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Synthesis and elaboration of functionalised carbohydrate-derived spiroketals

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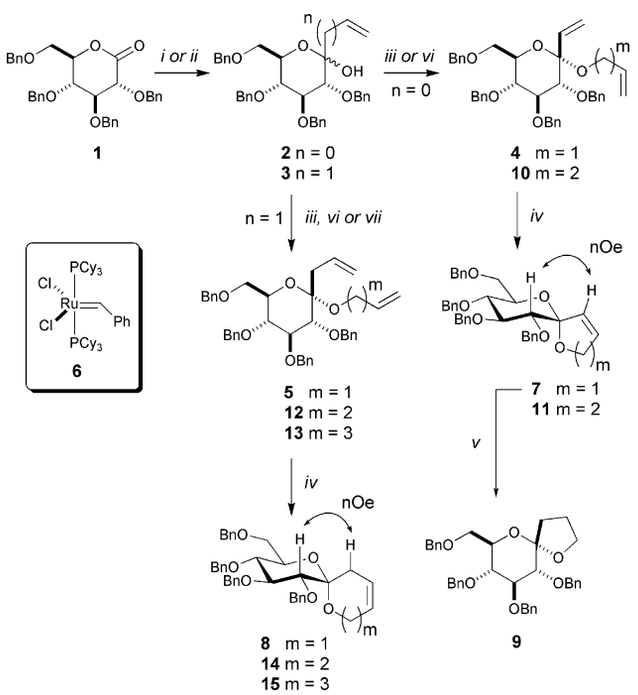
The scope of a stereoselective three-step approach for the synthesis of sugar derived spiroketals is presented. The methodology consists of Grignard addition of vinyl- or allylmagnesium bromide to a carbohydrate lactone, followed by K-10 clay mediated glycosidation with a terminal alkenol and subsequent ring-closing metathesis of the resulting diene. The generality of this procedure is demonstrated by the synthesis of various pyranose- and furanose-derived spiroketals, as well as more advanced tricyclic spiroketal derivatives. It is shown that functionalisation of the double bond in the resulting spiroketals leads to fused polycyclic ethers.

Introduction

Spiroketals, particularly 1,6-dioxa-spiro[4.5]decanes and 1,7-dioxa-spiro[5.5]undecanes, which are common structural features of many natural products,[1] have attracted considerable interest from synthetic organic chemists over the past several decades. An attractive approach towards functionalised spiroketals involves the use of carbohydrates as readily available chiral synthons. For instance, Hanessian and Ugolini[2] reported the acid-catalysed intramolecular glycosidation of a ketose derivative to a 1,7-dioxa-spiro[5.5]undecene. Similarly, [4.4] as well as [4.5] spiroketals were produced by acid-catalysed *trans*-ketalisation of *keto*-furanosides.[3] Alternatively, a 1,6-dioxa-spiro[4.5]undecane framework was constructed by radical promoted cyclisation of *C*-glycosides.[4] However, the spiroketalisations described above lead to epimeric mixtures which require additional acid treatment to force the equilibrium to the thermodynamically most stable isomer. Sinaÿ and Haudrechy[5] nicely evaded this drawback by predispositioning the configuration at the future spirocentre through a stereoselective glycosidation of a ketose derivative. The resulting ketoglycoside was successively converted into a spiroketal *via* radical mediated ring-closure.[6] In line with this approach, we developed a three-step procedure,[7] comprising Grignard addition of vinyl- or allylmagnesium bromide to perbenzylated D-gluconolactone, followed by stereoselective Montmorillonite K-10 clay[8] mediated condensation with different terminal alkenols and subsequent formation of the spiroketal by ring-closing metathesis using Grubbs' catalyst.[9] We present here the scope of this approach in full detail by the transformation of pyranose and furanose derived lactones into [4.4], [4.5], [4.6] and [5.5] spiroketals, as well as the synthesis of more advanced tricyclic compounds.



