Glycosylidene Carbenes

Part 29[1])

Insertion into B–C and Al–C Bonds: Glycosylborinates, -boranes, and -alanes

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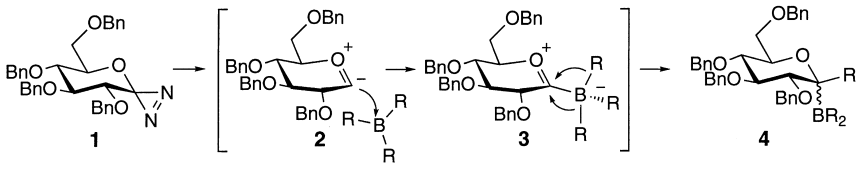
Insertion of the glycosylidene carbenes derived from the diazirines **1**, **14**, and **15** into the B–alkyl bond of the *B*-alkyl-9-oxa-10-borabicyclo[3.3.2]decanes **5**, **6**, and **7** yielded the stable glycosylborinates **8**/**9** (55%, 55:45), **10**/**11** (31%, 65:35), **12**/**13** (47%, 60:40), **16**/**17** (55%, 55:45), **18**/**19** (47%, 45:55), and **20**/**21** (31%, 30:70). Crystal-structure analysis of **17** and NOEs of **9** and **19** show that **17**, **9**, and **19** adopt similar conformations. The glycosylborinates are stable under acidic, basic and thermal conditions. The unprotected glycosylborinate **25** was obtained in 80% by hydrogenolysis of **12**. Insertion of the glycosylidene carbene derived from the diazirine **1** into a B–C bond of BEt_3, BBu_3, and BPh_3 led to unstable glycosylboranes that were oxidised to yield the hemiacetals **29** (55%), **31** (45%), and **33** (48%), respectively, besides the glucals **30** (13%), **32** (20%), and **34** (20%), respectively. Insertion of the glycosylidene carbenes derived from **14** and **15** into a B–C bond of BEt_3 led exclusively to hemiacetals; only **15** yielding traces of the glucal **40** besides the hemiacetal **39**. The glycosylidene carbene derived from **1** reacted with $Al(^iBu)_3$ and $AlMe_3$ to generate reactive glycosylalanes that were hydrolysed, yielding the *C*-glycosides **46** (21%) and **49** (30%), respectively, besides the glucals **48** (26%) and **51** (30%); deuteriolysis instead of protonolysis led to the monodeuterio analogues of **46** and **49**, respectively, which possess an equatorial ^{2}H-atom at the anomeric center.

Introduction. – Glycosylidene carbenes, generated by thermolysis or photolysis of diazirines, insert into X–H bonds to form *O*-, *C*-, and *N*-glycosides [2–6], glycosylphosphines [7], and glycosylstannanes [8].

We considered that the nucleophilic attack[2]) of glycosylidene carbenes (*e.g.*, **2**) on triligated B or Al derivatives should lead to tetraligated intermediates, such as the B-ylide **3** (*Scheme 1*). These ylides are expected to undergo (axial or equatorial) migration of a B or Al substituent, respectively, as shown in *Scheme 1* for glycosylboranes **4**, by analogy to the known migration of a B substituent in tetraligated borates that possess a vicinal leaving group [12][13]. They should lead to C(1)-substituted

Scheme 1



[1]) Part 28: [1].

[2]) For reviews on the synthesis of *C*-glycosides including reactions of nucleophilic *C*-glycosyl donors, see [9–11].

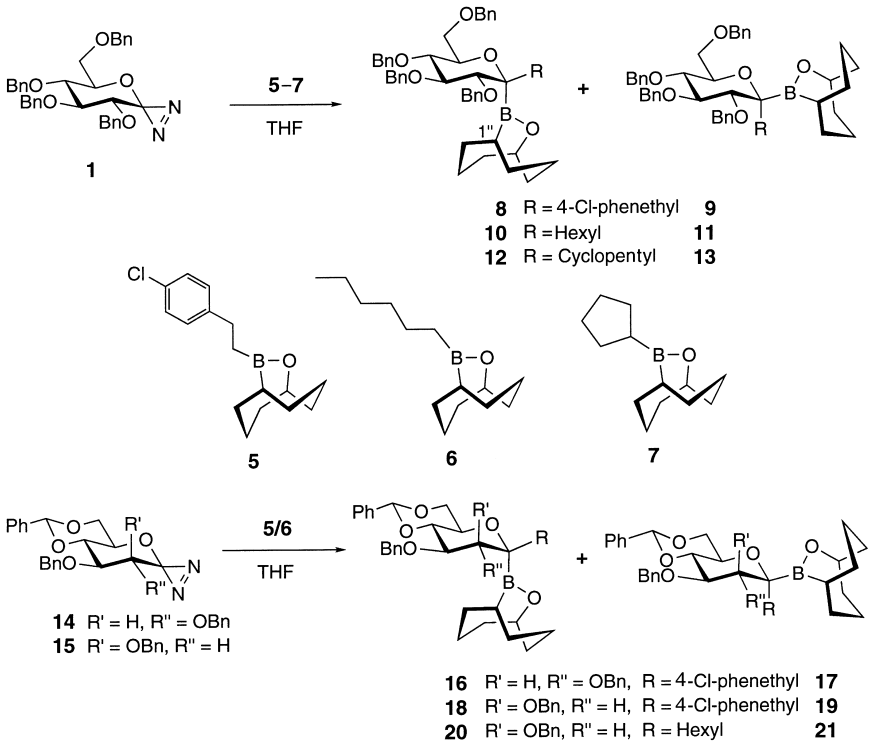
B- and *Al*-glycosides. The structure and reactivity of glycosylboranes and -alanes are of interest. No anomeric effect is possible for these compounds, and they are expected to yield geminally disubstituted *C*-glycosides.

A few examples of the insertion of carbenes and carbenoids into Al–C bonds are known for methylene derived from CH_2N_2 and from α-halo organolithium compounds [14][15]. Examples of the insertion of substituted and unsubstituted methylene [12][16][17], an imidazol-2-ylidene carbene [18], dichlorocarbene [19], a phosphanylcarbene [20], and methoxycarbene [21] into B–C bonds of trialkylboranes have been reported.

We have already briefly reported [1] the insertion of the glycosylidene carbene **2** into the B–alkyl bond of B-alkyl-9-oxa-10-borabicyclo[3.3.2]decanes that lead to stable glycosylborinates, and into a B–C bond of BEt_3 to yield unstable glycosylboranes, which were transformed further by oxidation, elimination, or rearrangements. We now describe details of these reactions, additional transformations, and the crystal structure of a glycosylborinate that possesses an equatorial B–C bond.

Results and Discussion. – 1. *Synthesis of Stable Glycosylborinates.* We selected the tetrabenzylated *gluco*-diazirine **1** [22], the *manno*-isomer **15** [23], and the benzylidene-protected analogue **14** of **1** as precursors of glycosylidene carbenes (*Scheme 2*). This

Scheme 2



should allow to determine the effect of the configuration at C(2) and of the annulated benzylidene ring that is known to increase the life-time of glycosylidene diazirines [23]. The selected diazirines show half-lives at 25° in MeOH of 33 (**1** [23]), 23 (**15** [23]), and 130 min (**14**). To obtain stable glycosylboron compounds, we chose the *B*-alkyl-9-oxa-10-borabicyclo[3.3.2]decanes (*B*-alkyl-OBBD) **5**–**7** as reaction partners, considering the exceptional stability of these borinates [24][25].

Thermolysis of the diazirines **1**, **14**, and **15** at 25° in THF in the presence of B-4-chlorophenethyl-OBBD **5** yielded the anomeric glycosylborinates **8/9** (55%, 55:45), **16/17** (55%, 55:45), and **18/19** (47%, 45:55), which were separated by HPLC. Similarly, thermolysis of the diazirines **1** and **15** in the presence of **6** yielded the anomeric glycosylborinates **10/11** (31%, 65:35) and **20/21** (31%, 30:70), respectively, and thermolysis of **1** in the presence of **7** yielded the anomers **12/13** (42%, 60:40). The anomers **12/13** and **20/21** were separated by HPLC. All glycosylborinates can be handled without special precautions and stored at −14° for several months. Except for **17** and **19**, all glycosylborinates are oils. Crystals obtained from **17** were suitable for crystal-structure analysis.

The structure of the glycosylborinates **8**–**13** and **16**–**19** was evidenced by ^{13}C-, ^{11}B-, and ^{1}H-NMR spectroscopy. The ^{13}C-NMR spectra show 5 *doublets* (65–86 ppm) for CH−O, one *triplet* (69–70 ppm) for CH_2−O, 6 *triplets* (38–20 ppm) for aliphatic CH_2 groups, and a small broad *doublet* (20–23 ppm) for a CH−B besides the signals for the benzyl, benzylidene, and C(1) alkyl substituents (*cf. Table 2*). The signals of the anomeric C-atom are missing as expected for a quarternary C−B [26]. A broad *singlet* in the ^{11}B-NMR spectra at 52–53 ppm is typical for borinates [27]. H-COB resonates as a broad *singlet* at 4.6 ppm. The ^{1}H-NMR signals of the glycosylborinates **20/21** correspond to those of **18/19** ($\Delta\delta < 0.08$ ppm; *cf. Table 3*) except for the signals of the alkyl substituents at C(1). The coupling constants $J(2,3)$[3]) (8.7–9.6 Hz for **8**–**13** and **16/17**, and 2.5–2.8 Hz for **18**–**21**) and the vicinal coupling constants of the other pyranose-ring H-atoms (8.4–10.0 Hz; *cf. Table 3*) imply a $^{4}C_1$ conformation for the *gluco*- and *manno*-configured glycopyranoses, respectively.

The β-D-configuration of **17** was established by crystal-structure analysis (*Fig. 1*)[4]). The glycosylborinate **17** adopts two conformations in the solid state, which differ in the orientation of the bicyclic system and the aromatic substituents. The endocyclic torsion angles of the pyranose ring are in the same range for both conformers (*Table 1*), indicating a slightly distorted $^{4}C_1$ conformation. The eight-membered ring is chair-like in both conformers, avoiding steric interactions of H−C(3″) and H−C(7″). Except for the bond between C(1) and O(5), which is slightly longer ($\Delta = 0.03$ Å) than in other geminally disubstituted glycosides [28–30], the bond lengths correspond to standard values. Due to the almost *anti*-periplanar orientation of the C(1′)−C(2′) and the C(1)−C(2) bonds in both conformers, one H−C(1′) is oriented towards H−C(3) and H−C(5) (distance: 2.1–2.3 Å; *Table 1*). The *anti*-periplanar orientation of the C(1′)−C(1) bond and the 4-chlorophenethyl substituent leads to a short distance between one H−C(2′) and H−C(5) (2.34/2.66 Å; *Table 1*). NOEs for the borinates **9** and **19** imply a β-D-configuration and indicate a similar position of the 4-chlorophen-

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[3]) To facilitate the comparison, the numbering of the C-atoms of the pyranose rings in the theoretical part is the same as for hexopyranoses; it does not correspond to the systematic numbering in the *Exper. Part.*

[4]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC 142256. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

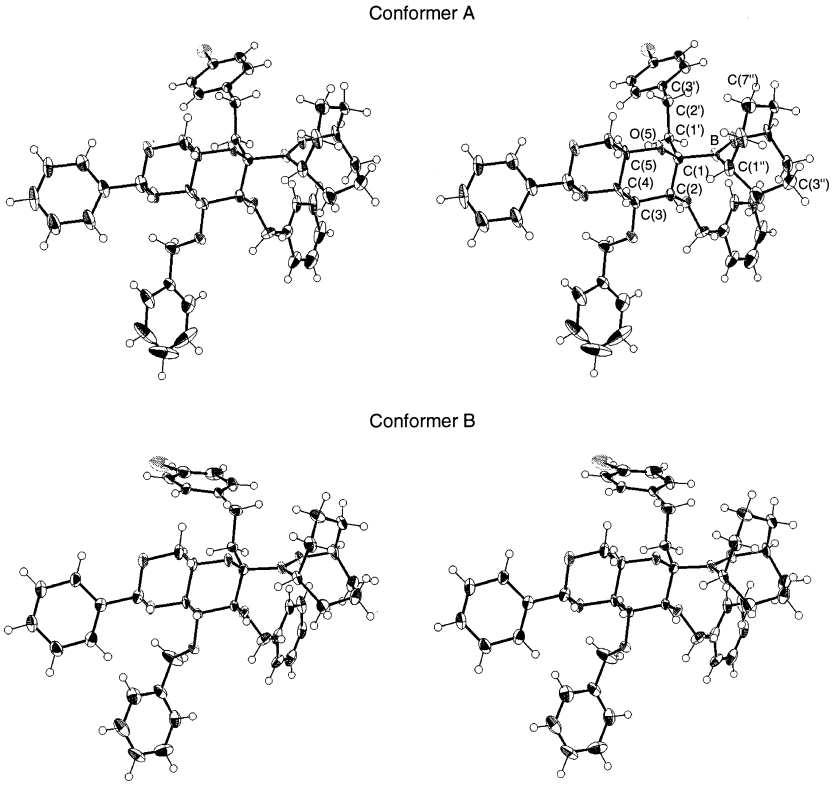


Fig. 1. *Stereoview of the crystal structure of the glycosylborinate* **17** (ORTEP [49] representation)

ethyl substituent in solution as in the solid state of **17**: one H−C(1′) signal is enhanced upon irradiation at C(3) or C(5), and one H−C(2′) signal is enhanced upon irradiation at C(5), as depicted for **19** (*Fig. 2*). Analogous NOEs were found for **9** [1]. The smaller coupling constants ($\Delta J \approx 1$ Hz; *cf. Table 3*) between the pyranose-ring H-atoms indicate a slightly more strongly distorted chair conformation of the β-D-glycosylborinates **9**, **11**, and **13** in solution, as compared to the α-D-anomers **8**, **10**, and **12**.

