Hz, 1H, H-5′), 3.94 (d, J=11.0 Hz, 1H, H-5′), 4.08 (br s, 1H, H-4′), 4.16 (dd, J=4.1, 4.0 Hz, 1H, H-3′), 4.50 (dd, J=4.9, 4.0 Hz, 1H, H-2′), 5.50

(d, J=4.9 Hz, 1H, H-1), 5.72 (d, J=7.6 Hz, 1H), 7.69 (d, J=7.6 Hz, 1H), 9.35 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.8 (2C), −4.7, −4.4, 17.9, 18.0, 25.7, 25.8, 61.4, 71.5, 73.9, 85.8, 93.4, 102.0, 142.9, 150.4, 163.7. HRMS (EI) Calcd for $C_{21}H_{41}N_2O_6Si_2$ $[M+H]^+$: 473.2503. Found: 473.2520.

4.2.19. 2,3-di-*O*-*tert*-Butyldimethylsilyl-β-D-adenosine (8c). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.58 (s, 3H), −1.13 (s, 3H), 0.11 (s, 3H), 0.12 (s, 3H), 0.75 (s, 9H), 0.94 (s, 9H), 3.71 (dd, J=12.4, 1.2 Hz, 1H, H-5′), 3.95 (dd, J=12.4, 1.5 Hz, 1H, H-5′), 4.16 (m, 1H, H-4′), 4.33 (d, J=4.5 Hz, 1H, H-3′), 4.97 (dd, J=7.5 Hz, 4.5, 1H, H-2′), 5.80 (d, J=7.5 Hz, 1H, H-1′), 6.48 (br s, 2H, NH_2), 7.94 (s, 1H), 8.33 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.4, −5.1, −4.7, −4.4, 17.8, 18.5, 25.8, 26.0, 62.3, 72.0, 75.7, 85.4, 88.3, 120.1, 139.6, 150.0, 152.8, 155.5. HRMS (EI) Calcd for $C_{22}H_{42}N_5O_4Si_2$ $[M+H]^+$: 496.2775. Found: 496.2768.

4.2.20. 2,3-di-*O*-*tert*-Butyldimethylsilyl-β-D-guanosine (8d). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.28 (s, 3H), 0.00 (s, 3H), 0.11 (s, 3H), 0.13 (s, 3H), 0.84 (s, 9H), 0.93 (s, 9H), 3.73 (dd, J=12.6, 1.9 Hz, 1H, H-5′), 4.11 (dd, J=12.6, 1.0 Hz, 1H, H-5′), 4.20 (m, 1H, H-4′), 4.28 (dd, J=4.7, 2.8 Hz, 1H, H-3′), 4.57 (dd, J=5.9, 4.7 Hz, 1H, H-2′), 6.00 (d, J=5.9 Hz, 1H, H-1′), 6.35 (br s, 2H, NH_2), 6.75 (br s, 1H, NH_2), 7.97 (s, 1H), 8.33 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.5, −5.0, −4.5, −4.3, 17.9, 18.3, 25.6, 26.1, 61.9, 71.9, 74.5, 81.0, 83.2, 120.1, 138.0, 149.0, 151.0, 155.2. HRMS (EI) Calcd for $C_{22}H_{42}N_5O_5Si_2$ $[M+H]^+$: 512.2724. Found: 512.2738.

4.2.21. Benzyl (*p*-tolyl 5-azido-4,7,8-tri-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-2-thio-D-glycero-α-galacto-non-2-ulpyranosid)onate (10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 6H), 0.01 (s, 3H), 0.07 (s, 3H), 0.13 (s, 3H), 0.20 (s, 3H), 0.87 (s, 9H), 0.88 (m, 1H, H-3), 0.88 (s, 9H), 0.98 (s, 9H), 1.73 (dd, J=11.6, 9.2 Hz, 1H, H-3), 2.34 (s, 3H), 2.69 (dd, J=7.6, 3.5 Hz, 1H, H-5), 3.09 (dd, J=9.5, 1.8 Hz, 1H), 3.30 (dd, J=7.2, 1.8 Hz, 1H), 3.51–3.59 (m, 3H), 3.83 (m, 1H), 4.03 (br s, 1H, OH), 5.03 (d, J=2.2 Hz, 2H), 7.10 (d, J=7.8 Hz, 2H), 7.23–7.27 (m, 3H), 7.34–7.38 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.8, −5.1, −5.0, −4.8, −4.7, −4.1, −3.4, −3.0, 14.4, 17.8, 18.1, 18.4, 25.6, 25.7, 26.1, 26.3, 31.6, 41.0, 62.8, 65.8, 67.6, 71.7, 77.8, 87.5, 125.8, 128.5, 128.6, 129.6, 134.9, 136.3, 139.6, 168.3. HRMS (EI) Calcd for $C_{41}H_{70}N_3O_7SSi_3$ $[M+H]^+$: 832.4242. Found: 832.4267.