Scheme 1 *Reagents and conditions*: i, vinylmagnesium bromide (1.2 equiv.), Et_2O, −78 °C (**2**: 91%). ii, Allylmagnesium bromide (1.2 equiv.), Et_2O, −78 °C (**3**: 83%). iii, Allyl alcohol (6 equiv.), K-10 clay (200 mass%), 4 Å sieves, CH_2Cl_2 (**4**: 75%, **5**: 69%). iv, **6** (0.06 equiv.), toluene, 60 °C (**7**: 95%, **8**: 88%, **11**: 88%, **14**: 95%, **15**: 90%). v, PtO_2, H_2, EtOAc (85%). vi, 3-Buten-1-ol (6 equiv.), K-10 clay (200 mass%), 4 Å sieves, CH_2Cl_2 (**10**: 68%, **12**: 69%, **13**: 80%). vii, 4-Penten-1-ol (6 equiv.), K-10 clay (200 mass%), 4 Å sieves, CH_2Cl_2 (80%).

Results and discussion

In a preliminary paper[7a] we showed that 1,6-dioxa-(5*S*)-spiro[4.5]dec-3-ene **7**[10,11] (see Scheme 1) and 1,7-dioxa-(6*S*)-spiro[5.5]undec-9-ene **8**[11] could be assembled with a high degree of stereoselectivity following the three-step reaction sequence mentioned above. In the first instance, fully benzylated gluconolactone **1**[12] was converted into the known[13] α-epimer of vinylketose **2** by nucleophilic addition of vinylmagnesium bromide. Treatment of the same lactone with allylmagnesium bromide afforded the known[14] allylketose **3** as a mixture of anomers (α : β = 4; 1). Next, Montmorillonite K-10 clay mediated glycosidation of donors **2** and **3** with an excess of allyl alcohol afforded the corresponding isomerically pure α-ketoglycosides **4** and **5**. The last step, comprising RCM of dienes **4** and **5** using Grubbs' catalyst **6** (6 mol%) in toluene at 60 °C, gave the respective spiroketal derivatives **7** and **8** in 65% and 50% overall yield from **1**. The *S*-configuration of the spirocentres in compounds **7** and **8** was unambiguously assigned by NOESY experiments (see Scheme 1).[15] In addition, the NMR-data of saturated spiroketal **9**, obtained by hydrogenation of **7**

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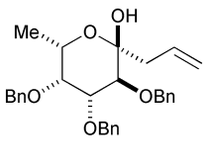
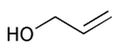
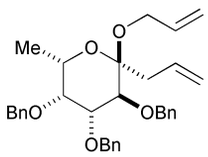
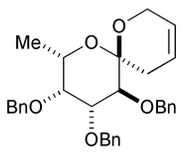
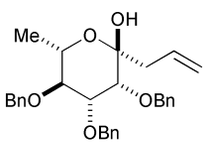
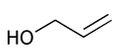
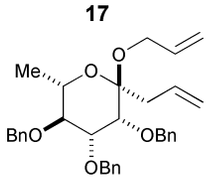
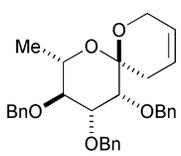
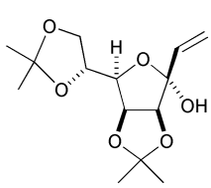
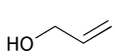
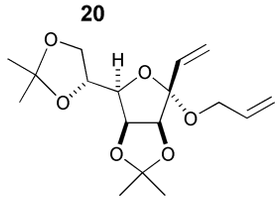
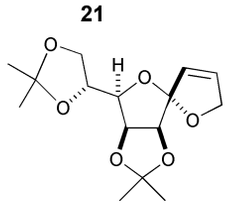
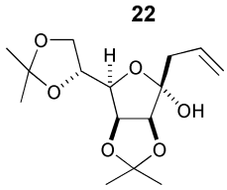
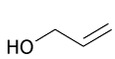
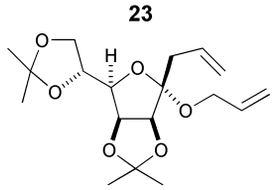
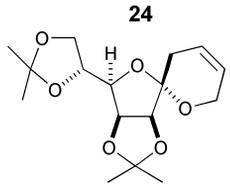
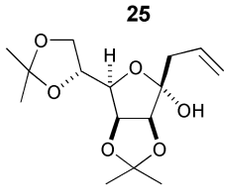
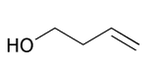
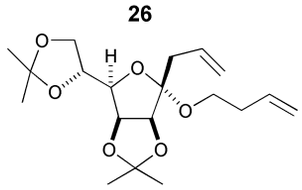
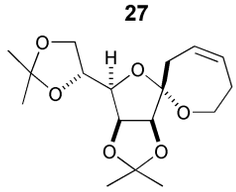
Table 1 Examples of the K-10/RCM approach towards monosaccharide-derived spiroketals