The anomeric configuration of **10**/**11**, **12**/**13**, and **20**/**21** was assigned by comparison of the ^{13}C- and ^{1}H-NMR data with those of **8**/**9**, **16**/**17**, and **18**/**19**: the axial B substituent has a deshielding effect on C(5) in **8**, **16**, and **18** ($\Delta\delta = 3.7$, 4.3, and 5.6 ppm, resp.; *Table 2*), as compared to the anomers possessing an equatorial B substituent. This corresponds to the shift to lower field of the ^{13}C-NMR signal of C(5) of **10**, **12**, and **20** ($\Delta\delta = 4.2$, 2.8, and 5.6 ppm, resp.; *Table 2*), indicating the α-D-configuration. The tetrabenzyl-protected α-D-glycosylborinates **8**, **10**, and **12** show a shift to lower field for the ^{1}H-NMR signals of H−C(5) (3.96, 3.90, and 4.21 ppm, resp.) as compared to the other signals of the pyranosyl-ring H-atoms (< 3.7 ppm; *Table 3*). The corresponding β-D-glycosylborinates **9**, **11**, and **13** show typically a shift to lower field for the signals of H−C(3) (3.91, 3.94, and 3.98 ppm, resp.). The anomeric configuration of the *manno*-glycosylborinates **20**/**21** is indicated by the same set of ^{1}H-NMR signals as for **18**/**19** ($\Delta\delta < 0.08$ ppm, except for the alkyl substituent at C(1); *Table 3*).

Table 1. *Selected Atom Distances, and Bond and Torsion Angles of the Glycosylborinate* **17**. Standard deviations in parentheses.

Bond lengths and atom distances [Å]		Bond angles [°]		Torsion angles [°]	
Conformer A					
B–C(1)	1.601	B–C(1)–O(5)	115.4(5)	C(1)–C(2)–C(3)–C(4)	– 53.6(6)
B–C(1″)	1.575	B–C(1)–C(2)	113.8(5)	C(2)–C(3)–C(4)–C(5)	55.0(6)
B–O	1.346	O–B–C(1)	115.4(5)	C(3)–C(4)–C(5)–O(5)	– 60.2(6)
C(1)–C(1′)	1.533	C(1)–B–C(1″)	123.3(5)	C(4)–C(5)–O(5)–C(1)	62.2
C(1)–O(5)	1.468			C(5)–O(5)–C(1)–C(2)	– 58.1(6)
				O(5)–C(1)–C(2)–C(3)	54.3(6)
H–C(3)···H–C(1′)	2.15			C(2)–C(1)–B–O	110.5(6)
H–C(5)···H–C(1′)	2.24			C(2′)–C(1′)–C(1)–C(2)	166.7(5)
H–C(5)···H–C(2′)	2.34			C(1)–C(1′)–C(2′)–C(3′)	173.7(5)
Conformer B					
B–C(1)	1.613	B–C(1)–O(5)	115.5(5)	C(1)–C(2)–C(3)–C(4)	– 51.0(6)
B–C(1″)	1.574	B–C(1)–C(2)	114.0(5)	C(2)–C(3)–C(4)–C(5)	56.5(6)
B–O	1.349	O–B–C(1)	115.5(5)	C(3)–C(4)–C(5)–O(5)	– 63.7(6)
C(1)–C(1′)	1.524	C(1)–B–C(1″)	123.4(5)	C(4)–C(5)–O(5)–C(1)	63.9
C(1)–O(5)	1.467			C(5)–O(5)–C(1)–C(2)	– 56.5(6)
				O(5)–C(1)–C(2)–C(3)	49.9(6)
H–C(3)···H–C(1′)	2.31			C(2)–C(1)–B–O	98.5(6)
H–C(5)···H–C(1′)	2.14			C(2′)–C(1′)–C(1)–C(2)	172.2(5)
H–C(5)···H–C(2′)	2.66			C(1)–C(1′)–C(2′)–C(3′)	– 167.9(5)

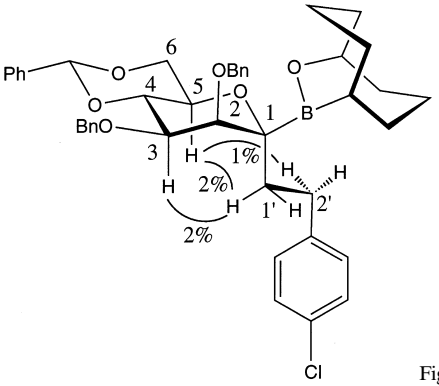


Fig. 2. *NOE Signals of the glycosylborinate* **19**

The formal insertion of the glycosylidene carbenes into the B–alkyl bond of *B*-alkyl-OBBDs shows a low diastereoselectivity, slightly favouring the glucosylborinates **8**, **10**, **12**, **16**, and the mannosylborinates **19** and **21**; all with the B substituent *cis* to the vicinal BnO group. This is rationalised by the intermediate formation of glycosylborates, such as **22** and **23**, respectively (*Scheme 3*)[5]), each one reacting *via* two conformers, where the migrating group is oriented in the π-plane of the C(1)–O bond. Presumably, the combination of the relative stability and reactivity of the four reactive conformers leads to the almost equal formation of the diastereoisomeric products.

[5]) Only one of the two diastereoisomeric glycosylborates is depicted in *Scheme 3*.

Table 2. *Selected ^{13}C-NMR Data of the Glycosylborinates* **8**–**13** *and* **16**–**19**[3])

	HC–B	HCO–B	C(2′)	C(1′)	C(2)	C(3)	C(4)	C(5)	C(6)
8	23.4	74.06	29.33	37.14	84.90	85.93	79.54	76.00	69.93
9	21.3	74.19	30.19	28.91	81.57	84.42	79.53	72.27	69.99
10	[a])	73.90	[b])	[b])	84.98	86.16	79.64	76.04	69.94
11	[a])	73.90	[b])	[b])	81.88	84.61	79.64	71.89	70.07
12	24	73.98	[b])	42.07	84.92	86.60	79.89	75.44	70.26
13	[a])	73.68	[b])	40.47	82.19	84.37	79.51	72.68	70.48
16	23.5	74.18	29.21	37.29	84.24	83.79	81.73	67.71	69.91
17	21.3	72.21	30.37	29.39	83.58	80.96	80.96	63.43	69.91
18	22.6	74.67	[b])	34.13	79.75[c])	79.54[c])	78.22	71.13	69.17
19	20.9	74.39	[b])	32.11	81.07[c])	78.36[c])	80.25	65.55	69.68

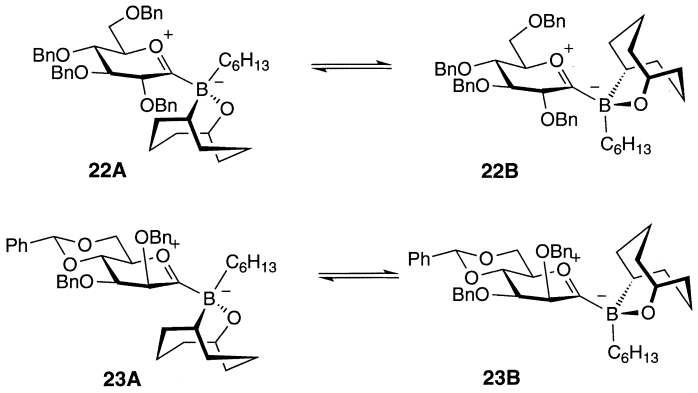
[a]) Hidden by the noise. [b]) Not assigned. [c]) Assignment may be interchanged.

Table 3. *Selected ^{1}H-NMR Data of the Glycosylborinates* **8**–**13** *and* **16**–**21**[3])

	Chemical shifts [ppm]						^{3}J [Hz]		
	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H′–C(6)	*J*(2,3)	*J*(3,4)	*J*(4,5)
8	3.50	~3.7	3.60	3.96	~3.7	~3.7	9.4	9.6	9.6
9	3.68	3.91	3.58	3.65	3.74	3.73	9.0	8.7	8.4
10	3.44	[a])	[a])	3.90	[a])	[a])	9.5	[a])	9.9
11	3.63	3.94	[a])	[a])	[a])	[a])	9.0	8.8	8.8
12	3.49	~3.7	~3.7	4.21	3.45	~3.7	9.6	9.9	9.9
13	3.82	3.98	3.57	~3.7	~3.7	~3.7	9.0	9.0	9.0
16	3.59	3.89	3.63	3.92	4.39	3.69	8.7	9.0	9.9
17	~3.7	4.01	~3.7	~3.7	4.31	~3.7	8.7	8.7	[a])
18	4.19	3.75	4.26	3.27	4.22	3.83	2.5	10.0	9.6
19	3.97	4.02	4.36	3.65	4.28	3.94	2.7	9.6	9.6
20	4.13	3.75	4.23	3.20	4.17	3.81	2.5	9.9	9.6
21	3.96	4.05	4.32	3.58	4.24	3.90	2.8	9.6	9.6

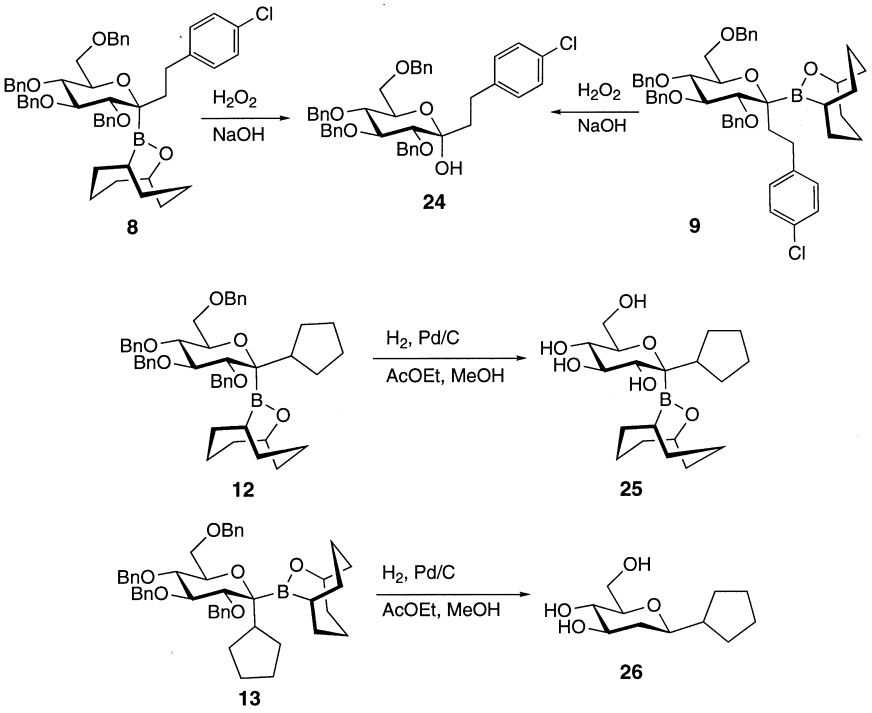
[a]) Not assigned.

Scheme 3



The glycosylborinates are thermally stable and also proved stable to acid and base treatment. Thus, the anomers **8**/**9** remained unchanged during heating to reflux in xylene and remained equally unaffected by boiling in 0.1M HCl in THF, in the presence of 2 equiv. of Bu_4NF in THF, or in the presence of 2 equiv. of NaOEt in toluene. Similarly, **10**/**11** remained stable during treatment with 10 equiv. of CF_3COOH at 25° in THF. The glycosylborinates are slowly oxidised by H_2O_2/NaOH, oxidation of **8**/**9** requiring 24 h to go to completion, to yield the hemiacetal **24** (*Scheme 4*). The borinate **9**, which possesses an equatorial B substituent, is oxidised noticeably faster than the corresponding diastereoisomer **8**, pointing at a (combined?) effect of a larger steric hindrance of **8**, or a decreased *Lewis* acidity, as a consequence of the *endo*-anomeric effect. Formation of the single hemiacetal **24** from either **8** or **9** denotes the rapid anomerisation of the hemiacetals. The axial position of the OH group in **24** is indicated by the deshielding of the pyranosyl C–*H* in a 1,3-diaxial relation to the anomeric OH group (4.00 ppm for H–C(3) and H–C(5)), typical for α-D-glucopyranoses.

Scheme 4



With the intention of preparing an unprotected glycosylborinate, we subjected the cyclopentyl rather than the 4-chlorophenethyl derivatives to hydrogenolysis, to avoid side reactions as far as possible. Hydrogenolysis of **12** at a pressure of 5 bar H_2 in the presence of prehydrogenated (at 5 bar H_2) 10% Pd/C in MeOH/AcOEt yielded the deprotected glycosylborinate **25** (80%; *Scheme 4*), while similar treatment of **13** led to a mixture of polar products. If Pd/C was prehydrogenated at ambient pressure,

hydrogenolysis of **12** at 5 bar did not go to completion, and hydrogenolysis of **13** yielded the triol **26** (60%), presumably by hydrogenation of an intermediate glycal. The ready formation of this glycal evidences a higher propensity of β-D-glucosylborinates towards elimination.