4.2.22. Methyl (*O*-allyl 5-acetamido-4,7,8,9-tetra-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-D-glycero-α-galacto-non-2-ulpyranosid)onate (11a). To a solution of sialic acid (280 mg, 0.77 mmol) in CH_2Cl_2 (5 mL) and lutidine (720 μL, 6.16 mmol) was added TBDMSOTf (1 mL, 4.62 mmol), and the mixture was stirred at room temperature for overnight. The solution was evaporated in vacuo, and the residue was purified by column chromatography (EA/Hexane=1/4) to yield product (505 mg, 80%). R_f 0.5 (EA/Hexane=1/4). ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.08 (s, 3H), −0.03 (s, 3H), 0.01 (s, 6H), 0.03 (s, 3H), 0.07 (s, 3H), 0.13 (s, 3H), 0.21 (s, 3H), 0.88 (s, 9H), 0.90 (s, 9H), 0.91 (s, 9H), 0.93 (s, 9H), 1.72 (t, J=12.4 Hz, 1H, H-3*ax*), 1.91 (s, 3H, Ac), 2.59 (dd, J_{3eq-4}=4.8 Hz, $J_{3eq-3ax}$=12.4 Hz, 1H, H-3*eq*), 3.28–3.35 (m, 1H, H-5), 3.54 (dd, J_{9a-8}=7.6 Hz, J_{9a-9b}=10.4 Hz, 1H, H-9a), 3.80 (s, 3H, Me), 3.90–3.93 (m, H-7, 2H, H-9b), 4.02 (dddd, J=1.6, 2.8, 6.0, 12.4 Hz, 1H, All), 4.02–4.06 (m, 2H, H-4, H-8), 4.09 (dd, 1H, J_{6-7}=2.0 Hz, J_{6-5}=10.8 Hz, H-6), 4.27 (dddd, 1H, All, J=1.6, 2.8, 5.2, 12.4 Hz), 5.14 (dddd, 1H, J=1.6, 2.8, 4.8, 10.4 Hz, All), 5.25 (dddd, 1H, J=1.6, 2.8, 4.8, 17.2 Hz, All), 5.45 (d, 1H, J=7.6 Hz, NH), 5.86 (dddd, 1H, J=5.2, 6.0, 10.4, 17.2 Hz, All). ^{13}C NMR (100 MHz, CD_3OD): δ −5.4, −5.3, −5.1, −5.0, −4.6, −4.6, −4.6, −3.9, 17.8, 18.2, 23.8, 25.6, 25.6, 25.6, 26.0, 26.0, 26.0, 26.0, 26.0, 26.0, 26.1, 26.1, 26.1, 41.2, 52.3, 55.5, 64.8, 65.0, 67.7, 74.2, 76.1, 76.8, 98.6, 112.3, 134.0, 168.9, 169.6. HRMS (FAB) calcd for $C_{39}H_{82}NO_9Si_4$ $[M+H]^+$: 820.5066 Found: 820.5081.

4.2.23. Methyl (*p*-tolyl 5-acetamido-4,7,8,9-tetra-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-2-thio-D-glycero-α-galacto-non-2-ulpyranosid)onate (11b). ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.10 (s, 3H), −0.04 (s, 3H), 0.00 (s, 6H), 0.05 (s, 3H), 0.08 (s, 3H), 0.14 (s, 3H), 0.21 (s, 3H), 0.84 (s, 9H), 0.91 (s, 9H), 0.93 (s, 9H), 0.96 (s, 9H), 1.62 (dd, J_{3ax-4}=11.6 Hz, $J_{3ax-3eq}$=12.8 Hz, 1H, H-3*ax*), 1.88 (s, 3H, Ac), 2.36 (s, 3H, CH_3), 2.60 (dd, J_{3eq-4}=4.8 Hz, $J_{3eq-3ax}$=12.8 Hz, 1H, H-3*eq*), 3.21–3.24 (m, 1H, H-5), 3.57 (dd, J_{9a-8}=7.2 Hz, J_{9a-9b}=10.4 Hz, 1H, H-9a), 3.62 (s, 3H, Me), 3.90 (dd, J_{7-8}=1.6 Hz, J_{7-6}=3.2 Hz, 1H, H-7), 3.94 (ddd, J_{8-7}=1.6 Hz, J_{8-9b}=4.0 Hz, J_{8-9a}=7.2 Hz, 1H, H-8), 4.00–4.04 (m, 1H, H-4), 4.01 (dd, J_{6-7}=3.2 Hz, J_{6-5}=10.4 Hz, 1H, 1H, H-6), 4.16 (dd, J_{9b-8}=4.0 Hz, J_{9b-9a}=10.4 Hz, 1H, H-9b), 5.52 (d, J=7.6 Hz, 1H, NH), 7.11 (d, J=8.0 Hz, 2H, Ar), 7.42 (d, J=8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, CD_3OD) δ −5.2, −5.2, −5.0, −4.8, −4.6, −4.5, −4.5, −4.1, 17.8, 18.2, 18.6, 18.6, 21.3, 23.9, 25.6, 25.6, 25.6, 26.1, 26.1, 26.1, 26.1, 26.1, 26.1, 26.2, 26.2, 26.2, 41.9, 52.3, 55.4, 65.0, 68.4, 76.2, 76.4, 76.6, 126.2, 129.4, 129.4, 136.4, 136.4, 139.6, 169.2, 169.5. HRMS (FAB) calcd for $C_{43}H_{84}NO_8SSi_4$ $[M+H]^+$: 886.4995 Found: 886.5009.

4.2.24. Methyl (*O*-allyl 5-acetamido-4,7,8-tri-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-D-glycero-α-galacto-non-2-ulpyranosid)onate (12a). A solution of saccharide (100 mg, 0.12 mmol), CBr_4 (6 mg, 0.018 mmol) and anhydrous MeOH (1.2 mL) in a pyrex round bottom was irradiated by a TLC-lamp (Uvltec Limited, 245 nm, 8 W) for 0.5 h, followed by stirring without irradiation at room temperature. After the reaction was completed (by TLC about 2 h), the organic solvent was removed directly under reduced pressure. Further purification was achieved on a flash chromatography with silica gel and ethyl acetate/hexane(1/2) to get product (57.9 mg, 67%). R_f 0.4 (EA/Hexane=1/4). ^{1}H NMR (400 MHz, $CDCl_3$) δ−0.08 (s, 3H), 0.01 (s, 6H), 0.05 (s, 3H), 0.10 (s, 3H), 0.20 (s, 3H), 0.87 (s, 9H), 0.93 (s, 9H), 0.94 (s, 9H), 1.75 (dd, J_{3ax-4} 11.6 Hz, $J_{3ax-3eq}$=12.8 Hz, 1H, H-3*ax*), 1.93 (s, 3H, Ac), 2.60 (dd, J_{3eq-4}=4.4 Hz, $J_{3eq-3ax}$=12.8 Hz, 1H, H-3*eq*), 3.35–3.42 (m, 1H, H-5), 3.60 (dd, J_{9a-8}=4.8 Hz, J_{9a-9b}= 11.2 Hz, 1H, H-9a), 3.83 (s, 3H, Me), 3.84–3.87 (m, 1H, OH), 3.93 (dd, J_{9b-8}=5.6 Hz, J_{9b-9a}=11.2 Hz, 1H, H-9b), 3.97 (m, 3H, H-4, H-8, H-7), 4.01 (dddd, J=1.2, 2.8, 6.0, 12.8 Hz, 1H, All), 4.14 (dd, J_{6-7}=0.8 Hz, J_{6-5}=10.4 Hz, 1H, H-6), 4.28 (dddd, J=1.2, 3.2, 5.6, 12.8 Hz, 1H, All),