Entry	Donor	Acceptor	K-10 product[a]	Yield (%)	RCM product[b]	Yield (%)
1	 **16**		 **17**	70	 **18**	90[c]
2	 **19**		 **20**	89	 **21**	85[c]
3	 **22**		 **23**	66	 **24**	95[d]
4	 **25**		 **26**	54	 **27**	87
5	 **25**		 **28**	42	 **29**	99[c]

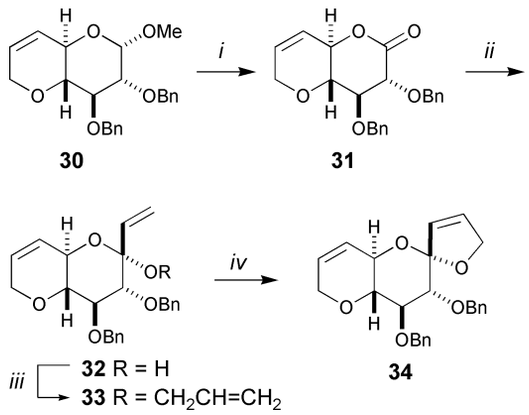
[a] Acceptor (6 equiv.), K-10 (200 mass%), 4 Å sieves, CH_2Cl_2, 20 °C. [b] **6** (0.06 equiv.), toluene, 60 °C. [c] **6** (0.06 equiv.), CH_2Cl_2, 20 °C. [d] **6** (0.03 equiv.), CH_2Cl_2, 20 °C.

under the influence of platinum(IV) oxide, were identical to those reported by the groups of Suárez and Taylor.[4d,16] Glycosidation of ketoses **2** and **3** with 3-buten-1-ol and 4-penten-1-ol and subsequent RCM as described above led to spiroketals **11**,[2,17] **14** and **15** in 60%, 66% and 72% yields, respectively, over the two steps.[7,11]

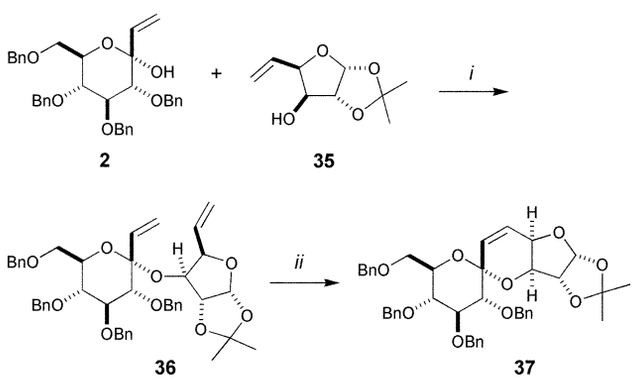
In the next stage, the influence of the carbohydrate configuration on the efficacy of the three-step methodology was studied. Therefore, the lactones derived from fully benzylated L-fuco- and L-rhamnopyranose[18,19] were subjected to Grignard addition of allylmagnesium bromide and K-10 mediated glycosidation with allyl alcohol (entries 1 and 2, Table 1) as described in Scheme 1. RCM of the resulting dienes **17** and **20** using Grubbs' catalyst (6 mol%) in dichloromethane at ambient temperature afforded the respective spiroketals **18** and **21** (55% and 68%, respectively), the structures of which were fully assigned by NMR-spectroscopy. Continuing our investigation, the acid-labile furanoid 2,3;5,6-di-*O*-isopropylidene-D-manno-1,4-lactone[20] was subjected to the three-step sequence. Reaction of this lactone with vinylmagnesium bromide led to the isolation of the expected vinylketose **22** (entry 3) in 45% as well as a side-product. Mass spectrometric and NMR-spectroscopic analysis indicated that the latter compound resulted from double vinyl addition which led to an acyclic bis-adduct.[21] However, subsequent glycosidation of **22** and RCM steps proceeded smoothly to give spiroketal **24** in 64% yield over two steps. Reaction of the same lactone with allylmagnesium bromide furnished allylketose **25** in excellent yield. Subjection of **25** to K-10 glycosidation with allyl alcohol as well as 3-butene-1-ol (entries 4 and 5 respectively), followed by RCM of the resulting dienes afforded spiroketals **27** and **29** in 47% and 42% yield over two steps.