The structure of **25** is supported by elemental analysis, and signals for $[M-H]^-$ (367) and $[M+Na]^+$ (391) in the ESI mass spectrum, signals for 5 *doublets* (79–73 ppm) for CH–O, a *triplet* (64 ppm) for CH_2–O, a *doublet* (45 ppm) for CH, 10 *triplets* (32–23 ppm) for aliphatic CH_2, and a small broad *doublet* (24 ppm) for CH–B. A signal for the anomeric C-atom is missing as in the protected glycosylborinate **12**. The B-atom is evidenced by a broad *singlet* at 55.6 ppm in the ^{11}B-NMR spectrum. The coupling constants J(2,3) (10.0 Hz), J(3,4) (9.7 Hz), and J(4,5) (10.0 Hz) indicate a $^4C_1$ conformation and the *gluco*-configuration. The structure of **26** was deduced from the ESI mass spectra (NH_4OAc) with peaks for $[M+OAc]^-$ (275) in the negative mode and peaks for $[M+Na]^+$ (239) and $[M+NH_4]^+$ (234) in the positive mode. C(2)-Atom gives rise to a *triplet* at 39.52 ppm and C(1) to a *doublet* at *ca.* 81 ppm. C(2)H_2 gives rise to a *ddd* (J = 12.8, 5.3, 1.9 Hz) at 1.98 ppm and to a *dt* (J = 12.8, 11.5 Hz) at 1.28 ppm. The J_{vic} value (11.5 Hz) of the signal at 1.28 ppm indicates the axial position of the corresponding H–C(2), H–C(3), and H–C(1). The $^4C_1$ conformation of the six-membered ring is confirmed by J(3,4) (8.4 Hz).

2. *Glycosylboranes.* Thermolysis of **1** in the presence of BEt_3 (25°, THF), followed by aqueous or non-aqueous workup, led to a mixture of products dominated by the hemiacetal **29**, and containing traces of the glucal **30** and the azines **39** (see below). This evidences the intermediate formation of the glycosylboranes **27**/**28** (*Scheme 5*), as well as their high susceptibility to oxidation. Indeed, ^{13}C-NMR signals at 28.9, 25.33, and 17.4 ppm, presumably of CH_2–C(1) of glycosylboranes **27**/**28**[6]), were detected in the NMR spectrum of the mixture resulting from thermolysis of **1** in the presence of BEt_3 in (D_8)THF.

To determine the yield of unstable glycosylboranes, we treated the crude product of the thermolysis of **1** in the presence of BEt_3, BBu_3, or BPh_3 with alkaline H_2O_2, and isolated the α-D-hemiacetals **29**, **31** [31], and **33** [32], respectively, in 45–55%, besides 13–20% of the glucals **30**, **32** [33], and **34**[7]) [33], respectively (*Scheme 5* and *Table 4*, *Entries 1–3*). The major side products are the (*E*,*E*)- and (*Z*,*Z*)-azines **35**, resulting from the reaction of the carbene with the diazirine **1** [23].

Thermolysis of **1** in the presence of the boronate **36** in THF and oxidation with alkaline H_2O_2 yielded only the hemiacetal **31** (62%) and no glucal, as expected for the decreased elimination tendency of boronates [34] (*Scheme 5* and *Table 4*, *Entry 4*).

Thermolysis of the diazirine **14** in the presence of BEt_3 (25°, THF), followed by oxidation with alkaline H_2O_2 yielded 60% of the hemiacetal **38**[7]) (*Scheme 5* and *Table 4*, *Entry 5*). The major side product was the (*E*,*E*)-configured azine **37**, which was also formed in 35% yield upon thermolysis of **14** in dry MeCN.

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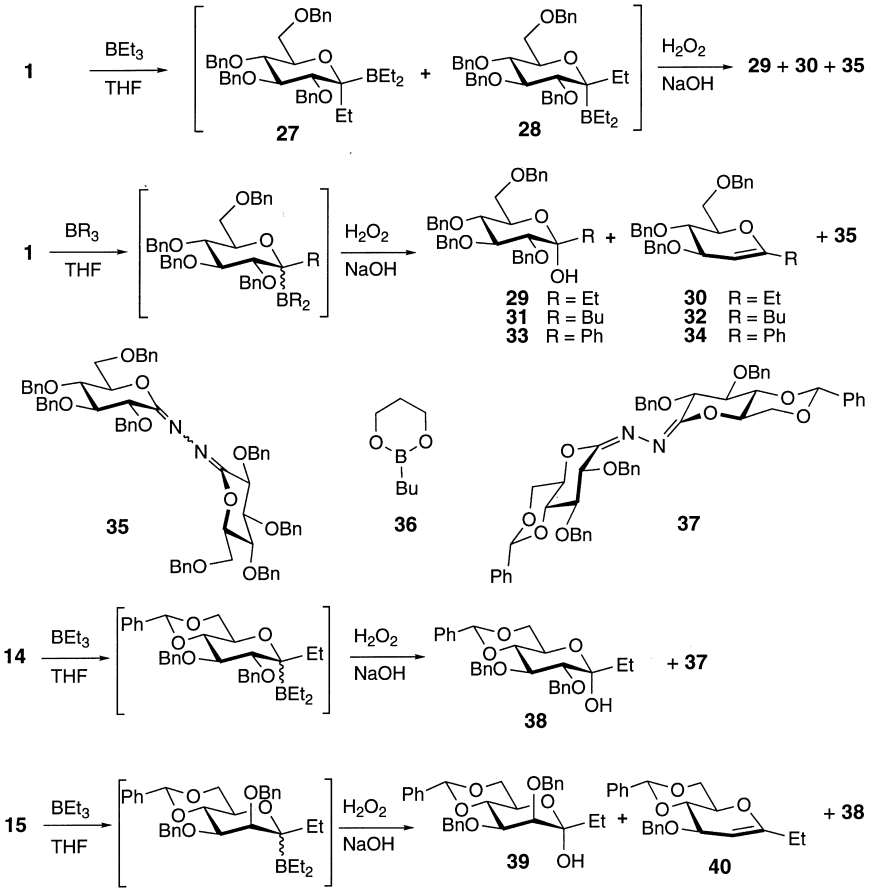
[6]) These signals are absent in the NMR spectrum of the crude resulting from a control thermolysis in the absence of BEt_3.

[7]) Formation of the hemiacetal **29** and the glucal **30** upon treatment of the crude with alkaline H_2O_2 is evidenced by new signals at 95.5 and 91.4 ppm. The ^{1}H-NMR signals for H–C(3) and H–C(5) of **29** (4.04 and 4.02 ppm, resp.), **31** (4.03 and 4.01 ppm, resp.), and **33** (4.10 and 4.21 ppm, resp.) are shifted downfield, indicating the axial position of the OH groups; similarly, the axial position of the OH group of **38** is indicated by the chemical shift of H–C(3) and H–C(5) (4.07 and 4.04 ppm, resp.), and that of **39** by the downfield shift of H–C(7) (4.00 ppm).

Scheme 5



The analogous thermolysis of the *manno*-diazirine **15** in the presence of BEt_3, followed by oxidation with alkaline H_2O_2, led to a mixture of products that were difficult to separate. Chromatographic purification led to the *manno* hemiacetal **39**[7]) (43%) and the *gluco*-isomer **38** (9%) (*Scheme 5* and *Table 4*, *Entry 6*); HPLC of the least polar fraction from the column chromatography yielded a 1:1 mixture of two compounds. One set of ^{1}H-NMR signals of this mixture evidenced an alkenyl H-atom (broad *d* at 4.57 ppm), one $PhCH_2$, one benzylidene, and one Et group (*t* for 3 H at 0.93 ppm, broad *q* for 2 H at 2.20 ppm). The similarity of these signals to those of **30** (*t* at 1.07 ppm, broad *q* at 2.13 ppm, and a broad *d* at 4.67 ppm) evidences the glucal **40**; other signals were not assigned (*Scheme 5*).

The 1,2-elimination of *β*-alkoxy organoboranes is known, including its configurational aspects [34–39]. There are two reaction pathways, an acid- or base-catalyzed *trans*-elimination, and an uncatalyzed *cis*-elimination [34]. Thus, the glucals **30**, **32**, and **34** are either formed *via* a glycosylborane with a *trans*-relation between the B-atom and the vicinal BnO substituents (such as **27**; *Scheme 5*), by attack of an external *Lewis* base

Table 4. *Yields of Hemiacetals and Glucals after Thermolysis of the Diazirines* **1**, **14**, *and* **15** *in the Presence of Organoboranes and Oxidation*

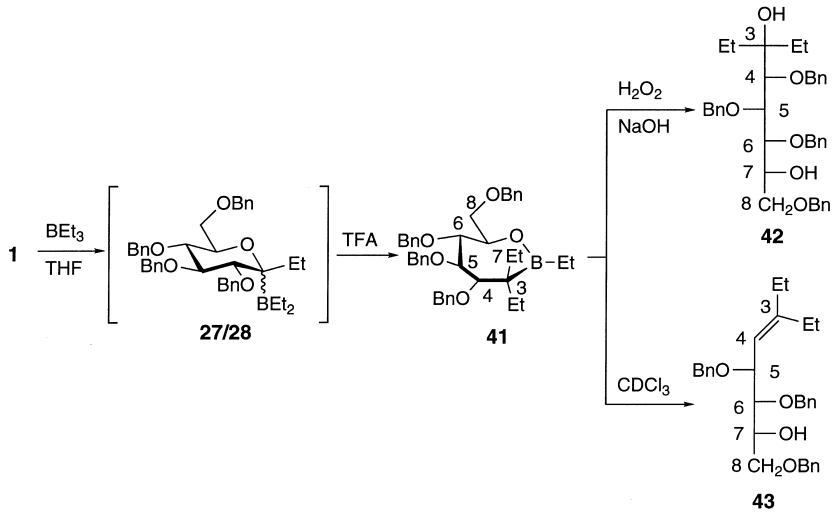
Entry	Diazirine	Organoborane	Products (yield [%])
1	**1**	BEt_3	**29** (55), **30** (13)
2	**1**	BBu_3	**31** (45), **32** (20)
3	**1**	BPh_3	**33** (48), **34** (20)
4	**1**	**36**	**31** (62)
5	**14**	BEt_3	**38** (60)
6	**15**	BEt_3	**39** (43), **38** (9), **40** (< 5)

at the B-atom and *trans*-elimination, or from an anomer, such as **28**, by intramolecular coordination and *cis*-elimination [34]. *trans*-Elimination appears more probable, since the glucal **30** is only formed upon addition of alkaline H_2O_2. *trans*-Elimination of a glycosylborane of type **27** requires a conformation with the B-atom and vicinal BnO substituents in axial positions. Indeed, glycosylboranes derived from the conformationally constrained diazirine **14** failed to give a glucal after oxidation with alkaline H_2O_2. They only lead to the hemiacetal **38** (*Scheme 5* and *Table 4*, *Entry 5*), in agreement with the requirements for a *trans*-elimination.

In contrast to the glycosylborinates, glycosylboranes were readily transformed by acids. Thermolysis of the diazirine **1** in the presence of BEt_3 in THF, followed by treatment with CF_3COOH, yielded 46% of the cyclic borinic ester **41**, resulting from the glycosylboranes **27**/**28** by migration of a second Et group [1] (*Scheme 6*).

The structure of **41** is evidenced by ^{13}C-NMR signals for 4 Bn groups, 4 *doublets* (81–74 ppm), a *triplet* (71.66 ppm), 2 *triplets* (26–21 ppm), and 3 *quadruplets* (10–8 ppm). The signal at 53.1 ppm in the ^{11}B-NMR spectrum is typical for borinates [27]. H–C(7) resonates at 4.77 ppm, its chemical shift indicating that the B-atom is attached to O–C(7). J(4,5) (4.7 Hz), J(5,6) (4.2 Hz), and J(6,7) (9.5 Hz) values do not correspond to a single conformation (by *Ampac* calculation [40]). There are no OH bands in the IR spectrum. The structure of

Scheme 6

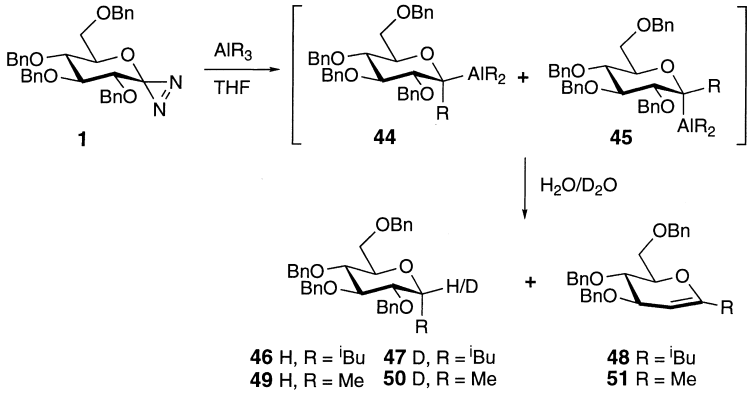


41 is further supported by its oxidation to the diol **42** and by its transformation to the alkene **43** upon storage in degassed $CDCl_3$ for several days (*Scheme 6*).

The structure of **42** and **43** is evidenced by elemental analysis, mass spectrometry, and by the IR and NMR spectra. The IR spectra show two OH bands (3599 and 3478 cm^{-1}) for **42** and one for **43** (3578 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra show signals of 4 (**42**) and 3 Bn groups (**43**), respectively. The OH groups resonate as a *doublet* (3.17 ppm) and as a *singlet* (2.33 ppm) for **42**, and as a *doublet* (2.93 ppm) for **43**. The C(3)-atom of **43** gives rise to a *singlet* at 148.66 ppm and C(4) to a *doublet* at 120.14 ppm.

3. *Reaction of the Carbene* **2** *with Organoalanes: Glycosylalanes.* Thermolysis of **1** in the presence of $Al(^iBu)_3$ in THF at 25°, followed by hydrolysis at 25°, gave the *C*-glycosides **46** (21%) [41] and the glucal **48** (26%) (*Scheme 7*). $AlMe_3$ reacted similarly, leading to **49** (30%) [42] and **51** (30%) [43]. Deuterolysis instead of hydrolysis led to the deuterated *C*-glycosides **47** and **50**, respectively, and the same undeuterated glucals as before, evidencing the intermediate formation of the glycosylalanes **44** and **45**. In contradistinction to the reaction of **1**, thermolysis of the diazirines **14** in the presence of $Al(^iBu)_3$ led to complex mixtures of products.