5.15 (dddd, J=1.2, 2.8, 4.8, 10.4 Hz, 1H, All), 5.21 (d, J=7.6 Hz, 1H, NH), 5.27 (dddd, J=1.2, 3.2, 4.8, 17.2 Hz, 1H, All), 5.82 (dddd, J=5.6, 6.0, 10.4, 17.2 Hz, 1H, All). ^{13}C NMR (100 MHz, CD_3OD) δ −5.2, −5.0, −4.8, −4.5, −4.5, −3.9, 17.8, 18.3, 18.5, 23.7, 25.6, 25.6, 25.6, 26.0, 26.0, 26.0, 26.0, 26.0, 26.0, 41.1, 52.6, 55.6, 63.3, 65.1, 67.3, 74.2, 74.7, 77.2, 98.8, 117.2, 133.8, 168.9, 169.7. HRMS (FAB) calcd for $C_{33}H_{68}NO_9Si_3$ $[M+H]^+$: 706.4202 Found: 706.4214.

4.2.25. Methyl (*p*-tolyl 5-acetamido-4,7,8-tri-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-2-thio-D-glycero-α-galacto-non-2-ulpyranosid)onate (12b). ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.06 (s, 3H), 0.01 (s, 3H), 0.03 (s, 3H), 0.07 (s, 3H), 0.10 (s, 3H), 0.20 (s, 3H), 0.86 (s, 9H), 0.91 (s, 9H), 0.98 (s, 9H), 1.70 (dd, J_{3ax-4}=11.6 Hz, $J_{3ax-3eq}$=12.8 Hz, 1H, H-3*ax*), 1.90 (s, 3H, Ac), 2.36 (s, 3H, CH_3), 2.72 (dd, J_{3eq-4}=4.8 Hz, $J_{3eq-3ax}$=12.8 Hz, 1H, H-3*eq*), 3.27–3.34 (m, 1H, H-5), 3.50 (dd, J_{9a-8}=4.8 Hz, J_{9a-9b}=11.6 Hz, 1H, H-9a), 3.64 (s, 3H, Me), 3.71–3.74 (m, 1H, H-8), 3.91 (dd, J_{9b-8}=6.0 Hz, J_{9b-9a}=11.6 Hz, 1H, H-9b), 3.95–4.03 (m, 3H, H-4, H-6, H-7), 5.19 (d, J=7.6 Hz, 1H, NH), 7.14 (d, J=8.0 Hz, 2H, Ar), 7.43 (d, J=8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, CD_3OD) δ −5.2, −5.0, −4.9, −4.6, −4.5, −3.9, 17.8, 18.3, 18.6, 23.7, 25.6, 25.6, 25.6, 26.0, 26.0, 26.0, 26.1, 26.1, 26.1, 41.7, 52.5, 55.7, 63.3, 67.8, 74.5, 76.1, 77.7, 87.4, 125.3, 129.5, 129.5, 136.8, 136.8, 140.2, 169.0, 169.7. HRMS (FAB) calcd for $C_{37}H_{70}NO_8S_1Si_3$ $[M+H]^+$: 772.4130 Found: 772.4127.

4.2.26. Methyl (*O*-allyl 5-acetamido-9-*O*-acetyl-4,7,8-tri-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-D-glycero-α-galacto-non-2-ulpyranosid)onate (13a). To a solution of sialic acid (50 mg, 0.07 mmol) in pyridine (2 mL) was added Ac_2O (0.5 mL) at 0 °C, and the mixture was stirred at room temperature for overnight. The solution was evaporated in vacuo, and the residue was purified by column chromatography (EA/Hexane=1/4) to yield product (50 mg, 94%). R_f 0.3 (EA/Hexane=1/4). ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.10 (s, 3H), 0.00 (s, 3H), 0.02 (s, 3H), 0.07 (s, 3H), 0.14 (s, 3H), 0.20 (s, 3H), 0.87 (s, 9H), 0.91 (s, 9H), 0.94 (s, 9H), 1.70 (dd, J_{3ax-4}=11.6 Hz, $J_{3ax-3eq}$=12.8 Hz, 1H, H-3*ax*), 1.92 (s, 3H, Ac), 2.04 (s, 3H, Ac), 2.63 (dd, J_{3eq-4}=4.8 Hz, $J_{3eq-3ax}$=12.8 Hz, 1H, H-3*eq*), 3.21–3.28 (m, 1H, H-5), 3.81 (s, 3H, Me), 3.94–3.95 (m, 1H, H-7), 3.97 (dddd, J=1.2, 2.8, 5.6, 12.4 Hz, 1H, All), 4.03 (dd, J_{9a-8}=4.4 Hz, J_{9a-8}=10.4 Hz, 1H, H-9a), 4.05–4.14 (m, 2H, H-4, H-8), 4.19 (dd, J_{6-7}=1.2 Hz, J_{6-5}=10.4 Hz, 1H, H-6), 4.27 (dddd, J=1.6, 3.2, 5.2, 12.4 Hz, 1H, All), 4.55 (d, J=10.4 Hz, 1H, H-9b), 5.14 (dddd, J=1.2, 2.8, 4.8, 10.4 Hz, 1H, All), 5.23–5.28 (m, 1H, All), 5.26 (dddd, J=1.6, 3.2, 4.8, 17.2 Hz, 1H, All), 5.85 (dddd, J=5.2, 5.6, 10.4, 17.2 Hz, 1H, All). ^{13}C NMR (100 MHz, CD_3OD) δ −5.3, −5.0, −4.9, −4.6, −4.5, −3.8, 17.8, 18.1, 18.4, 21.0, 23.7, 25.6, 25.6, 25.57, 25.8, 25.8, 25.8, 26.0, 26.0, 26.0, 41.6, 52.4, 55.9, 65.2, 66.9, 67.1, 73.8, 74.8, 75.2, 98.6, 117.0, 134.0, 168.8, 169.8, 170.8. HRMS (FAB) calcd for $C_{35}H_{70}NO_{10}Si_3$ $[M+H]^+$: 748.4307 Found: 748.4297.