The generality of the approach is further emphasised by its application in the synthesis of the more complex tricyclic spiroketal **34**. Lactone **31** (see Scheme 2) was synthesised from known[22] pyranopyran compound **30** in two steps. Liberation of the acetal function by acid hydrolysis with 3 M sulfuric acid in acetic acid at 80 °C, followed by subsequent oxidation furnished lactone **31** in 50% yield. Execution of the three-step reaction sequence on this lactone, as described for the conversion of **2** into **7**, proceeded in 20% overall yield to afford spiroketal **34**, the structure of which was ascertained by NOESY-experiments. A different tricyclic constellation, namely **37** (see Scheme 3), was accessible through K-10-mediated glycosidation of vinylketose **2** with sugar derived acceptor **35**.[23] Remarkably, this glycosidation only proceeded in satisfactory yield when **35** was used in a 20-fold excess. RCM of the resulting disaccharide **36** with Grubbs' catalyst **6** (6 mol%) furnished tricyclic adduct **37** in 64% yield.

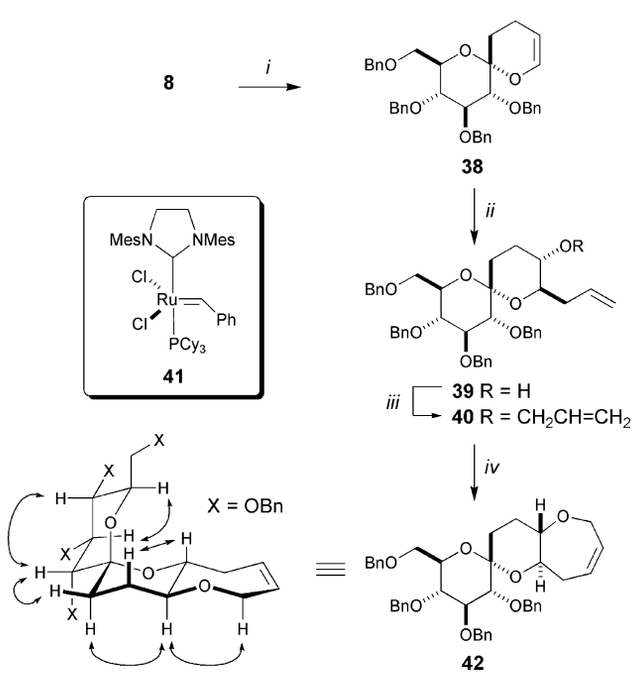
Interestingly, yet another opportunity to construct oligocyclic systems presents itself by elaboration of the double bond in the spiroketals, as is demonstrated for spiroketal **8** (see



Scheme 2 *Reagents and conditions*: i, a) 3 M H_2SO_4, HOAc, 80 °C, 6 h, b) DMSO, acetic anhydride, 16 h (50%). ii, Vinylmagnesium bromide, Et_2O, −78 °C (42%). iii, Allyl alcohol (6 equiv.), K-10 clay (200 mass%), 4 Å sieves, CH_2Cl_2 (50%). iv, **6** (0.06 equiv.), CH_2Cl_2 (95%).



Scheme 3 *Reagents and conditions*: i, **35** (20 equiv.), K-10 clay (200 mass%), 4 Å sieves, CH_2Cl_2 (45%). ii, **6** (0.06 equiv.), CH_2Cl_2 (64%).



Scheme 4 *Reagents and conditions:* i, $(Ph_3P)_3RhCl$ (cat.), DBU, EtOH, 60 °C (90%). ii, a) DMDO, CH_2Cl_2, 0 °C, b) allylmagnesium chloride, THF, 0 °C (61%). iii, Allyl bromide, NaH, DMF (93%). iv. catalyst **41** (0.5 mol%), CH_2Cl_2, Δ (80%).