Scheme 7



Since organoalanes are known to be configurationally stable in etheral solution at 25° [44], and hydrolytic cleavage of Al–C bonds proceeds with retention of configuration [45][46], the *C*-glycosides **46** and **49** most probably arise from *trans*-glycosylalanes **44**. We assume that both diastereoisomeric glycosylalanes **44**/**45** were formed, and that the *cis*-glycosylalane **45** lead to the glucals **48** and **51** *via* 1,2-*cis*-elimination.[8])

Deuteration at C(1) of **47** and **50** is indicated by the disappearance of the signal of H–C(1) in the ^{1}H-NMR spectra. A $^4C_1$ conformation and the equatorial position of the H-atom at C(1) of **46** is indicated by the coupling constants J(1,2) (5.3 Hz), J(2,3) (9.3 Hz), and J(3,4 or 4,5) (7.8 Hz).

We thank Dr. *B. Schweizer* for determining the crystal structure, Dr. *B. Bernet* for helpful discussions and for checking the *Exper. Part*, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous financial support.

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[8]) A 1,2-elimination of β-alkoxy organoalanes, which could not be isolated, has been proposed for the reductive cleavage of enol ethers by organoalanes [47][48].

Experimental Part

General. Solvents were distilled before use: THF from Na/benzophenone, CH_2Cl_2 from CaH_2. Solvents were degassed by flushing with a stream of Ar for 2 h. Reactions were run under Ar. Qual. TLC: precoated silica-gel plates (*Merck* silica gel *60* F_{254}); detection by spraying with 'mostain' (400 ml of 10% aq. H_2SO_4, 20 g of $(NH_4)_6Mo_7O_{24}\cdot H_2O$, 0.4 g of $Ce(SO_4)_2$) and heating. Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). Prep. HPLC: silica gel, *Spherisorb SW 5*, 250 × 20 mm column. Optical rotations: 1-dm cell at 25° and 589 nm. FT-IR: 1–2% soln. in the indicated solvent.

Thermolysis of the Diazirines **1** *and* **15** *in the Presence of Organoboranes and Organoalanes in Degassed THF*. A soln. of the diazirine in dry CH_2Cl_2 (0.1–0.15M) at −60° was taken into a cooled syringe[9]) and added in *ca*. 12 portions in 2 h to a soln. of the organoborane or the organoalane in THF at 30°. Stirring at 30° was continued until no more diazirine was detectable (1–3 h, depending on the reagents). Detection of diazirines: applying a sample of the mixture on a silica-gel plate, immersing immediately into a soln. of 4-(4-nitrobenzyl)pyridine in acetone and heating to 60–80°. Pink spots indicate the presence of diazirine.

10-[4,5,6,8-Tetra-O-*benzyl-1*-C-*(4-chlorophenyl)-1,2-dideoxy-α*-D-gluco-*oct-3-ulo-3,7-pyranosyl]-9-oxa-10-borabicyclo[3.3.2]decane* (**8**) *and 10-[4,5,6,8-Tetra*-O-*benzyl-1*-C-*(4-chlorophenyl)-1,2-dideoxy-β*-D-gluco-*oct-3-ulo-3,7-pyranosyl]-9-oxa-10-borabicyclo[3.3.2]decane* (**9**). The soln. of thermolysis of the diazirine **1** (77 mg, 0.14 mmol) in the presence of **5** (116 mg, 0.42 mmol) in THF (3 ml) was evaporated at 20°. FC (hexane/AcOEt/CH_2Cl_2 18:1:1) and prep. HPLC (hexane/AcOEt 12:1, 9 ml/min) gave **9** (28 mg, 25%) and **8** (33 mg, 30%) as colourless oils.

Data of **9**: R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.36. t_R(hexane/AcOEt 12:1; 9 ml/min) 11.8 min. $[\alpha]_D^{25} = +51.4$ ($c = 1.16$, CH_2Cl_2). IR (CH_2Cl_2): 3032*w*, 2927*m*, 2963*m*, 1604*w*, 1493*m*, 1453*m*, 1420*m*, 1364*m*, 1092*s*, 1027*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.62–7.11 (*m*, 24 arom. H); 4.87 (*d*, $J = 10.6$, PhC*H*); 4.85 (*d*, $J = 10.9$, PhC*H*); 4.83 (*d*, $J = 10.9$, PhC*H*); 4.77 (*d*, $J = 10.9$, PhC*H*); 4.72–4.68 (*m*, HCOB); 4.71 (*d*, $J = 12.1$, PhC*H*); 4.68 (*d*, $J = 10.9$, PhC*H*); 4.66 (*d*, $J = 10.9$, PhC*H*); 4.64 (*d*, $J = 12.1$, PhC*H*); 3.91 (*t*, $J = 8.7$, H−C(5)); 3.74 (*dd*, $J = 11.2, 4.0$, H−C(8)); 3.73 (*dd*, $J = 11.2, 1.9$, H′−C(8)); 3.68 (*d*, $J = 9.0$, irrad. at. 3.91 → *d*, $J \approx 4$, H−C(4)); 3.67–3.63 (*m*, H−C(7)); 3.58 (*t*, $J = 8.4$, irrad. at 3.91 → *dd*, $J \approx 9, 3$, H−C(6)); 2.65–2.56 (*m*, irrad. at 3.64 → NOE of 1%, 2 H−C(1)); 2.37–2.27 (*m*, irrad. at 2.6 → *d*, $J \approx 10$, H−C(2)); 2.21 (br. *s*, irrad. at 3.68 → NOE of 1%, HCB); 2.01–1.91 (*m*, irrad. at 2.6 → *d*, $J \approx 10$, irrad. at 3.9 → NOE of 2%; irrad. at 3.64 → NOE of 3%, H′−C(2)); 2.01–1.46 (*m*, 12 H). ^{11}B-NMR (160 MHz, $CDCl_3$): 52.02 (br. *s*). ^{13}C-NMR (75 MHz, $CDCl_3$, assignment based on ^{1}H/^{13}C-COSY spectrum): 142.03 (*s*); 139.00 (2*s*); 138.69, 138.29, 131.12 (3*s*); 129.79–127.12 (several *d*); 84.42 (*d*, C(5)); 81.57 (*d*, C(4)); 79.53 (*d*, C(6)); 75.60, 75.13, 74.73 (3*t*, 3 PhCH_2); 74.19 (*d*, HCOB); 73.51 (*t*, PhCH_2); 72.24 (*d*, C(7)); 69.99 (*t*, C(8)); 32.41, 30.63 (2*t*); 30.19 (*t*, C(1)); 28.91 (*t*, C(2)); 27.54, 25.63, 22.89, 21.91 (4*t*); 21.3 (small br. *d*, BCH); signal for C(3) missing. FAB-MS (3-NOBA): 821 (<1, $[M+Na]^+$), 799 (<1, $[M+H]^+$), 599 (38), 553 (43, $[M - OBn - C_8H_{14}BO]^+$), 447 (44), 181 (100). Anal. calc. for $C_{50}H_{56}BClO_6$ (799.25): C 75.14, H 7.06; found: C 74.87, H 7.23.

Data of **8**: R_f(hexane/AcOEt/CH_2Cl_2 10:1:1) 0.32. t_R(hexane/AcOEt 12:1; 9 ml/min) 18.4 min. $[\alpha]_D^{25} = +12.0$ ($c = 0.65$, CH_2Cl_2). IR (CH_2Cl_2): 3032*w*, 2927*m*, 1492*m*, 1453*m*, 1418*w*, 1364*m*, 1093*s*, 1027*m*, 1015*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–6.99 (*m*, 24 arom. H); 4.98 (*d*, $J = 11.8$, PhC*H*); 4.85 (*d*, $J = 10.9$, PhC*H*); 4.84 (*s*, PhCH_2); 4.72–4.68 (*m*, HCOB); 4.70 (*d*, $J = 11.8$, PhC*H*); 4.68 (*d*, $J = 12.1$; PhC*H*); 4.62 (*d*, $J = 10.9$, PhC*H*); 4.60 (*d*, $J = 12.1$, PhC*H*); 3.96 (*dt*, $J \approx 9, 4$, H−C(7)); 3.78–3.70 (*m*, H−C(5), 2 H−C(8)); 3.60 (*t*, $J =$ 9.6, irrad. at 3.96 → *d*, $J \approx 9$, H−C(6)); 3.50 (*d*, $J = 9.4$, H−C(4)); 2.74–2.67 (*m*, 2 H−C(1)); 2.25 (br. *s*, irrad. at 3.96 → NOE of <1%, HCB); 2.05–1.95 (*m*, irrad. at 2.70 → *d*, $J \approx 12$, H−C(2)); 1.99–1.26 (*m*, 13 H). ^{11}B-NMR (160 MHz, $CDCl_3$): 53.8 (br. *s*). ^{13}C-NMR (75 MHz, $CDCl_3$, assignment based on ^{1}H/^{13}C-COSY spectrum): 141.75 (*s*); 139.26 (2*s*); 138.2, 137.8, 133.6 (3*s*); 129.9–127.14 (several *d*); 85.93 (*d*, C(5)); 84.90 (*d*, C(4)); 79.54 (*d*, C(6)); 76.00 (*d*, C(7)); 75.37, 75.09, 74.80 (3*t*, 3 PhCH_2); 74.06 (*d*, CHOB); 73.22 (*t*, PhCH_2); 69.93 (*t*, C(8)); 37.14 (*t*, C(2)); 31.82, 30.91 (2*t*); 29.33 (*t*, C(1)); 26.79, 25.77 (2*t*); 23.4 (small br. *d*, BCH); 22.48, 21.92 (2*t*); signal for C(3) missing. FAB-MS (3-NOBA): 821 (<1, $[M+Na]^+$), 799 (<1, $[M+H]^+$), 553 (43, $[M - OBn - C_8H_{14}BO]^+$), 461 (28), 401 (41), 325 (60), 281 (87), 181 (100). Anal. calc. for $C_{50}H_{56}BClO_6$ (799.25): C 75.14, H 7.06; found: C 75.47, H 7.23.

10-(8,9,10,12-Tetra-O-*benzyl-1,2,3,4,5,6-hexadeoxy-α*-D-gluco-*dodec-7-ulo-7,11-pyranosyl)-9-oxa-10-borabicyclo[3.3.2]decane* (**10**) *and 10-(8,9,10,12-Tetra*-O-*benzyl-1,2,3,4,5,6-hexadeoxy-β*-D-gluco-*dodec-7-ulo-7,11-pyranosyl)-9-oxa-10-borabicyclo[3.3.2]decane* (**11**). The soln. of the thermolysis of the diazirine **1** (48 mg,

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[9]) The syringe containing the diazirine soln. was placed in a small container that was charged with dry-ice during the addition.

0.09 mmol) in the presence of **6** (160 mg, 0.72 mmol) in THF (3 ml) was evaporated at 20°. FC (hexane/AcOEt/CH_2Cl_2 25:1:1) gave **10/11** 65:35 (20 mg, 31%) as a colourless oil. R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.73. ^{1}H-NMR (500 MHz, $CDCl_3$; **10/11** 65:35): 7.36–7.21 (*m*, 20 arom. H); 4.94 (*d*, *J* = 11.7, 0.65 H), 4.91 (*d*, *J* = 10.8, 0.35 H) (PhC*H*); 4.86–4.79 (*m*, 3 H); 4.71–4.62 (*m*, 3.7 H), 4.60 (*d*, *J* = 10.9, 0.65 H), 4.59 (*d*, *J* = 12.2, 0.65 H) (PhC*H*); 3.94 (*t*, *J* = 8.8, 0.35 H, H–C(9)); 3.90 (*ddd*, *J* = 9.9, 3.8, 2.3, 0.65 H, H–C(11)); 3.79–3.68 (*m*, 2.7 H); 3.63 (*d*, *J* = 9.0, 0.35 H, H–C(8)); 3.58–3.53 (*m*, 1.3 H); 3.44 (*d*, *J* = 9.5, 0.65 H, H–C(8)); 2.25–2.23 (*m*, 0.65 H); 2.19–2.17 (*m*, 0.35 H); 1.88–1.22 (*m*, 22 H); 0.9–0.86 (*m*, 3 H). ^{11}B-NMR (160 MHz, $CDCl_3$): 52.6 (br. *s*). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.36, 139.22, 139.09, 138.71, 138.45 (5*s*); 128.44–127.01 (several *d*); 86.16 (*d*, C(9) (*α*)); 84.98 (*d*, C(8) (*α*)); 84.61 (*d*, C(9) (*β*)); 81.88 (*d*, C(8) (*β*)); 79.64 (*d*, C(10)); 76.04 (*d*, C(11) (*α*)); 75.58, 75.28, 75.13, 75.05, 74.81 (5*t*, 5 PhCH); 73.90 (*d*, CHOB); 73.50, 73.17 (2*t*, 2 PhCH); 71.89 (*d*, C(11) (*β*)); 70.07 (*t*, C(12) (*β*)); 69.94 (*t*, C(12) (*α*)); 35.19, 32.28, 31.94, 31.00, 30.76, 30.22, 30.13, 26.91, 25.92, 25.63, 23.59, 22.67, 22.01 (13*t*); 14.09 (*q*, Me). FAB-MS (3-NOBA): 767 (<1, $[M+Na]^+$), 745 (<1, $[M+H]^+$), 545 (5), 499 (22, $[M-OBn-C_8H_{14}BO]^+$), 358 (100). Anal. calc. for $C_{48}H_{61}BO_6$ (744.82): C 77.41, H 8.25; found: C 77.35, H 8.27.

10-(2,3,4,6-Tetra-O-*benzyl-1*-C-*cyclopentyl-α*-D-*glucopyranosyl)-9-oxa-10-borabicyclo[3.3.2]decane* (**12**) *and 10-(2,3,4,6-Tetra*-O-*benzyl-1*-C-*cyclopentyl-β*-D-*glucopyranosyl)-9-oxa-10-borabicyclo[3.3.2]decane* (**13**). The soln. of the thermolysis of the diazirine **1** (97 mg, 0.18 mmol) in the presence of **7** (370 mg, 1.8 mmol) in THF (5.5 ml) was evaporated at 20°. FC (hexane/AcOEt/CH_2Cl_2 18:1:1) and prep. HPLC (hexane/AcOEt 12:1, 9 ml/min) gave **13** (22 mg, 17%) and **12** (33 mg, 25%) as colourless oils.