4.2.27. Methyl (*p*-tolyl 5-acetamido-9-acetyl-4,7,8-tri-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-2-thio-D-glycero-α-galacto-non-2-ulpyranosid)onate (13b). ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.09 (s, 3H), −0.01 (s, 3H), 0.02 (s, 3H), 0.05 (s, 3H), 0.12 (s, 3H), 0.19 (s, 3H), 0.87 (s, 9H), 0.89 (s, 9H), 0.98 (s, 9H), 1.71 (dd, J_{3ax-4}=11.6 Hz, $J_{3ax-3eq}$=12.8 Hz, 1H, H-3*ax*), 1.90 (s, 3H, Ac), 2.04 (s, 3H, Ac), 2.34 (s, 3H, CH_3), 2.75 (dd, J_{3eq-4}=4.4 Hz, $J_{3eq-3ax}$=12.8 Hz, 1H, H-3*eq*), 3.15–3.22 (m, 1H, H-5), 3.59 (s, 3H, Me), 3.91–3.93 (m, 2H, H-7, H-9a), 4.01–4.07 (m, 2H, H-4, H-6), 4.24–4.33 (m, 1H, H-8), 4.31 (dd, J_{9b-8}=7.6 Hz, J_{9b-9a}=12.0 Hz, 1H, H-9b), 5.25 (d, J=7.6 Hz, 1H, NH), 7.09 (d, J=8.0 Hz, 2H, Ar), 7.39 (d, J=8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, CD_3OD) δ −5.6, −5.2, −5.0, −4.5, −3.8, −3.6, 17.8, 18.0, 18.5, 21.1, 21.3, 23.7, 25.6, 25.6, 25.6, 25.8, 25.8, 25.8, 26.0, 26.0, 26.0, 42.0, 52.2, 56.0, 66.6, 67.8, 74.7, 75.0, 76.0, 87.4, 125.7, 129.4, 129.4, 136.7, 136.7, 139.8, 169.1, 169.7, 170.6. HRMS (FAB) calcd for $C_{39}H_{72}NO_9S_1Si_3$ $[M+H]^+$: 814.4235 Found: 814.4241.

4.2.28. Methyl (*O*-allyl 5-acetamido-7,8-di-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-9-sulfate-D-glycero-α-galacto-non-2-ulpyranosid)onate (14a). To a solution of sialic acid (50.0 mg, 0.07 mmol) in dry DMF (5 mL) was added $(Et_3)_3\cdot SO_3$ (192.5 mg, 1.06 mmol) and the mixture was stirred overnight at 50 °C under Ar. Then, TLC showed the disappearance of starting material and the formation of a new spot. After the addition of MeOH (5 mL), stirring was continued for 15 min. The mixture was concentrated and a solution of residue in MeOH (10 mL) was stirred with Dowex 50 (Na^+) for 1 h, the solution was filtrated and concentrated under reduced pressure. Further purification was achieved on a flash chromatography with silica gel and MeOH/CH_2Cl_2 (1/4) to get product (44.6 mg, 75%). R_f 0.3 (MeOH/CH_2Cl_2=1/4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.05 (s, 3H), 0.12 (s, 3H), 0.19 (s, 3H), 0.97 (s, 9H), 0.98 (s, 9H), 1.69 (t, 1H, J=12.4 Hz, H-3*ax*), 1.99 (s, 3H, Ac), 2.63 (dd, J_{3eq-4}=4.4 Hz, $J_{3eq-3ax}$=12.4 Hz, 1H, H-3*eq*), 3.51–3.56 (m, 1H, H-4), 3.76–3.81 (m, 2H, H-5, H-7), 3.83 (s, 3H, Me), 4.01–4.09 (m, 4H, H-6, H-8, H-9a, All), 4.37 (dddd, J=1.2, 3.2, 5.2, 13.2 Hz, 1H, All), 4.65 (d, J=10.4 Hz, 1H, H-9b), 5.09 (m, 1H, All), 5.26–5.31 (m, 1H, All), 5.85–5.91 (m, 1H, All). ^{13}C NMR (100 MHz, CD_3OD) δ −4.7, −4.2, −3.9, −3.2, 19.3, 19.5, 23.4, 26.8, 26.9, 41.7, 53.1, 54.5, 66.7, 70.0, 71.7, 76.3, 77.0, 77.8, 100.3, 116.8, 135.7, 170.6, 173.8. HRMS (FAB) calcd for $C_{27}H_{54}NO_{12}SSi_2$ $[M+H]^+$: 672.2905 Found: 672.2890.