Scheme 4). Conversion of **8** into enol ether **38** was effected in 90% yield by reaction with Wilkinson's catalyst[24] in the presence of a catalytic amount of DBU in ethanol at 60 °C.[22a] Next, **38** was treated with a freshly prepared solution of 3,3-dimethyldioxirane (DMDO) in acetone at 0 °C,[25] followed by opening of the crude epoxide with allylmagnesium bromide in THF[26] at 0 °C. The resulting alkenol **39** was isolated in 61% yield. Allylation under standard conditions, followed by RCM using 0.5 mol% Grubbs' catalyst **41**[27] in refluxing dichloromethane afforded tricyclic product **42** in 74% over two steps. The structure of **42** was confirmed by NOESY-experiments, of which the most important signals are depicted in Scheme 4.

Conclusion

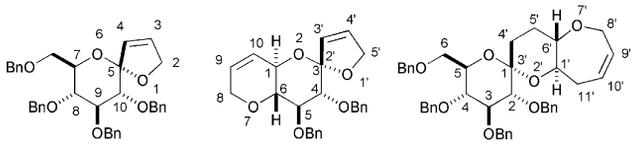
In this paper, the scope of a stereoselective and versatile three-step approach towards the construction of pyranose (D-*gluco*, L-*fuco* and L-*rhamno*) and furanose (D-*manno*) derived unsaturated spiroketals is presented. The methodology has proven to be effective for the construction of [4.4], [4.5], [5.5], [5.6] and [5.7] spiroketals and also of the more advanced tricyclic compounds **34** and **37**. It was demonstrated that the double bond in the newly formed spirosystem is amenable to further elaboration, to furnish fused oxacyclic compounds such as **42**. It is of interest to note that the allylic ether **42** can be subjected to the same sequence of reactions, to give entrance to a reiterative procedure.[28] Its broad applicability, as well as the potential to further elaborate the produced spiroketals, make this three-step methodology a valuable tool in the synthesis of natural products containing highly functionalised spiroketal moieties.

Experimental

General

Dichloromethane, dimethylsulfoxide (DMSO), ethyl acetate, chloroform, *N,N*-dimethylformamide (DMF), pyridine (p.a. grade, Baker) and tetrahydrofuran (THF, Baker, HPLC grade) were stored over molecular sieves (4 Å). Toluene was boiled under reflux with P_2O_5 for 3 h, distilled and stored over molecular sieves (4 Å). Anhydrous diethyl ether was freshly destilled from $LiAlH_4$ prior to use. Sulfuric acid, acetic acid, acetic anhydride (p.a. grade, Baker), ethanol (96%, technical grade) and acetone (Acros, p.a.) were used as received. Vinylmagnesium bromide (1 M in THF, Aldrich), allyl alcohol (Aldrich), platinum(IV) oxide (Acros), allylmagnesium bromide (1 M in Et_2O, Aldrich), 3-buten-1-ol (Aldrich), chlorotris(triphenylphosphine)rhodium(I) ($(PPh_3)_3Rh(I)Cl$, Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich), allylmagnesium chloride (2 M in THF, Aldrich), allyl bromide (Aldrich), and sodium hydride (60% dispersion in mineral oil, Acros) were used as received. Montmorillonite K-10 clay (Aldrich) was dried (110 °C, 1 mm Hg, 10 h) before use. Reactions were executed at ambient temperature unless stated otherwise. Drying of organic layers after work-up was effected by addition of $MgSO_4$. TLC analysis was conducted on DC-Fertigfolien (Schleicher & Schuell, F1500, LS254) or HPTLC aluminum sheets (Merck, silica gel 60, F254) with detection by UV-absorption (254 nm) and charring with 20% H_2SO_4in ethanol. Column chromatography was performed either on Baker silica gel (0.063–0.200 mm) or Merck silica gel 60 (0.040–0.063 mm). Solvents used for column chromatography were of technical grade and distilled before use. ^1H- and ^{13}C-spectra were recorded on a Jeol JNM-FX-200 (200 MHz and 50.1 MHz, respectively) or a Bruker DPX-300 (300 MHz and 75.1 MHz, respectively). NMR shifts are reported in ppm (δ) relative to tetramethylsilane. Mass spectrometry was performed on a PE/SCIEX API 165 equipped with an electrospray interface. Optical rotation values were measured at 20 °C on a Propol Automatic Polarimeter at 589 nm and are given in unit of 10^{-1} deg cm^2 g^{-1}.