Data of **13**: R_f(hexane/AcOEt/CH_2Cl_2 10:1:1) 0.38. t_R(hexane/AcOEt 12:1; 9 ml/min) 9.6 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.23 (*m*, 20 arom. H); 4.89–4.77 (*m*, 5 PhC*H*); 4.69 (*d*, *J* = 12.1, PhC*H*); 4.64 (*d*, *J* = 11.2, PhC*H*); 4.62–4.58 (*m*, HCOB); 4.60 (*d*, *J* = 12.4, PhC*H*); 3.98 (*t*, *J* = 8.7, irrad. at 3.57 → *d*, *J* ≈ 9, H–C(3)); 3.82 (*d*, *J* = 9.0, irrad. at 3.98 → *m*, H–C(2)); 3.78–3.69 (*m*, 3 H); 3.57 (*t*, *J* = 9.0, irrad. at 3.98 → *d*, *J* ≈ 9, H–C(4)); 2.51–2.45 (*m*, 1 H); 2.16–2.10 (*m*, 1 H); 2.01–1.41 (*m*, 20 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.83, 139.20, 138.95, 138.60 (4*s*); 128.37–127.01 (several *d*); 84.37 (*d*, C(3)); 82.91 (*d*, C(2)); 79.51 (*d*, C(4)); 75.25 (*t*, Ph*C*H$_2$); 74.73 (*t*, 2 Ph*C*H$_2$); 73.68 (*d*, CHOB); 73.50 (*t*, Ph*C*H$_2$); 72.68 (*d*, C(5)); 70.48 (*t*, C(6)); 40.47 (*d*, C(1′)); 32.13, 31.03, 29.92, 29.38 (4*t*); 26.46 (3*t*); 24.95, 22.58, 22.06 (3*t*); signals of HCB and of C(1) missing. FAB-MS (3-NOBA): 751 (<1, $[M+Na]^+$), 729 (<1, $[M+H]^+$), 529 (23), 483 (67), 377 (92).

Data of **12**: R_f(hexane/AcOEt/CH_2Cl_2 10:1:1) 0.36. t_R(hexane/AcOEt 12:1; 9 ml/min) 11.4 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.25 (*m*, 20 H); 4.98 (*d*, *J* = 11.5, PhC*H*); 4.89 (*d*, *J* = 10.9, PhC*H*); 4.85 (*s*, PhC*H*$_2$); 4.76 (*d*, *J* = 11.5, PhC*H*); 4.68 (*d*, *J* = 12.1, PhC*H*); 4.68–4.65 (*m*, HCOB); 4.66 (*d*, *J* = 10.5, PhC*H*); 4.63 (*d*, *J* = 11.9, PhC*H*); 4.21 (*dt*, *J* ≈ 10, 3, H–C(5)); 3.75–3.66 (*m*, 3 H); 3.49 (*d*, *J* = 9.6, H–C(2)); 3.45 (*t*, *J* = 9.9, irrad. at 4.21 → *d*, *J* ≈ 10, H–C(4)); 2.52–2.47 (*m*, 1 H); 2.21 (br. *s*, 1 H); 1.93–1.27 (*m*, 20 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.44, 139.36, 138.80, 138.69 (4*s*); 128.32–127.01 (several *d*); 86.60 (*d*, C(3)); 84.92 (*d*, C(2)); 79.89 (*d*, C(4)); 75.44 (*d*, C(5)); 75.33, 74.98 (2*t*, 3 Ph*C*H$_2$); 73.89 (*d*, CHOB); 73.18 (*t*, Ph*C*H$_2$); 70.26 (*t*, C(6)); 42.07 (*d*, C(1′)); 32.39, 30.44, 28.16, 27.47, 26.83, 26.57, 26.08, 25.76 (8*t*); 24 (small br. *s*, HCB); 23.01, 21.75 (2*t*); signal of C(1) missing. FAB-MS (3-NOBA): 751 (<1, $[M+Na]^+$), 729 (<1, $[M+H]^+$), 529 (23), 483 (67), 377 (92).

10-[4,5-Di-O-*benzyl-6,8*-O-*benzylidene-1*-C-*(4-chlorophenyl)-1,2-dideoxy-α*-D-gluco-*oct-3-ulo-3,7-pyranosyl]-9-oxa-10-borabicyclo[3.3.2]decane* (**16**) *and 10-[4,5-Di*-O-*benzyl-6,8*-O-*benzylidene-1*-C-*(4-chlorophenyl)-1,2-dideoxy-β*-D-gluco-*oct-3-ulo-3,7-pyranosyl]-9-oxa-10-borabicyclo[3.3.2]decane* (**17**). A soln. of **14** (50 mg, 0.11 mmol) in dry CH_2Cl_2 (0.6 ml) was treated with a soln. of **5** (155 mg, 0.56 mmol) in dry THF (3 ml), stirred at 30° for 6 h (TLC: complete consumption of **14**), and evaporated at 0°. FC (hexane/AcOEt/CH_2Cl_2 25:1:1) and prep. HPLC (hexane/AcOEt 22:1, 9 ml/min) gave **16** (23 mg, 30%) as a colourless oil and **17** (19 mg, 25%) as a crystalline solid.

Data of **16**: R_f(hexane/AcOEt/CH_2Cl_2 10:1:1) 0.36. t_R(hexane/AcOEt 22:1, 9 ml/min) 24.4 min. $[\alpha]_D^{25} = -28.8$ (*c* = 0.29, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.56–7.52 (*m*, 2 H); 7.43–7.18 (*m*, 15 arom. H); 7.02–6.98 (*m*, 2 arom. H); 5.60 (*s*, PhC*H*); 5.06 (*d*, *J* = 11.8, PhC*H*); 4.97 (*d*, *J* = 11.2, PhC*H*); 4.82 (*d*, *J* = 11.5, PhC*H*); 4.72–4.68 (*m*, HCOB); 4.70 (*d*, *J* = 11.8, PhC*H*); 4.39 (*dd*, *J* = 9.9, 4.7, H_{eq}–C(8)); 3.92 (*td*, *J* = 9.9, 4.9, irrad. at 4.39 → *t*, *J* ≈ 9, H–C(7)); 3.89 (*t*, *J* = 9.0, H–C(5)); 3.69 (*t*, *J* = 9.9, irrad. at 4.39 → *d*, *J* ≈ 9, H_{ax}–C(8)); 3.63 (*t*, *J* = 9.0, H–C(6)); 3.59 (*d*, *J* = 8.7, H–C(4)); 2.63 (br. *t*, *J* ≈ 9, 1 H); 2.16–1.26 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.27, 138.79, 138.55, 137.77, 131.35 (5*s*); 129.76–126.01 (several *d*); 100.99 (*d*, PhC*H*); 84.24 (*d*, C(4)); 83.79 (*d*, C(5)); 81.73 (*d*, C(6)); 75.70, 74.62 (2*t*, 2 Ph*C*H$_2$); 74.18 (*d*, HCOB); 69.91 (*t*, C(8)); 67.71 (*d*, H–C(7)); 37.29 (*t*, C(2)); 31.85, 30.93 (2*t*); 29.21 (*t*, C(1)); 26.86, 25.55 (2*t*); 23.5 (small br. *d*, HCB); 22.54, 22.03 (2*t*); signal for C(3) missing. FAB-MS (3-NOBA): 707 (100, M^+), 601 (30). Anal. calc. for $C_{43}H_{48}BClO_6$ (707.11): C 73.04, H 6.84; found: C 73.12, H 6.87.

Data of **17**: R_f(hexane/AcOEt/CH_2Cl_2 10:1:1) 0.36. t_R(hexane/AcOEt 22:1, 9 ml/min) 25.4 min. M.p. 120°. $[\alpha]_D^{25} = +50.0$ ($c = 0.10$, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.54–7.50 (*m*, 2 arom. H); 7.42–7.22 (*m*, 15 arom. H); 7.18–7.15 (*m*, 2 arom. H); 5.60 (*s*, PhC*H*); 4.96 (*d*, $J = 10.9$, PhC*H*); 4.95 (*d*, $J = 11.2$, PhC*H*); 4.71–4.68 (*m*, HCOB); 4.69 (*d*, $J = 10.9$, PhC*H*); 4.65 (*d*, $J = 11.2$, PhC*H*); 4.31 (*dd*, $J = 9.6$, 3.4, H_{eq}–C(8)); 4.01 (*t*, $J = 8.7$, H–C(5)); 3.78–3.64 (*m*, 4 H); 2.60 (*td*, $J = 13.7$, 5.3, 1 H); 2.52 (*td*, $J = 12.8$, 5.3, 1 H); 2.38 (*td*, $J = 13.7$, 5.3, 1 H); 2.10–1.40 (*m*, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.72, 139.05, 138.65, 137.61, 131.28 (5*s*); 129.78–125.96 (several *d*); 101.05 (*d*, PhCH); 83.58 (*d*, C(4)); 80.96 (*d*, C(5), C(6)); 75.31, 75.12 (2*t*, 2 PhCH_2); 72.21 (*d*, HCOB); 69.91 (*t*, C(8)); 63.43 (*d*, C(7)); 32.22, 30.75 (2*t*); 30.37 (*t*, C(1)); 29.39 (*t*, C(2)); 27.40, 25.59, 22.76, 21.93 (4*t*); 21.3 (small br. *d*, HCB); signal for C(3) missing. FAB-MS (3-NOBA): 730 (12, $[M + Na]^+$), 707 (52, M^+), 461 (70), 355 (100). Anal. calc. for $C_{43}H_{48}BClO_6$ (707.11): C 73.04, H 6.84; found: C 73.5, H 6.90.

X-Ray Crystal-Structure Analysis of **17**. Crystals were obtained by isothermic evaporation of MeOH from a soln. of **17** in MeOH. $C_{43}H_{48}BClO_6$ (707.07). Orthorhombic. $P2_12_12_1$. $a = 13.358(5)$ Å, $b = 13.225(2)$ Å, $c = 43.246(10)$ Å, $V = 7640(4)$ Å^3, $Z = 8$, $D_{calc.} = 1.229$ Mg/m^3. From a crystal of size $0.20 \times 0.15 \times 0.10$ mm 7506 reflexions were measured on an *Enraf Nonius CAD-4* Diffractometer with CuK_α radiation (graphite monochromator, $\lambda = 1.54184$ Å) at 103(2) K. Part of the structure was solved by direct methods with SIR97 [50], the remaining non-H-atoms were found from a difference *Fourier* map with SIR97 [50]. The non-H-atoms were refined anisotropically with SHELXL97 [51]. H-Atoms were calculated at idealyzed positions and included in the structure factor calculation with fixed isotropic displacement parameters. The structure converged at an *R* value of 0.0530 using 5038 reflections with $I > 3\sigma(I)$.

10-[4,5-Di-O-*benzyl-6,8*-O-*benzylidene-1*-C-*(4-chlorophenyl)-1,2-dideoxy-α*-D-manno-*oct-3-ulo-3,7-pyranosyl]-9-oxa-10-borabicyclo[3.3.2]decane* (**18**) *and 10-[4,5-Di*-O-*benzyl-6,8*-O-*benzylidene-1*-C-*(4-chlorophenyl)-1,2-dideoxy-β*-D-manno-*oct-3-ulo-3,7-pyranosyl]-9-oxa-10-borabicyclo[3.3.2]decane* (**19**). The soln. resulting from the thermolysis of the diazirine **15** (40 mg, 0.087 mmol) in the presence of **5** (100 mg, 0.37 mmol) in degassed THF (5 ml) was evaporated at 20°. FC (hexane/AcOEt/CH_2Cl_2 20:1:1) and prep. HPLC (hexane/AcOEt 12:1, 9 ml/min) gave **18** (13 mg, 21%) as a colourless oil and **19** (16 mg, 26%) as a white solid.

Data of **18**: R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.62. t_R(hexane/AcOEt 12:1, 9 ml/min) 14.4 min. $[\alpha]_D^{25} = +24.5$ ($c = 0.47$, CH_2Cl_2). IR (CH_2Cl_2): 2928*w*, 2864*w*, 1605*w*, 1493*w*, 1453*m*, 1419*w*, 1366*w*, 1093*s*, 1027*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.61–7.14 (*m*, 17 arom. H); 6.98–6.89 (*m*, 2 arom. H); 5.63 (*s*, PhC*H*); 5.27 (*d*, $J = 11.2$, PhC*H*); 4.93 (*d*, $J = 12.4$, PhC*H*); 4.85 (*d*, $J = 12.4$, PhC*H*); 4.64 (*d*, $J = 11.5$, PhC*H*); 4.56–4.54 (*m*, HCOB); 4.26 (*t*, $J = 9.6$, H–C(6)); 4.22 (*dd*, $J = 10.3$, 5.0, H_{eq}–C(8)); 4.19 (*d*, $J = 2.5$, H–C(4)); 3.83 (*t*, $J = 10.3$, H_{ax}–C(8)); 3.75 (*dd*, $J = 10.0$, 2.5, H–C(5)); 3.27 (*td*, $J = 9.6$, 4.6, H–C(7)); 2.53 (*td*, $J \approx 13$, 5, H–C(1)); 2.40 (*td*, $J \approx 13$, 5, H′–C(1)); 2.01–1.26 (*m*, 15 H). ^{11}B-NMR (160 MHz, $CDCl_3$): 53.9 (br. *s*). ^{13}C-NMR (125 MHz, $CDCl_3$): 140.66, 139.17, 138.75, 137.96, 131.40 (5*s*); 129.41–126.06 (several *d*); 101.26 (*d*, PhCH); 79.75, 79.54, 78.22 (3*d*, C(4), C(5), C(6)); 75.62 (*t*, PhCH_2); 74.67 (*d*, HCOB); 72.32 (*t*, PhCH_2); 71.13 (*d*, C(7)); 69.17 (*t*, C(8)); 34.13 (*t*, C(2)); 32.73, 29.79, 29.71, 27.30, 26.21, 22.80 (6*t*); 22.64 (small br. *d*, HCB); 21.22 (*t*); signal for C(3) missing. FAB-MS (3-NOBA): 707 (31, M^+), 599 (100). HR-FAB-MS: 707.3302 ($[M + H]^+$; calc. 707.3311).