4.2.29. Methyl (*p*-tolyl 5-acetamido-4,7,8-tri-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-9-sulfate-2-thio-D-glycero-α-galacto-non-2-ulpyranosid)onate (14b). ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.04 (s, 3H), 0.00 (s, 3H), 0.03 (s, 3H), 0.10 (s, 3H), 0.12 (s, 3H), 0.20 (s, 3H), 0.85 (s, 9H), 0.93 (s, 9H), 1.00 (s, 9H), 1.60 (dd, J_{3ax-4}=11.2 Hz, $J_{3ax-3eq}$=12.4 Hz, 1H, H-3*ax*), 1.90 (s, 3H, Ac), 2.35 (s, 3H, CH_3), 2.60 (dd, J_{3eq-4}=3.2 Hz, $J_{3eq-3ax}$=12.4 Hz, 1H, H-3*eq*), 3.50–3.53 (m, 1H, H-5), 3.53 (s, 3H, Me), 3.60–3.64 (m, 2H, H-4, H-9a), 3.91–3.96 (m, 2H, H-8, H-6), 4.10 (dd, J_{9b-8}=9.2 Hz, J_{9b-9a}=10.0 Hz, 1H, H-9b), 4.54–4.55 (d, 1H, H-7), 7.20 (d, J=8.0 Hz, 2H, Ar), 7.45 (d, J=8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, CD_3OD): −4.5, −4.3, −4.2, −4.1, −3.8, −3.2, 18.8, 19.4, 19.6, 21.5, 23.7, 23.6, 26.3, 26.9, 27.1, 43.0, 53.2, 71.4, 77.3, 78.1, 89.2, 127.4, 130.9, 137.8, 141.5, 170.9, 173.0, 173.1. HRMS (FAB)

calcd for $C_{37}H_{68}NO_{11}S_2Si_3Na_2$ $[M+Na]^+$: 896.3337 Found: 896.3350.

4.2.30. Methyl (*O*-allyl 5-acetamido-4-acetyl-7,8-di-*O*-*tert*-butyldimethylsilyl-3,5-dideoxy-9-sulfate-D-glycero-α-galacto-non-2-ulpyranosid)onate (15a). ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.03 (s, 3H), 0.01 (s, 3H), 0.10 (s, 3H), 0.18 (s, 3H), 0.93 (s, 9H), 0.95 (s, 9H), 1.77 (t, J=12.0 Hz, 1H, H-3*ax*), 1.88 (s, 3H, Ac), 2.01 (s, 3H, Ac), 2.60 (dd, J_{3eq-4}=4.4 Hz, $J_{3eq-3ax}$=12.0 Hz, 1H, H-3*eq*), 3.86–4.07 (m, 5H, H-6, H-7, H-8, H-9a, All), 4.36 (dddd, J=1.6, 2.4, 5.2, 11.2 Hz, 1H, All), 4.62 (d, J=9.2 Hz, 1H, H-9b), 4.90 (ddd, J_{4-3eq}=4.4 Hz, J_{4-5}=7.2 Hz, J_{4-3ax}=12.0 Hz, 1H, H-4), 5.06–5.09 (m, 1H, All), 5.23–5.28 (m, 1H, All), 5.85 (dddd, J=5.2, 6.0, 10.8, 17.2 Hz, 1H, All). ^{13}C NMR (100 MHz, CD_3OD) δ −5.0, −4.2, −3.9, −2.9, 19.3, 19.5, 21.0, 23.1, 26.8, 26.8, 26.8, 26.9, 26.9, 26.9, 38.5, 51.8, 53.3, 66.8, 71.5, 71.5, 76.2, 76.9, 77.6, 100.1, 116.8, 135.8, 170.4, 172.1, 173.5. HRMS (FAB) calcd for $C_{29}H_{56}NO_{13}SSi_2$ $[M+H]^+$: 714.3011 Found: 714.3031.

4.2.31. Methyl [*p*-tolyl 5-(*N*-acetyl-*N*-benzoyl)amido-4,7,8-tri-*O*-benzoyl-9-*O*-tert-butyldimethylsilyl-3,5-dideoxy-2-thio-D-glycero-α-galacto-non-2-ulpyranosid]-onate (16). ^{1}H NMR (400 MHz, CD_3OD) δ 0.72 (s, 9H), 1.93 (t, J_{3ax-4}=$J_{3ax-3eq}$=12.0 Hz, 1H, H-3*ax*), 2.39 (s, 3H, Ac), 3.15 (dd, J_{3eq-4}=4.8 Hz, $J_{3eq-3ax}$=12.0 Hz, 1H, H-3*eq*), 3.29 (s, 3H, CH_3), 3.87 (dd, J_{9a-8}=3.2 Hz, J_{9a-9b}=11.6 Hz, 1H, H-9a), 4.15 (dd, J_{9b-8}=7.6 Hz, J_{9b-9a}=11.6 Hz, 1H, H-9b), 4.87–4.98 (m, 2H, H-5, H-6), 5.50–5.52 (m, 1H, H-8), 5.82–5.87 (m, 2H, H–4, H-7), 7.14–7.22 (m, 3H, Ar), 7.31–7.76 (m, 15H, Ar), 7.81–7.92 (m, 3H, Ar), 8.13–8.20 (m, 3H, Ar). ^{13}C NMR (100 MHz, CD_3OD) δ −5.7, 18.1, 21.4, 25.6, 28.0, 39.0, 52.6, 55.8, 60.8, 68.0, 69.4, 72.4, 72.6, 87.4, 125.6, 126.0, 128.2, 128.4, 128.9, 129.1, 129.6, 129.7, 129.8, 123.0, 130.2, 132.8, 133.1, 133.6. HRMS (FAB) calcd for $C_{53}H_{58}NO_{12}SSi$ $[M+H]^+$: 960.3449 Found: 960.3457.