The atom numbering used for the bi- and tricyclic products is given in Fig. 1.



7 34 42

Fig. 1 The atom numbering used for the bi- and tricyclic products.

General procedure for the Grignard reactions

A solution of the lactone in anhydrous Et_2O (5 mL mmol^{-1}) was cooled to −78 °C under a nitrogen atmosphere. The Grignard reagent (1.0 M solution, 1.2 equiv.) was added dropwise and the mixture was stirred at −78 °C until TLC analysis (33% EtOAc–light petroleum ether) revealed completion of the reaction. The reaction was quenched by addition of sat. NH_4Cl and extracted with Et_2O. The organic layer was washed with sat. NH_4Cl, dried and concentrated. Silica gel chromatography (10 to 30% EtOAc–light petroleum ether) yielded the ketose.

General procedure for the K-10-mediated condensation reactions

To a flask containing Montmorillonite K-10 clay and powdered molecular sieves 4 Å (both flame-dried under vacuum, 200 mass% each), was added a mixture of the ketose and the acceptor (6 equiv.) in anhydrous CH_2Cl_2 (10 mL mmol^{-1}) under an argon atmosphere. The resulting suspension was stirred vigorously until TLC analysis (25% EtOAc–light petroleum ether) revealed completion of the reaction. A mixture of methanol–pyridine (10 mL mmol^{-1}, 1 : 1) was added and stirring was continued for 10 min. The suspension was filtered over Hyflo® and concentrated. Silica gel chromatography (5 to 20% EtOAc–light petroleum ether) of the residue yielded the glycosidation product.

General procedures for ring-closing metathesis

Method A: A 0.08 M solution of the diene in anhydrous toluene was purged for 15 min with argon. Grubbs' catalyst **6** (0.06 equiv.) was added and the mixture was purged with argon for an additional 15 min, after which the solution was heated to 60 °C. Stirring was continued under an argon atmosphere until TLC analysis (20% EtOAc–light petroleum ether) revealed complete disappearance of the starting material. The mixture was allowed to cool to room temperature and was concentrated. The residue was subjected to silica gel chromatography (5 to 20% EtOAc–light petroleum ether) to give the product.

Method B: A 0.08 M solution of the diene in anhydrous dichloromethane was purged for 15 min with argon. Grubbs' catalyst **6** (0.06 equiv.) was added and the mixture was purged with argon for an additional 15 min. Stirring was continued under an argon atmosphere until TLC analysis (20% EtOAc–light petroleum ether) revealed complete disappearance of the starting material. The mixture was concentrated, and purified by silica gel chromatography (5 to 20% EtOAc–light petroleum ether) to give the product.

4,5,6,8-Tetra-*O*-benzyl-1,2-dideoxy-α-D-*gluco*-oct-1-eno-3-ulopyranose (2). Prepared from **1** by Grignard addition, according to the general procedure. Colourless syrup (3.82 g, 6.87 mmol, 91%); $[\alpha]_D$ +46.5 (*c* 1 in $CHCl_3$); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.14–7.28 (m, 20H, CH_{arom}), 5.99 (dd, 1H, *J* 11.0 and 17.5 Hz, H-2), 5.26 and 5.60 (2d, 2H, *J* 10.2 and 16.8 Hz, 2 × H-1), 4.54, 4.63, 4.79 and 4.88 (4d, 8H, CH_2 Bn), 4.05–4.10 (m, 1H, H-7), 4.01 (br t, 1H, *J* 9.5 Hz, H-5), 3.65–3.78 (m, 2H, H-6,8), 3.46 (dd, 1H, *J* 3.7 and 7.3 Hz, H-8), 3.42 (br d, 1H, *J* 9.5 Hz, H-4), 3.20 (br s, 1H, OH); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.6 (C-2), 137.7, 138.1 and 138.6 (C_q Bn), 127.4–128.2 (CH_{arom}), 117.0 (C-1), 96.4 (C-3), 71.4, 78.0, 82.6 and 83.2 (C-4,5,6,7), 73.1, 74.8, 75.5 and 76.4 (CH_2 Bn), 68.6 (C-8); MS (ESI): calc. for $C_{33}H_{38}O_6$ 566.3, found *m*/*z* 589.3 (M + Na$^+$).