Data of **19**: R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.62. t_R(hexane/AcOEt 12:1, 9 ml/min) 12 min. $[\alpha]_D^{25} = -18.4$ ($c = 0.37$, CH_2Cl_2). IR (CH_2Cl_2): 2929*w*, 1605*w*, 1492*m*, 1453*m*, 1367*w*, 1094*s*, 1028*w*, 1015*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.60–7.51 (*m*, 2 arom. H); 7.40–7.21 (*m*, 15 arom. H); 7.10–7.05 (*m*, 2 arom. H); 5.70 (*s*, PhC*H*); 5.30 (*d*, $J = 10.6$, PhC*H*); 4.91 (*d*, $J = 12.4$, PhC*H*); 4.71 (*d*, $J = 12.4$, PhC*H*); 4.64–4.62 (*m*, HCOB); 4.57 (*d*, $J = 10.9$, PhC*H*); 4.36 (*t*, $J = 9.3$, H–C(6)); 4.28 (*dd*, $J = 10.3$, 4.6, irrad. at 3.94 → *d*, $J \approx 5$, H_{eq}–C(8)); 4.02 (*dd*, $J = 9.6$, 2.5, H–C(5)); 3.97 (*d*, $J = 2.7$, H–C(4)); 3.94 (*t*, $J = 10.3$, H_a–C(8)); 3.65 (*td*, $J = 9.6$, 4.7, irrad. at 3.94 → *t*, $J \approx 6$, H–C(7)); 2.59 (br. *td*, $J \approx 13$, 5, irrad. at 2.05 → *m*, irrad. at 3.65 → NOE of 1%, H–C(1)); 2.41 (br. *td*, $J \approx 13$, 5, irrad. at 2.05 → *m*, H′–C(1)); 2.05 (br. *td*, $J \approx 13$, 5, irrad. at 2.50 → change, irrad. at 4.02 → NOE of 2%, irrad. at 3.65 → NOE of 2%, H–C(2)); 2.17–1.26 (*m*, 14 H). ^{11}B-NMR (160 MHz, $CDCl_3$): 53.2 (br. *s*). ^{13}C-NMR (125 MHz, $CDCl_3$): 140.73, 139.20, 138.82, 137.88, 131.64 (5*s*); 129.54–126.00 (several *d*); 101.26 (*d*, PhCH); 81.07, 80.51, 78.36 (3*d*, C(4), C(5), C(6)); 74.40 (*d*, CHOB); 74.30, 73.35 (2*t*, 2 PhCH_2); 69.68 (*t*, C(8)); 65.55 (*d*, C(7)); 32.92 (*t*); 32.11 (*t*, C(2)); 30.60, 30.52, 25.91, 25.27, 23.10, 21.60 (6*t*); 20.91 (small *d*, BCH); signal for C(3) missing. FAB-MS (3-NOBA): 707 (100, M^+), 663 (37), 461 (14), 355 (26). HR-FAB-MS: 707.3302 ($[M + H]^+$; calc. 707.3311).

10-(8,9-Di-O-*benzyl-10,12*-O-*benzylidene-1,2,3,4,5,6-hexadeoxy-α*-D-manno-*dodec-7-ulo-7,11-pyranosyl)-9-oxa-10-borabicyclo[3.3.2]decane* (**20**) *and 10-(8,9-Di*-O-*benzyl-10,12*-O-*benzylidene-1,2,3,4,5,6-hexadeoxy-β*-D-manno-*dodec-7-ulo-7,11-pyranosyl)-9-oxa-10-borabicyclo[3.3.2]decane* (**21**). The soln. of the thermolysis of the diazirine **15** (24 mg, 0.05 mmol) in the presence of **6** (50 mg, 0.22 mmol) in THF (1.5 ml) was evaporated at

20°. FC (hexane/AcOEt/CH_2Cl_2 25:1:1) gave **20**/**21** 30:70 (10 mg, 31%) as a colourless oil. Anal. samples of **21** and **20** were obtained by prep. HPLC (hexane/AcOEt 15:1, 9 ml/min).

Data of **21**: R_f(hexane/AcOEt/CH_2Cl_2 5:1:1) 0.54. t_R(hexane/AcOEt 15:1, 9 ml/min) 9 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.55–7.51 (*m*, 2 arom. H); 7.40–7.20 (*m*, 13 arom. H); 5.68 (*s*, PhC*H*); 5.9 (*d*, *J* = 10.9, PhC*H*); 4.93 (*d*, *J* = 12.4, PhC*H*); 4.75 (*d*, *J* = 12.1, PhC*H*); 4.6–4.55 (*m*, BCH); 4.55 (*d*, *J* = 10.9, PhC*H*); 4.32 (*t*, *J* = 9.6, H–C(10)); 4.24 (*dd*, *J* = 10.3, 4.7, H_{eq}–C(12)); 4.05 (*dd*, *J* = 9.9, 2.8, H–C(9)); 3.96 (*d*, *J* = 2.8, H–C(8)); 3.90 (*t*, *J* = 10.3, H_{ax}–C(12)); 3.58 (*td*, *J* = 9.6, 4.7, H–C(11)); 1.91–1.12 (*m*, 23 H); 0.88 (*t*, *J* = 6.2, Me). FAB-MS (3-NOBA): 653 (3, $[M+H]^+$), 301 (14).

Data of **20**: R_f(hexane/AcOEt/CH_2Cl_2 5:1:1) 0.51. t_R(hexane/AcOEt 15:1, 9 ml/min) 11.8 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52–7.26 (*m*, 15 arom. H); 5.60 (*s*, PhC*H*); 5.19 (*d*, *J* = 11.2, PhC*H*); 4.89 (*d*, *J* = 12.6, PhC*H*); 4.83 (*d*, *J* = 12.4, PhC*H*); 4.63 (*d*, *J* = 11.2, PhC*H*); 4.53–4.48 (*m*, BCH); 4.23 (*t*, *J* = 9.6, H–C(10)); 4.17 (*dd*, *J* ≈ 10, 6, H_{eq}–C(12)); 4.13 (*d*, *J* = 2.5, H–C(8)); 3.81 (*t*, *J* = 10.3, H_{ax}–C(12)); 3.75 (*dd*, *J* = 9.9, 2.5, H–C(9)); 3.20 (*td*, *J* = 9.9, 5.0, H–C(11)); 1.90–1.10 (*m*, 23 H); 0.85 (*t*, *J* = 6.5, Me). FAB-MS (3-NOBA): 653 (7, $[M+H]^+$), 545 (14), 455 (12).

4,5,6,8-Tetra-O-*benzyl-1*-C-*(4-chlorophenyl)-1,2-dideoxy-α*-D-gluco-*oct-3-ulo-3,7-pyranose* (**24**). A soln. of **9**/**8** 25:30 (16 mg, 0.02 mmol) in THF (1 ml) was treated with 3M aq. NaOH (0.6 ml) and 30% H_2O_2 (0.6 ml), stirred at 25° for 24 h (TLC showed complete disappearance of **9** after 10 h and complete disappearance of **8** after 24 h). The mixture was diluted with CH_2Cl_2, washed with sat. aq. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt/CH_2Cl_2 10:1:1) yielded **24** (13 mg, 100%) as a colourless oil. R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.17. $[\alpha]_D^{25} = +12.0$ (*c* = 0.44, CH_2Cl_2). IR (CH_2Cl_2): 3566*w*, 3032*m*, 2926*m*, 2867*m*, 1605*w*, 1492*m*, 1453*m*, 1361*m*, 1091*s*, 1065*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.20 (*m*, 2 arom. H); 7.05–7.02 (*m*, 2 arom. H); 4.94 (*d*, *J* = 11.2, 2 PhC*H*); 4.86 (*d*, *J* = 10.9, PhC*H*); 4.84 (*d*, *J* = 10.9, PhC*H*); 4.76 (*d*, *J* ≈ 10, PhC*H*); 4.64 (*d*, *J* ≈ 10, PhC*H*); 4.63 (*d*, *J* ≈ 12, PhC*H*); 4.55 (*d*, *J* = 12.4, PhC*H*); 4.03–3.97 (*d*, H–C(7)); 4.00 (*t*, *J* = 9.0, irrad. at 3.44 → *d*, *J* ≈ 9, H–C(5)); 3.79 (*dd*, *J* = 10.9, 3.7, H–C(8)); 3.73–3.66 (*d*, H–C(6), H′–C(8)); 3.44 (*d*, *J* = 9.3, H–C(4)); 2.75–2.59 (*m*, 2 H–C(1)); 2.64 (*s*, OH); 2.01–1.85 (*m*, 2 H–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 140.73, 138.81, 138.64, 138.52, 138.00, 131.75 (6*s*); 130.01–127.83 (several *d*); 98.14 (*s*, C(3)); 84.03 (*d*, C(5)); 82.07 (*d*, C(4)); 78.50 (*d*, C(6)); 75.76, 75.63, 75.05, 73.50 (4*t*, 4 PhCH_2); 71.83 (*d*, C(7)); 68.90 (*t*, C(8)); 40.21 (*t*, C(2)); 28.12 (*t*, C(1)). FAB-MS (3-NOBA): 701 (27, $[M+Na]^+$), 553 (95), 253 (61), 181 (100). Anal. calc. for $C_{42}H_{43}ClO_6$ (679.27): C 74.27, H 6.38; found: C 74.44, H 6.32.

10-(1-C-*Cyclopentyl-α*-D-*glucopyranosyl)-9-oxa-10-borabicyclo[3.3.2]decane* (**25**). A suspension of 10% Pd on activated charcoal (10 mg) in AcOEt/MeOH (1:1, 1 ml) was hydrogenated for 10 min. at 1 bar, added to **12** (10 mg, 0.141 mmol) and hydrogenated for 14 h at 5 bar. The suspension was filtered through *Celite* and evaporated. FC (CH_2Cl_2/MeOH 93:7) yielded **25** (4 mg, 80%) as a colourless oil. R_f(CH_2Cl_2/MeOH 10:1) 0.37. ^{1}H-NMR (300 MHz, CD_3OD): 4.76–4.75 (*m*, HCOB); 3.80 (*dd*, *J* = 11.5, 2.2, H–C(6)); 3.57 (*dd*, *J* = 11.5, 5.9, irrad. at 3.80 → *t*, *J* ≈ 5, H′–C(6)); 3.40 (*dd*, *J* = 10.0, 8.7, irrad. at 3.11 → *dd*, *J* ≈ 10, 3, H–C(3)); 3.37–3.25 (*m*, 2 H); 3.11 (*dd*, *J* = 10.0, 8.7, H–C(4)); 2.30–2.24 (*m*, 1 H); 2.27–1.41 (*m*, 21 H). ^{11}B-NMR (160 MHz, CD_3OD): 55.6 (br. *s*). ^{13}C-NMR (75 MHz, CD_3OD): 79.50, 79.29, 78.63, 76.83 (4*d*); 73.19 (*d*, CHOB); 64.33 (*t*, C(6)); 45.35 (*d*, C(1′)); 32.33, 32.26, 28.07, 27.88, 27.73, 27.60, 26.96, 26.08 (8*t*); 24.3 (small br. *d*, HCB); 23.49, 23.10 (2*t*). ESI-MS: 367 (100, $[M-H]^-$), 391 (100, $[M+Na]^+$). Anal. calc. for $C_{19}H_{33}BO_6$ (368.28): C 61.97, H 9.03; found: C 61.79, H 9.00.

*(1*R*)-1,5-Anhydro-1*-C-*cyclopentyl-1,2-dideoxy*-D-arabino-*hexitol* (**26**). A suspension of 10% Pd on activated charcoal (10 mg) in AcOEt/MeOH (1:1, 1 ml) was hydrogenated at 5 bar for 30 min, added to **13** (10 mg, 0.141 mmol), hydrogenated at 5 bar for 14 h, and filtered through *Celite*. Evaporation and FC (CH_2Cl_2/MeOH 9:1) yielded **26** (2 mg, 60%) as a white solid. R_f(CH_2Cl_2/MeOH 10:1) 0.27. ^{1}H-NMR (300 MHz, CD_3OD): 3.82 (*dd*, *J* = 11.8, 2.2, irrad. at 3.19 → *d*, *J* ≈ 11, H–C(6)); 3.64 (*dd*, *J* = 11.8, 5.3, irrad. at. 3.19 → *d*, *J* ≈ 11, H′–C(6)); 3.51 (*ddd*, *J* = 11.2, 8.4, 5.0, irrad. at 3.19 → *dd*, *J* ≈ 11, 6, irrad. at. 1.98 → *dd*, *J* ≈ 10, 8, irrad. at 1.3 → *m*, H–C(3)); 3.21–3.12 (*m*, irrad. at 3.51, 1.98, or 1.3 → change, H–C(1), H–C(4), H–C(5)); 1.98 (*ddd*, 12.8, 5.3, 1.9, irrad. at 3.51 → *dd*, *J* ≈ 13, 2, H_{eq}–C(2)); 1.94–1.39 (*m*, 8 H); 1.34–1.22 (*m*, 1 H); 1.28 (*dt*, *J* = 12.8, 11.5, irrad. at 3.51, 3.19, or 1.98 → *t*, *J* ≈ 12, H_{ax}–C(2)). ^{13}C-NMR (75 MHz, CD_3OD): 81.69, 81.08 (2*d*, C(1), C(5)); 74.27, 73.81 (2*d*, C(3), C(4)); 63.43 (*t*, C(6)); 46.20 (*d*, C(1′)); 39.52 (*t*, C(2)); 30.33, 29.79, 26.64, 26.47 (4*t*). ESI-MS (NH_4OHc): 275 (100, $[M+OAc]^-$), 239 (95, $[M+Na]^+$), 234 (56, $[M+NH_4]^+$).