4.2.32. Methyl [*p*-tolyl 5-(*N*-acetyl-*N*-benzoyl)amido-4,7,8-tri-*O*-benzoyl-3,5-dideoxy-2-thio-D-glycero-α-galacto-non-2-ulpyranosid]onate (17). ^{1}H NMR (400 MHz, CD_3OD) δ 2.01 (dd, 1H, J_{3ax-4}=11.2 Hz, $J_{3ax-3eq}$=12.4 Hz, H-3*ax*), 2.41 (s, 3H, Ac), 3.21 (s, 3H, Me), 3.21–3.30 (m, 1H, H-3*eq*), 3.74–3.80 (m, 1H, H-9a), 4.10–4.23 (m, 1H, H-9b), 5.04–5.05 (m, 2H, H-5, H-6), 5.43–5.45 (m, 1H, H-8), 5.68–5.72 (2H, H-4, H-7), 7.16–7.21 (m, 4H), 7.36–7.48 (m, 5H), 7.51–7.78 (m, 10H), 7.91 (d, J=7.6 Hz, 1H, Ar), 8.02–8.04 (m, 2H, Ar), 8.14–8.21 (m, 2H, Ar). ^{13}C NMR (100 MHz, CD_3OD) δ 21.4, 27.9, 39.2, 52.7, 55.8, 60.6, 68.2, 68.5, 72.9, 73.0, 87.5, 125.4, 126.0, 128.3, 128.5, 128.7, 128.9, 129.0, 129.3, 129.7, 129.9, 130.1, 132.7, 133.0, 133.3, 133.8, 136.1, 136.7, 140.2, 164.9, 165.5, 167.1, 168.3, 173.3, 174.0. HRMS (FAB) calcd for $C_{47}H_{44}NO_{12}S$ $[M+H]^+$: 846.2584 Found: 846.2592.

4.2.33. 1,2-Isopropylidene-3-*O*-(*m*-methoxyphenyl)-β-D-galactofuranose (19f). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.47 (s, 3H), 2.72 (br s, 2H, OH), 3.68 (dd, J=11.5, 5.4 Hz, 1H, H-6), 3.79 (s, 3H), 3.80 (dd, J=11.5, 3.3 Hz, 1H, H-6), 4.01 (m, 1H), 4.08–4.13 (m, 2H), 4.53 (d, J=11.9 Hz, 1H), 4.60 (d, J=3.7 Hz, 1H, H-2), 4.67 (d, J=11.9 Hz, 1H), 4.68 (d, J=12.0 Hz, 1H), 5.91 (d, J=3.7 Hz, 1H, H-1). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 26.6, 55.2, 64.2, 69.1, 71.9, 79.9, 81.9, 82.1, 105.1, 111.7, 113.4, 119.9, 129.7, 138.8, 160.0. HRMS (EI) Calcd for $C_{17}H_{25}O_7$ $[M+H]^+$: 341.1600. Found: 341.1612.

4.2.34. 1,2-Isopropylidene-3-*O*-(*p*-toluenesuphonyl)-β-D-galactofuranose (19h). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 3H), 1.46 (s, 3H), 2.45 (s, 3H), 2.57 (br s, 2H), 3.65–3.68 (m, 1H), 3.84–3.88 (m, 1H), 4.11–4.17 (m, 2H), 4.56 (d, J=3.7 Hz, 1H, H-2), 5.00 (d, J=2.6 Hz, 1H, H-3), 5.86 (d, J=3.7 Hz, 1H, H-1), 7.37 (d, J=8.6 Hz, 2H), 7.83 (d, J=8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 21.7, 26.5, 64.0, 68.0, 79.0, 81.9, 82.8, 104.9, 112.6, 128.1, 130.1, 132.4, 145.7. HRMS (EI) Calcd for $C_{16}H_{23}O_8S$ $[M+H]^+$: 375.1113. Found: 375.1120.

4.2.35. 1,2-Isopropylidene-β-D-arabinofuranose (23). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 3H), 1.46 (s, 3H), 3.64 (br s, 2H, OH), 3.96 (dd, J=12.3, 3.7 Hz, 1H, H-5), 4.03 (dd, J=12.3, 4.1 Hz, 1H, H-5), 4.13–4.16 (m, 1H, H-4), 4.27 (br d, J=2.6 Hz, 1H, H-3), 4.50 (br d, J=3.6 Hz, 1H, H-2), 5.95 (d, J=3.6 Hz, 1H, H-1). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1, 26.6, 60.7, 76.4, 79.1, 85.5, 104.7, 111.8. HRMS (EI) Calcd for $C_8H_{15}O_5$ $[M+H]^+$: 191.0919. Found: 191.0914.

4.2.36. (2*R*,3*S*,4*R*,5*R*)-4,5-*O*-Isopropylidene-1,2,3,4,5-dodecanepentol (29). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J=6.8 Hz, 3H), 1.28–1.36 (m, 10H), 1.36 (s, 6H), 1.73–1.76 (m, 2H), 3.56 (ddd, J=10.6, 8.1, 2.4 Hz, 1H), 3.62–3.70 (m, 3H), 3.80–3.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 25.0, 26.8, 26.9, 29.3, 29.6, 31.8, 34.4, 63.9, 73.0, 73.2, 80.2, 82.8, 109.2. HRMS (EI) Calcd for $C_{15}H_{31}O_5$ $[M+H]^+$: 291.2171. Found: 291.2175.

4.2.37. (2*R*,3*S*,4*R*,5*R*)-3-Azido-4,5-*O*-isopropylidene-1,2,4,5-decanetetrol (31). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J=6.6 Hz, 3H), 1.33–1.40 (m, 12H), 1.38 (s, 3H), 1.50 (s, 3H), 1.86 (br s, 2H), 3.21–3.24 (m, 1H), 3.68–3.75 (m, 2H), 3.81–3.84 (m, 1H), 3.99–4.07 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (2C), 22.5, 26.2, 26.7, 31.0, 31.5, 48.2, 61.6, 63.8, 72.8, 81.8, 104.5. HRMS (EI) Calcd for $C_{13}H_{26}N_3O_4$ $[M+H]^+$: 288.1923. Found: 288.1931.