5,6,7,9-Tetra-*O*-benzyl-1,2,3-trideoxy-D-*gluco*-non-1-eno-4-ulopyranose (3). Prepared from **1** by Grignard addition, according to the general procedure. Colourless syrup (3.13 g, 5.40 mmol, 32 %, α/β = 4 : 1); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.29–7.43 (m, 20H, CH_{arom}), 5.99–6.03 (m, 1H, H-2), 5.30 (dd, 2H, 2x H-1), 4.68, 4.71, 4.81, 4.97 and 5.05 (5d, 8H, CH_2 Bn), 4.18 (br t, 1H, *J* 9.5 Hz, H-6), 4.10–4.17 (m, 1H, H-8), 3.66–3.89 (m, 2H, 2 × H-9), 3.78 (br t, 1H, *J* 10.2 Hz, H-7), 3.57 (br d, 1H, *J* 9.5 Hz, H-5), 2.58 (d, 2H, *J* 6.6 Hz, H-3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 137.8, 138.0 and 138.4 (C_q Bn), 132.1 (C-2), 126.7–128.2 (CH_{arom}), 119.8 (C-1), 97.6 (C-4), 71.3, 78.3, 81.2 and 83.5 (C-5,6,7,8), 73.1, 74.7, 75.1 and 75.4 (CH_2 Bn), 68.5 (C-9), 42.6 (C-3); MS (ESI): calc. for $C_{37}H_{40}O_6$ 580.3, found *m*/*z* 603.4 (M + Na)$^+$.

Allyl (4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy)-α-D-*gluco*-oct-1-eno-3-ulopyranoside (4). Prepared from **2** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (238 mg, 0.39 mmol, 74%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.34–7.43 (m, 20H, CH_{arom}), 5.99–6.12 (m, 2H, *J* 11.0, 17.5 Hz, H-2 and CH All), 5.69 (dd, 1H, *J* 1.5, 17.5 Hz, H-1), 5.40 (dd, 1H, *J* 1.5, 11.0 Hz, H-1), 5.35 (d, 1H, *J* 6.6 Hz, CH_2 All), 5.23 (d, 1H, *J* 10.2 Hz, CH_2 All), 4.68, 4.73, 4.78, 4.99, and 5.00 (5d, 8H, CH_2 Bn), 4.29 (br t, 1H, *J* 8.8 Hz, H-5), 4.06 (t, 2H, *J* 5.9 Hz, CH_2 All), 3.81–3.94 (m, 4H, H-6,7 and 2 × H-8), 3.50 (d, 1H, *J* 9.5 Hz, H-4); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.3, 138.4 and 138.8 (C_q Bn), 135.4 (C-2), 134.8 (CH All), 127.6–128.4 (CH_{arom}), 118.7 (C-1), 116.6 (CH_2 All), 99.8 (C-3), 71.9, 78.5, 83.0 and 84.3 (C-4,5,6,7), 73.3, 75.0, 75.6 and 75.8 (CH_2 Bn), 68.8 (C-8), 63.0 (CH_2 All); MS (ESI): calc. for $C_{39}H_{42}O_6$ 606.3, found *m*/*z* 629.5 (M + Na)$^+$.