4,5,6,8-Tetra-O-*benzyl-1,2-dideoxy-α*-D-gluco-*oct-3-ulo-3,7-pyranose* (**29**) *and 3,7-Anhydro-5,6,8-tri*-O-*benzyl-1,2,4-trideoxy*-D-arabino-*oct-3-enitol* (**30**). The soln. of the thermolysis of the diazirine **1** (112 mg, 0.2 mmol) in the presence of 1M BEt_3 (in hexane, 300 µl, 0.3 mmol) in degassed THF (3 ml) at 30° was cooled to 0°, treated with 3M aq. NaOH (0.7 ml) and 30% H_2O_2 (0.7 ml), and stirred at 25° for 12 h. The suspension was diluted with

CH_2Cl_2, washed with sat. aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt/CH_2Cl_2 8:1:1) gave **30** (12 mg, 13%) and **29** (40 mg, 55%) as colourless oils.

Data of **30**: R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.57. $[\alpha]_D^{25} = +1.3$ ($c = 1.30$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3065*w*, 3000*w*, 2920*w*, 2870*m*, 1675*m*, 1495*w*, 1455*m*, 1365*w*, 1170*w*, 1090*s*, 1025*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.27 (*m*, 15 arom. H); 4.82 (*d*, $J = 11.4$, PhC*H*); 4.67 (br. *d*, $J \approx 4$, H–C(4)); 4.66 (*d*, $J = 11.3$, PhC*H*); 4.63 (*d*, $J = 11.7$, PhC*H*); 4.61 (*d*, $J = 12.1$, PhC*H*); 4.57 (*d*, $J = 12.1$, PhC*H*); 4.55 (*d*, $J = 11.7$, PhC*H*); 4.19–4.17 (*m*, H–C(5)); 4.10 (*ddd*, $J = 8.0$, 5.0, 3.0, H–C(7)); 3.84 (*dd*, $J = 8.1$, 5.6, H–C(6)); 3.82 (*dd*, $J = 10.8$, 5.0, H–C(8)); 3.78 (*dd*, $J = 10.8$, 3.0, H′–C(8)); 2.14–2.09 (*m*, 2 H–C(2)); 1.07 (*t*, $J = 7.5$, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 157.68 (*s*, C(3)); 138.57, 138.31, 138.28 (3*s*); 128.33–127.50 (several *d*); 93.76 (*d*, C(4)); 76.71 (*d*); 76.04 (*d*); 74.34 (*d*); 73.39, 73.29, 70.25 (3*t*, 3 Ph*C*H_2); 68.91 (*t*, C(8)); 26.56 (*t*, C(2)); 11.20 (*q*, C(1)). CI-MS: 445 (1.4, M^+), 337 (100), 253 (12), 91 (28). Anal. calc. for $C_{29}H_{32}O_4$ (444.67): C 78.35, H 7.26; found: C 78.26, H 7.13.

Data of **29**: R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.25. $[\alpha]_D^{25} = +29.0$ ($c = 1.32$, $CHCl_3$). IR ($CHCl_3$): 3585*w*, 3090*w*, 3065*w*, 3000*m*, 2980*m*, 2870*m*, 1600*w*, 1495*w*, 1453*m*, 1360*m*, 1290*w*, 1085*s*, 1025*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.23 (*m*, 20 arom. H); 4.95 (*d*, $J = 11.1$, PhC*H*); 4.94 (*d*, $J = 11.0$, PhC*H*); 4.89 (*d*, $J = 11.0$, PhC*H*); 4.86 (*d*, $J = 10.9$, PhC*H*); 4.71 (*d*, $J = 11.1$, PhC*H*); 4.65 (*d*, $J = 12.3$, PhC*H*); 4.64 (*d*, $J = 10.9$, PhC*H*); 4.57 (*d*, $J = 12.3$, PhC*H*); 4.04 (*t*, $J = 9.2$, H–C(5)); 4.02 (*ddd*, $J = 10.0$, 3.9, 1.9, H–C(7)); 3.80 (*dd*, $J = 11.0$, 3.9, H–C(8)); 3.71–3.67 (*m*, H–C(6), H′–C(8)); 3.47 (*d*, $J = 9.4$, H–C(4)); 2.61 (*s*, OH); 1.78–1.72 (*m*, 2 H–C(2)); 0.93 (*t*, $J = 7.4$, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.59, 138.36, 138.24, 137.89 (4*s*); 128.36–127.36 (several *d*); 98.36 (*s*, C(3)); 83.77 (*d*, C(5)); 81.11 (*d*, C(4)); 78.46 (*d*, C(6)); 75.45, 75.27, 74.75 (3*t*, 3 Ph*C*H_2); 74.49 (*d*, C(7)); 73.21 (*t*, Ph*C*H_2); 68.78 (*t*, C(8)); 31.33 (*t*, C(2)); 6.86 (*q*, C(1)). CI-MS: 551 (12, $[M - OH]^+$), 443 (100). Anal. calc. for $C_{36}H_{40}O_6$ (568.71): C 76.03, H 7.09; found: C 75.88, H 7.05.

3′,7-Anhydro-4,5,6,8-tetra-O-*benzyl-3*-C-*ethyl-3*-C-*(ethylhydroxyboryl)-1,2,3-trideoxy*-D-gluco-*octitol* (**41**). The soln. of the thermolysis of the diazirine **1** (25 mg, 0.045 mmol) in the presence of 1M BEt_3 (in THF, 61 µl, 0.061 mmol) in degassed THF (2 ml) was cooled to 0°, treated with CF_3COOH (18 µl, 0.24 mmol), and stirred for 12 h at 25°. The soln. was diluted with AcOEt, washed with sat. aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated at 25°. FC (hexane/AcOEt/CH_2Cl_2 8:1:1) yielded **41** (13 mg, 46%) as a colourless oil. R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.53. IR (CH_2Cl_2): 3031*m*, 2962*m*, 1496*w*, 1454*w*, 1095*s*, 1013*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.20 (*m*, 20 arom. H); 4.77 (*ddd*, $J = 9.6$, 3.7, 2.2, H–C(7)); 4.74 (*d*, $J = 12.1$, PhC*H*); 4.65 (*d*, $J = 12.1$, PhC*H*); 4.59 (*s*, PhCH_2); 4.58 (*d*, $J \approx 12$, PhC*H*); 4.55 (*d*, $J \approx 12$, PhC*H*); 4.47 (*d*, $J = 11.8$, PhC*H*); 4.34 (*d*, $J = 11.5$, PhC*H*); 3.94 (*t*, $J = 4.3$, H–C(5)); 3.88 (*dd*, $J = 10.9$, 4.0, irrad. at 4.77 → *d*, $J \approx 11$, H–C(8)); 3.81 (*dd*, $J = 11.0$, 2.1, irrad. at 4.77 → *d*, $J \approx 11$, H′–C(8)); 3.79 (*dd*, $J = 9.4$, 4.1, irrad. at 4.77 → *d*, $J \approx 4$, H–C(6)); 3.60 (*d*, $J = 4.9$, H–C(4)); 1.72 (*dq*, $J = 14.3$, 7.2, MeCH_2); 1.59–1.51 (*m*, 1 H); 1.41 (*dq*, $J = 14.6$, 7.8, MeCH_2); 0.92–0.74 (*m*, 11 H). ^{11}B-NMR (160 MHz, $CDCl_3$): 53.16 (br. *s*). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.39, 139.23, 138.73, 138.34 (4*s*); 128.57–127.45 (several *d*); 81.55 (*d*); 81.27 (*d*); 78.47 (*d*); 74.46 (*d*); 73.86, 73.81, 72.70, 72.57 (4*t*, 4 PhCH_2); 71.66 (*t*, C(8)); 26.43, 21.79 (2*t*, 2 MeCH_2); 9.96, 8.42, 8.16 (3*q*, 3 Me); signals for C(3) and B–CH_2Me missing.

4,5,6,8-Tetra-O-*benzyl-1,2-dideoxy-3*-C-*ethyl*-D-gluco-*octitol* (**42**). A soln. of **41** (10 mg, 0.106 mmol) in $CDCl_3$ (0.7 ml) was diluted with THF (2 ml), cooled to 0°, treated with 3M aq. NaOH (0.7 ml) and 30% H_2O_2 (0.7 ml), and stirred for 3 h at 25°. The suspension was diluted with CH_2Cl_2, washed with sat. aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt/CH_2Cl_2 8:1:1) gave **42** (7 mg, 73%) as a colourless oil. R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.17. $[\alpha]_D^{25} = -8.2$ ($c = 0.32$, CH_2Cl_2). IR (CH_2Cl_2): 3599*m*, 3478*m*, 3032*m*, 2966*m*, 1605*m*, 1496*m*, 1454*m*, 1093*s*, 1069*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37–7.26 (*m*, 20 arom. H); 4.94 (*d*, $J = 11.2$, PhC*H*); 4.75 (*d*, $J = 10.9$, PhC*H*); 4.69 (*d*, $J = 11.5$, PhC*H*); 4.56–4.47 (*m*, 5 PhC*H*); 4.17 (br. *t*, $J \approx 6$, 1 H); 4.13 (*dd*, $J = 6.2$, 3.1, 1 H); 3.66–356 (*m*, 4 H); 3.17 (br. *d*, $J \approx 6$, exchangeable with D_2O, HO–C(7)); 2.33 (*s*, exchangeable with D_2O, HO–C(3)); 1.71–1.24 (*m*, 4 H); 0.77 (*t*, $J = 7.5$, Me); 0.73 (*t*, $J = 7.5$, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.92, 137.96, 137.90, 137.67 (4*s*); 128.69–127.34 (several *d*); 79.99 (*d*); 78.50 (*d*); 77.55 (*d*); 76.70 (*s*, C(3)); 74.54, 74.40, 73.48, 73.04 (4*t*, 4 PhCH_2); 71.49 (*t*, C(8)); 70.45 (*d*, C(7)); 29.68, 27.61 (2*t*, 2 MeCH_2); 7.98, 7.30 (2*q*, 2 Me). DCI-MS (NH_4): 599 (< 1, $[M + H]^+$), 581 (< 1, $[M - OH]^+$), 491 (< 1, $[M - OBn]^+$), 337 (19), 253 (75), 91 (100). Anal. calc. for $C_{38}H_{46}O_6$ (598.78): C 76.22, H 7.74; found: C 76.05, H 7.74.

5,6,8-Tri-O-*benzyl-1,2,3,4-tetradeoxy-3*-C-*ethyl*-D-arabino-*oct-3-enitol* (**43**). A soln. of **41** (9 mg, 0.014 mmol) in degassed $CDCl_3$ (0.7 ml) was kept at 25° for 80 h and evaporated. FC (hexane/AcOEt/CH_2Cl_2 8:1:1) gave **43** (6 mg, 88%). R_f(hexane/AcOEt/CH_2Cl_2 4:1.1) 0.34. $[\alpha]_D^{25} = -20.0$ ($c = 0.18$, CH_2Cl_2). IR (CH_2Cl_2): 3587*w*, 3032*w*, 2966*m*, 2874*m*, 1662*w*, 1605*w*, 1496*w*, 1454*m*, 1086*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.33–7.18 (*m*, 15 arom. H); 5.31 (br. *d*, $J \approx 9$, C=CH); 4.65 (*d*, $J = 11.5$, PhC*H*); 4.59 (*d*, $J = 12.1$, PhC*H*); 4.56 (*d*, $J = 11.5$, PhC*H*); 4.49 (*s*, PhCH_2); 4.41 (*dd*, $J = 9.3$, 3.8, irrad. at 5.31 → *d*, $J \approx 4$, H–C(5)); 4.31 (*d*, $J = 12.1$, PhC*H*);

4.06–4.00 (*m*, addn. of D_2O → change, H–C(7)); 3.55–3.59 (*m*, 3 H); 2.93 (*d*, *J* = 5.3, exchangeable with D_2O, OH); 2.08 (*qd*, *J* = 7.5, 1.2, irrad. at 5.31 → *q*, *J* ≈ 7, MeCH_2); 1.99 (*m*, MeCH_2); 1.01 (*t*, *J* = 7.5, Me); 0.91 (*t*, *J* = 7.5, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 148.66 (*s*, C(3)); 138.35, 138.27, 138.09 (3*s*); 128.35–127.58 (several *d*); 120.14 (*d*, C(4)); 81.34 (*d*, C(6)); 74.74 (*d*, C(5)); 74.18, 73.24, 71.25 (3*t*, 3 PhCH_2); 70.61 (*d*); 69.85 (*t*, C(8)); 28.87, 23.69 (2*t*, 2 MeCH_2); 13.13, 12.67 (2*q*, 2 Me). DCI-MS (NH_4): 492 (< 1, $[M+NH_4]^+$), 475 (< 1, $[M+H]^+$), 259 (11), 203 (70, $[M-CHOBn-CHOH-CH_2OBn]^+$), 91 (100). Anal. calc. for $C_{31}H_{38}O_4$ (474.64): C 78.45, H 8.07, O 13.48; found: C 78.62, H 7.99.