4.2.38. (2*R*,3*S*,4*R*,5*R*)-1,2-*O*-Isopropylidene-3-*O*-methanesulfonyl-1,2,3,4,5-decanepentol (33a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J=6.7 Hz, 3H), 1.28–1.50 (m, 8H), 1.36 (s, 3H), 1.42 (s, 3H), 1.91 (br s, 2H), 3.16 (s, 3H), 3.53–3.62 (m, 2H), 3.98 (dd, J=8.8, 7.3 Hz, H-1, 1H), 4.13 (dd, J=8.8, 6.4 Hz, 1H, H-1), 4.32–4.36 (m, 1H), 5.12 (d, J=4.3 Hz, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (2C), 22.6, 25.1, 26.5, 31.8, 32.9, 38.8, 65.7, 70.4, 73.7, 75.9, 79.1, 109.2. HRMS (EI) Calcd for $C_{14}H_{29}O_7S$ $[M+H]^+$: 341.1634. Found: 341.1644.

4.2.39. (2*R*,3*S*,4*R*,5*R*)-4,5-*O*-Isopropylidene-3-*O*-methanesulfonyl-1,2,3,4,5-decanepentol (33b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J=6.7 Hz, 3H), 1.27–1.51 (m, 8H), 1.38 (s, 3H), 1.42 (s, 3H), 1.90 (br s, 2H), 3.15 (s, 3H), 3.82–3.88 (m, 2H), 4.18–4.25 (m, 2H), 4.32 (dd, J=6.0, 4.3 Hz, 1H, H-4), 4.76 (d, J=4.3 Hz, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (2C), 23.6, 26.0, 26.5, 32.5, 34.6, 38.7, 63.8, 71.1, 72.8, 74.1, 82.3, 109.2. HRMS (EI) Calcd for $C_{14}H_{29}O_7S$ $[M+H]^+$: 341.1634. Found: 341.1645.

4.2.40. *p*-Methylphenylsulfinyl 2,3-di-*O*-*p*-methylbenzyl-β-D-glucopyranoside (45). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (br s, 1H, OH), 2.33 (s, 3H), 2.34 (s, 3H), 2.36 (s, 3H), 3.41 (br s, 1H, OH), 3.58 (m, 1H), 3.82–3.90 (m, 2H), 4.00 (dd, $J=11.8$, 3.7 Hz, 1H), 4.86–4.90 (m, 1H), 5.33–5.40 (m, 2H), 7.09–7.19 (m, 6H), 7.35 (dd, $J=6.6$, 1.7 Hz, 2H), 7.83 (d, $J=8.2$ Hz, 2H), 7.85 (d, $J=8.2$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 21.5, 21.6, 62.4, 69.8, 70.0, 78.2, 80.0, 86.2, 126.0, 126.5, 128.1, 129.0, 129.1, 129.7, 129.8, 130.0, 133.4, 138.5, 144.0, 144.3, 165.2, 167.6. HRMS (EI) Calcd for $C_{29}H_{31}O_7S$ $[M+H]^+$: 523.1790. Found: 523.1802.

Acknowledgements

We thank the Academia Sinica and National Science Council in Taiwan (NSC 91-2113-M-001-013 and 92-2751-B-001-014-Y) for their financial support. M.Y.C. also thanks National Taipei College of Nursing for their financial support.

References and notes

1. (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1999; pp 113–148. (b) Kocienski, P. J. *Protecting Groups*; Georg Thieme: New York, 1994; pp 28–42.
2. Tandon, M.; Begley, T. P. *Synth. Commun.* **1997**, *27*, 2953–2959.
3. (a) Chen, M.-Y.; Patkar, L. N.; Jan, M.-D.; Lee, A. S.-Y.; Lin, C.-C. *Tetrahedron Lett.* **2004**, *45*, 635–639. (b) Chen, M.-Y.; Lu, K.-C.; Lee, A. S.-Y.; Lin, C.-C. *Tetrahedron Lett.* **2002**, *43*, 2777–2780.
4. (a) Lee, A. S.-Y.; Su, F.-Y.; Liao, Y.-C. *Tetrahedron Lett.* **1999**, *40*, 1323–1326. (b) Johnstone, C.; Kerr, W. J.; Scott, J. S. *J. Chem. Soc. Chem. Commun.* **1996**, 341–342. (c) Wagner, A.; Heitz, M. P.; Mioskowski, C. *Tetrahedron Lett.* **1990**, *31*, 3141–3144. (d) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769–3772.
5. Lee, A. S.-Y.; Yeh, H.-C.; Shie, J.-J. *Tetrahedron Lett.* **1998**, *39*, 5249–5252.
6. Lee, A. S.-Y.; Hu, Y.-J.; Chu, S.-F. *Tetrahedron* **2001**, *57*, 2121–2126.
7. Yadav, J. S.; Reddy, B. V. S. *Carbohydr. Res.* **2000**, *329*, 885–888.
8. Yadav, J. S.; Reddy, B. V. S. *Chem. Lett.* **2000**, 566–567.
9. Chen, M.-Y.; Lee, A. S.-Y. *J. Org. Chem.* **2002**, *67*, 1384–1387.
10. (a) Bartoli, G.; Bosco, M.; Marcantoni, E.; Sambri, L.; Torregiani, E. *Synlett* **1998**, 209–211. (b) Muzart, J. *Synthesis* **1993**, 11–27. (c) Lalonde, M.; Chan, T. H. *Synthesis* **1985**, 817–845.
11. For the deprotection of TBDMS group see Refs. 3b,10c, and the references cited therein.
12. Nelson, T. D.; Crouch, R. D. *Synthesis* **1996**, 1031–1069.
13. For recent examples (a) Hattori, K.; Sajiki, H.; Hirota, K. *Tetrahedron* **2001**, *57*, 2109–2114. (b) Higashibayashi, S.; Shinko, K.; Ishizu, T.; Hashimoto, K.; Shirahama, H.; Nakata, M. *Synlett* **2000**, 1306–1308. (c) Hunter, R.; Hinz, W.; Richards, P. *Tetrahedron Lett.* **1999**, *40*, 3643–3646. (d) Ramasamy, K.; Averett, D. *Synlett* **1999**, 709–712. (e) Farras, J.; Serra, C.; Vilarrasa, J. *Tetrahedron Lett.* **1998**, *39*, 327–330.
14. (a) De Groot, A. H.; Dommisse, R. A.; Lemière, G. L. *Tetrahedron* **2000**, *56*, 1541–1549. (b) Firouzabadi, H.; Etemadi, S.; Karimi, B.; Jarrahpour, A. A. *Synth Commun.* **1999**, *29*, 4333–4339. (c) Maiti, G.; Roy, S. C. *Tetrahedron Lett.* **1997**, *38*, 495–498. (d) Feixas, J.; Capdevila, A.; Guerrero, A. *Tetrahedron* **1994**, *50*, 8539–8550.
15. (a) Yang, Y.-Y.; Yang, W.-B.; Teo, C.-Fen; Lin, C.-H. *Synlett* **2000**, 1634–1636. (b) Cormier, J. F. *Tetrahedron Lett.* **1991**, *32*, 187–188. (c) Kawai, A.; Hara, O.; Hamada, Y.; Shioiri, T. *Tetrahedron Lett.* **1988**, *29*, 6331–6334. (d) McInnes, A. G. *Can. J. Chem.* **1965**, *43*, 1998–2003.
16. (a) Barone, G.; Bedini, E.; Iadonisi, A.; Manzo, E.; Parrilli, M. *Synlett* **2002**, 1645–1648. (b) Ramalingam, T.; Srinivas, R.; Reddy, B. V. S.; Yadav, J. S. *Synth. Commun.* **2001**, *31*, 1091–1095. (c) Rao, B. V.; Sarma, B. V. N. B. S.; Ravindranadh, S. V.; Gurjar, M. K.; Chorghade, M. S. *Carbohydr. Letts.* **1997**, *2*, 377–380. (d) Fernandez, J. M. G.; Mallet, C. O.; Marin, A. M.; Fuentes, J. *Carbohydr. Res.* **1995**, *274*, 263–268. (e) Park, K. H.; Yoon, Y. J.; Lee, S. G. *Tetrahedron Lett.* **1994**, *35*, 9737–9740.
17. Khalafi-Nezad, A.; Alamdari, R. F. *Tetrahedron* **2001**, *57*, 6805–6807 and references cited therein.
18. Bosques, C. J.; Tai, V. W.-F.; Imperiali, B. *Tetrahedron Lett.* **2001**, *42*, 7207–7210.
19. Corey, E. J.; Cho, H.; Rucker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455–3458.
20. Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190–6197.
21. *Biology of the Sialic Acids*; Rosenberg, A., Ed.; Plenum: New York, 1995.
22. Kiefel, M. J.; von Itzstein, M. *Chem. Rev.* **2002**, *102*, 471–490.
23. Compounds **19** and **21** have been reported (a) **19a**: Mehltretter, C. L.; Alexander, B. H.; Mellies, R. L.; Rist, C. E. *J. Am. Chem. Soc.* **1951**, *73*, 2425–2426. (b) **19b**: Stepowska, H.; Zamojski, A. *Carbohydr. Res.* **1994**, *265*, 133–137. (c) **19c**: Qureshi, S.; Shaw, G.; Burgess, G. E. *J. Chem. Soc., Perkin. Trans. 1* **1985**, 1557–1563. (d) **19d**: zu Reckendorf, W. M.; Schultz, N.; Kreimeier, R. *Liebigs Ann. Chem.* **1994**, 337–346. (e) **19e**: Fleet, G. W. J.; Witty, D. R. *Tetrahedron: Asymmetry* **1990**, *1*, 119–136. (f) **19g**: Horita, K.; Nagato, S.; Oikawa, Y.; Yonemitsu, O. *Chem. Pharm. Bull.* **1989**, *37*, 1705–1716. (g) **19i**: Park, J.; Pedersen, S. F. *Tetrahedron* **1992**, *48*, 2069–2080. (h) **21**: Balza, F.; Perlin, A. S. *Carbohydr. Res.* **1982**, *107*, 270–278.
24. Compounds **25**, **27**, **35** and **37** have been reported. (a) **25**: Miyajima, K.; Achiwa, K. *Chem. Pharm. Bull.* **1997**, *45*, 312–320. (b) **27** and **35**: Lin, C.-C.; Hsu, T.-S.; Lu, K.-C.; Huang, I.-T. *J. Chin. Chem. Soc.* **2000**, *47*, 921–928. (c) See Ref. 3b.
25. Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, *2*, 95–98.
26. Compounds **39**, **41**, **47**, **49** and **51** have been reported. (a) **39**: Lin, C.-C.; Hsu, T.-S.; Lu, K.-C.; Huang, I.-T. *J. Chin. Chem. Soc.* **2000**, *47*, 921–928. (b) **41**: Horton, D.; Lauterbach, J. H. *Carbohydr. Res.* **1975**, *43*, 9–33. (c) **47**: Argas-Berenguel, A.; Meldal, M.; Paulsen, H.; Jensen, K. J.; Bock, K. *J. Chem. Soc., Perkin. Trans. 1* **1994**, 3287–3294. (d) **49**: Takahashi, H.; Kittaka, H.; Ikegami, S. *J. Org. Chem.* **2001**, *66*, 2705–2716. (e) **51**: Lu, X.-A.; Chou, C.-H.; Wang, C.-H.; Hung, S.-C. *Synlett* **2003**, *9*, 1364–1366.