4,5-Di-O-*benzyl-6,8*-O-*benzylidene-1,2-dideoxy-α*-D-gluco-*oct-3-ulo-3,7-pyranose* (**38**). A soln. of 1M BEt_3 (in THF, 0.1 ml, 0.1 mmol) in dry THF (1.5 ml) was treated with a soln. of **14** (30 mg, 0.065 mmol) in dry CH_2Cl_2 (1.9 ml) and stirred at 30° for 6 h (complete consumption of **14**). The soln. was cooled to 0°, treated with 3M aq. NaOH (0.3 ml) and 30% H_2O_2 (0.3 ml), stirred at 25° for 12 h, diluted with CH_2Cl_2, washed with aq. sat $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt/CH_2Cl_2 8:1:1) gave **38** (19 mg, 60%) as a colourless oil. R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.27. $[\alpha]_D^{25} = -3.1$ (*c* = 0.35, CH_2Cl_2). IR (CH_2Cl_2): 3596*w*, 2927*m*, 2856*m*, 1605*m*, 1497*w*, 1454*m*, 1373*m*, 1094*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52–7.22 (*m*, 15 arom. H); 5.58 (*s*, PhC*H*); 5.00 (*d*, *J* = 11.2, PhC*H*); 4.98 (*d*, *J* = 10.9, PhC*H*); 4.78 (*d*, *J* = 11.2, PhC*H*); 4.70 (*d*, *J* = 10.9, PhC*H*); 4.31 (*dd*, *J* = 10.3, 5.0, H_{eq}–C(8)); 4.07 (*t*, *J* = 9.3, irrad. at 3.48 → *dd*, *J* ≈ 10, 2, H–C(5)); 4.04 (*td*, *J* = 10.3, 5.0, irrad. at 4.31 → *t*, *J* ≈ 10, H–C(7)); 3.71 (*t*, *J* = 10.3, irrad. at 4.31 → *d*, *J* ≈ 10, H_{ax}–C(8)); 3.64 (*t*, *J* = 9.7, H–C(6)); 3.48 (*d*, *J* = 8.7, H–C(4)); 2.79 (*s*, OH); 1.77–1.67 (*m*, 2 H–C(2)); 0.86 (*t*, *J* = 7.2, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.81, 138.06, 137.80 (3*s*); 129.15–126.28 (several *d*); 101.39 (*d*, PhCH); 99.56 (*s*, C(3)); 82.68 (*d*, C(6)); 80.76, 80.66 (2*d*, C(4), C(5)); 75.84, 75.36 (2*t*, 2 PhCH_2); 69.35 (*t*, C(8)); 63.18 (*d*, C(7)); 31.73 (*t*, C(2)); 6.83 (*q*, C(1)). Anal. calc. for $C_{29}H_{32}O_6$ (476.57): C 73.09, H 6.77; found: C 73.28, H 6.87.

*(*E,E*)-2,3-Di*-O-*benzyl-4,6*-O-*benzylidene*-D-*glucono-1,5-lactone Azine* (**37**). A soln. of **14** (38 mg, 0.083 mmol) in CH_2Cl_2 (0.45 ml) was diluted with MeCN (2 ml, dried over molecular sieves), stirred at 25° for 20 h, and evaporated at 20°. FC (hexane/AcOEt/CH_2Cl_2 8:1:1) gave **37** (15 mg, *ca.* 35%), together with traces of other products. Crystallisation (AcOEt/hexane) gave an anal. sample of **37**. R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.63. IR (CH_2Cl_2) 3040*m*, 2986*s*, 1636*m*, 1496*w*, 1453*w*, 1441*s*, 1087*s*, 1028*m*, 1009*m*, 885*s*. ^{1}H-NMR (300 MHz, C_6D_6): 7.59–7.05 (*m*, 15 arom. H); 6.03 (br. *s*, H–C(2)); 5.16 (*s*, PhC*H*); 4.76–4.67 (*m*, H–C(5)); 4.74 (*d*, *J* = 11.2, PhC*H*); 4.69 (*d*, *J* = 11.5, PhC*H*); 4.52 (*d*, *J* = 12.4, PhC*H*); 4.43 (*d*, *J* = 12.4, PhC*H*); 4.24 (*dd*, *J* = 10.3, 5.3, irrad. at 3.46 → *d*, *J* ≈ 5, H_{eq}–C(6)); 4.23 (*d*, *J* = 6.8, irrad. at 3.79 → *s*, H–C(3)); 3.79 (*dd*, *J* = 10.3, 6.8, irrad. at 4.23 → *d*, *J* ≈ 10, H–C(4)); 3.46 (*t*, *J* = 10.3, irrad. at 4.23 → *d*, *J* ≈ 10, H_{ax}–C(6)). ^{13}C-NMR (75 MHz, C_6D_6): 164.56 (*s*, C(1)); 138.17, 137.99, 137.91 (3*s*); 129.12–126.62 (several *d*); 101.64 (*d*, PhC*H*); 81.47, 80.63 (2*d*, C(3), C(4)); 72.02, 71.62 (2*t*, 2 PhCH_2); 70.95 (*d*, C(2)); 68.99 (*t*, C(6)); 65.55 (*d*, C(5)). MALDI-MS: 889 (60, $[M+H]^+$), 888 (100, M^+).

4,5-Di-O-*benzyl-6,8*-O-*benzylidene-1,2-dideoxy-α*-D-manno-*oct-3-ulo-3,7-pyranose* (**39**) *and 3,7-Anhydro-5*-O-*benzyl-6,8*-O-*benzylidene-1,2,4-trideoxy*-D-arabino-*oct-3-enitol* (**40**). The soln. of the thermolysis of the diazirine **15** (20 mg, 0.043 mmol) in the presence of 1M BEt_3 (in THF, 92 µl, 0.092 mmol) in degassed THF (1 ml) was cooled to 0°, treated with 3M aq. NaOH (0.5 ml) and 30% H_2O_2 (0.5 ml), and stirred at 25° for 12 h. The mixture was diluted with CH_2Cl_2, washed with sat. aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt/CH_2Cl_2 8:1:1) gave an apolar mixture of **39** (9 mg, 43%) and **38** (2 mg, 9%) as colourless oils. HPLC (hexane/AcOEt 8:1; 9 ml/min) of the apolar mixture yielded a 1:1 mixture of the glucal **40** (< 1 mg, < 5%) and another product.

Data of **39**: R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.23. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.54–7.26 (*m*, 15 arom. H); 5.63 (*s*, PhC*H*); 5.09 (*d*, *J* = 11.2, PhC*H*); 4.95 (*d*, *J* = 12.4, PhC*H*); 4.76 (*d*, *J* = 12.2, PhC*H*); 4.67 (*d*, *J* = 11.5, PhC*H*); 4.29–4.19 (*m*, H–C(5), H–C(6), H_{eq}–C(8)); 4.00 (*td*, *J* = 11.3, 4.7, H–C(7)); 3.84 (*t*, *J* = 10, H_{ax}–C(8)); 3.83 (*d*, *J* = 2.5, H–C(4)); 2.19 (*s*, exchangeable with CD_3OD, OH); 1.81 (*dq*, *J* = 14.3, 7.5, 1 H, MeCH_2); 1.70 (*dq*, *J* = 14.6, 7.3, 1 H, MeCH_2); 0.85 (*t*, *J* = 7.7, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.90, 138.37, 137.77 (3*s*); 128.81–126.10 (several *d*); 101.46 (*d*, PhCH); 100.75 (*s*, C(3)); 79.57, 77.94, 77.84 (3*d*, C(4), C(5), C(6)); 75.25, 73.42 (2*t*, 2 PhCH_2); 69.11 (*t*, C(8)); 64.88 (*d*, C(7)); 30.45 (*t*, C(2)); 6.67 (*q*, C(1)).

Data of **40**: R_f(hexane/AcOEt/CH_2Cl_2 8:1:1) 0.50. t_R(hexane/AcOEt 8:1, 9 ml/min) 10.6 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.61–7.02 (*m*, 15 arom. H); 5.59 (*s*, PhCH); 4.90–4.62 (*m*, PhCH_2, H_{ax}–C(8)); 4.57 (*dq*, *J* ≈ 7, 1, H–C(4)); 4.41 (*dd*, *J* = 10.3, 5.0, H_{eq}–C(8)); 4.16 (*dd*, *J* = 9.9, 7.2, H–C(5)); 3.99 (*td*, *J* = 10.3, 5.0, H–C(7)); 3.85 (*t*, *J* = 10.3, H–C(6)); 2.23–2.16 (*m*, MeCH_2); 0.93 (*t*, *J* = 7.5, *Me*CH_2); further signals: 7.61–7.02 (*m*, 15 arom. H); 5.58 (*s*, PhC*H*); 4.90–4.62 (*m*, 3 H); 4.57 (*d*, *J* = 7.1); 4.37 (*dd*, *J* = 10.3, 5.0); 4.08 (*dd*, *J* = 9.9, 7.2); 3.84 (*t*, *J* = 10.3); 3.72 (*td*, *J* = 10.3, 5.0).

*4,8-Anhydro-2-*C*-methyl-5,6,7,9-tetra-*O*-benzyl-1,2,3-trideoxy-*D*-glycero-*D*-gulo-nonitol* (**46**) *and 4,8-Anhydro-2-*C*-methyl-1,2,3,5-tetradeoxy-6,7,9-tri-*O*-benzyl-*D*-arabino-non-4-enitol* (**48**). The soln. of the thermolysis of the diazirine **1** (35 mg, 0.064 mmol) in the presence of 1M $Al(^iBu)_3$ (in heptane, 84 µl, 0.084 mmol) in THF (1.5 ml) was cooled to 0°, treated with H_2O (0.5 ml), and stirred for 12 h. The mixture was diluted wtih CH_2Cl_2, washed with sat. aq. NH_4Cl, $NaHCO_3$, and H_2O, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt/CH_2Cl_2 18:1:1) yielded **48** (8 mg, 26%) and **46** (8 mg, 21%) as colourless oils.

Data of **46**: R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.62. IR (CH_2Cl_2): 3032*w*, 2956*m*, 2869*m*, 1496*m*, 1453*m*, 1364*m*, 1208*m*, 1083*s*, 1027*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.10 (*m*, 20 arom. H); 4.95 (*d*, *J* = 10.9, PhC*H*); 4.82 (*d*, *J* = 10.9, PhC*H*); 4.80 (*d*, *J* = 10.9, PhC*H*); 4.69 (*d*, *J* = 11.8, PhC*H*); 4.64 (*d*, *J* = 12.5, PhC*H*); 4.60 (*d*, *J* = 11.8, PhC*H*); 4.47 (*d*, *J* = 12.1, PhC*H*); 4.45 (*d*, *J* = 10.6, PhC*H*); 4.13 (*ddd*, *J* = 11.8, 5.3, 2.8, irrad. at 3.73 → *dd*, *J* ≈ 11, 3, irrad. at 1.74 → *d*, *J* ≈ 5, H–C(4)); 3.80 (*dd*, *J* = 9.3, 7.8, H–C(6) or H–C(7)); 3.73 (*dd*, *J* = 9.3, 5.6, irrad. at 4.13 → *d*, *J* ≈ 9, H–C(5)); 3.69–3.55 (*m*, 4 H); 1.80–1.68 (*m*, 2 H–C(3)); 1.40–1.32 (*m*, H–C(2)); 0.95–0.89 (*m*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.85, 138.37, 138.26, 138.09 (4*s*); 128.44–127.76 (several *d*); 82.63 (*d*, C(6)); 80.38 (*d*, C(5)); 78.26 (*d*, C(7)); 75.55, 75.14, 73.53, 73.10 (4*t*, 4 PhCH_2); 72.08, 71.03 (2*d*, C(4), C(8)); 68.99 (*t*, C(9)); 33.01 (*t*, C(3)); 24.00 (*d*, C(2)); 23.82, 21.36 (2*q*, 2 Me). FAB-MS (3-NOBA): 581 (9, $[M+H]^+$), 502 (17), 391 (36), 349 (100).

Data of **48**: R_f(hexane/AcOEt/CH_2Cl_2 4:1:1) 0.70. IR (CH_2Cl_2): 3032*w*, 2957*m*, 2869*m*, 1673*m*, 1496*w*, 1453*m*, 1367*w*, 1097*s*, 1027*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34–7.26 (*m*, 15 arom. H); 4.80 (*d*, *J* = 11.5, PhC*H*); 4.67 (*d*, *J* = 3.4, irrad. at 4.18 → change, H–C(5)); 4.65 (*d*, *J* = 10.9, PhC*H*); 4.62 (*d*, *J* = 11.5, PhC*H*); 4.60 (*d*, *J* = 11.8, PhC*H*); 4.55 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 11.8, PhC*H*); 4.18 (*dd*, *J* = 5.6, 3.2, H–C(6)); 4.09 (*ddd*, *J* = 7.8, 5.0, 2.8, H–C(8)); 3.83 (*dd*, *J* = 8.0, 5.6, irrad. at 4.18 or 4.09 → *m*, H–C(7)); 3.82 (*dd*, *J* = 10.9, 5.0, irrad. at 4.09 → *m*, H–C(9)); 3.75 (*dd*, *J* = 10.6, 2.8, irrad. at 4.09 → *d*, *J* ≈ 10, H′–C(9)); 1.97–1.87 (*m*, 3 H); 0.92–0.89 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.40 (*s*, C(4)); 138.63 (*s*, 1 arom. C); 138.37 (*s*, 2 arom. C); 128.37–127.53 (several *d*); 96.02 (*d*, C(5)); 75.90, 74.27 (2*d*); 73.39, 73.25, 70.11 (3*t*, 3 PhCH_2); 68.77 (*t*, C(9)); 43.02 (*t*, C(3)); 26.01 (*d*, C(2)); 22.41, 22.38 (2*q*, 2 Me).

Reaction of **1** *with* $AlMe_3$. A soln. of 2M $AlMe_3$ in heptane (52 µl, 0.103 mmol) and **1** (47 mg, 0.086 mmol) in THF (1.5 ml) was stirred for 4.5 h at 18°, cooled to 0°, and treated with H_2O (0.5 ml) and CH_2Cl_2 (20 ml). The org. layer was separated, washed with 2N NaOH soln. and H_2O, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt/CH_2Cl_2 10:1:1) gave **51** [43] (11 mg, 30%) and **49** [42] (14 mg, 30%).

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