Allyl (5,6,7,9-tetra-*O*-benzyl-1,2,3-trideoxy)-α-D-*gluco*-non-1-eno-4-ulopyranose (5). Prepared from **3** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (228 mg, 0.37 mmol, 69%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.21–7.30 (m, 20H, CH_{arom}), 5.81–6.02 (m, 2H, H-2 and CH allyl), 5.28 (d, 1H, *J* 17.5 Hz, H-1), 5.05–5.14 (m, 3H, H-1 and CH_2 allyl), 4.52, 4.57, 4.63, 4.71, 4.84 and 4.93 (6d, 8H, CH_2 Bn), 4.14 (br t, 1H, *J* 9.5 Hz, H-6), 4.07 (d, 2H, *J* 5.8, CH_2 All), 3.61–3.77 (m, 4H, H-7,8 and 2 × H-9), 3.53 (br d, 1H, *J* 9.5 Hz, H-4), 2.63 (d, 2H, *J* 7.3 Hz, 2 × H-3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.3 and 138.7 (C_q Bn), 135.0 (C-2), 133.6 (CH allyl), 127.5–128.4 (CH_{arom}), 118.1 (CH_2 allyl), 116.4 (C-1), 101.9 (C-4), 72.0, 78.8, 81.2 and 83.6 (C-5,6,7,8), 73.3, 74.9, 75.1 and 75.5 (CH_2 Bn), 68.9 (C-9), 61.7 (CH_2allyl), 42.6 (C-3); MS (ESI): calc. for $C_{40}H_{44}O_6$ 620.3, found *m*/*z* 643.4 (M + Na)$^+$.

(5*S*,7*R*,8*R*,9*S*,10*R*)-8,9,10-Tris-benzyloxy-7-benzyloxymethyl-1,6-dioxa-spiro[4.5]dec-3-ene (7). Obtained by RCM of **4**, *via* method A of the general procedure, as a greenish syrup (216 mg, 0.37 mmol, 95%); $[\alpha]_D$ + 67.2 ° (*c* 1 in CH_2Cl_2); δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.11–7.24 (m, 20H, CH_{arom}), 6.19 (d, 1H, *J* 5.8 Hz, H-4), 5.62 (m, 1H, H-3), 4.44, 4.54, 4.59, 4.71, 4.74, 4.84, 4.85 and 4.93 (8d, 8H, CH_2 Bn), 4.04 (br t, 1H, *J* 9.5 Hz, H-9), 3.98 (dd, 1H, *J* 6.6 Hz, H-11), 3.71–3.80 (m, 3H, H-7,8,11), 3.64 (d, 1H, *J* 9.5 Hz, H-10), 2.25 (d, 2H, *J* 11.7 Hz, 2 × H-2); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.0 (C_q Bn), 138.3 and 138.7 (C_q Bn), 132.2 (C-4), 127.2–128.2 (C-3 and CH_{arom}), 112.1 (C-5), 72.3, 77.8, 81.3 and 83.6 (C-7,8,9,10), 73.3 and 74.7 (CH_2 Bn), 72.2 (C-2), 68.5 (CH_2OBn); MS (ESI): calc. for $C_{37}H_{38}O_6$ 578.3, found *m*/*z* 601.3 (M + Na)$^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris-benzyloxy-2-benzyloxymethyl-1,7-dioxa-spiro[5.5]undec-9-ene (8). Obtained by RCM of **5** *via* method A of the general procedure as a greenish syrup (634 mg, 1.1 mmol, 90%); $[\alpha]_D$ +34.2 (*c* 0.57 in CH_2Cl_2); δ_H (300 MHz;

$CDCl_3$; Me_4Si) 7.25–7.40 (m, 20H, CH_{arom}), 5.77 (m, 2H, H-9,10), 4.60, 4.66, 4.71, 4.78, 4.96 and 5.07 (6d, 8H, CH_2 Bn), 4.30 (br t, 1H, *J* 8.8 Hz, H-4), 4.22 (br s, 2H, 2 × H-8), 3.78–3.89 (m, 4H, H-2,3 and CH_2OBn), 3.47 (d, 1H, *J* 9.5 Hz, H-5), 2.63 (d, 1H, *J* 17.5 Hz, H-11), 1.88 (d, 1H, *J* 16.8 Hz, H-11); δ_C (50 MHz; $CDCl_3$; Me_4Si) 137.7, 138.0 and 138.5 (C_q Bn), 127.5–128.5 (CH_{arom}), 123.6 (C-9), 121.2 (C-10), 97.2 (C-6), 71.6, 78.5, 82.0 and 83.3 (C-2,3,4,5), 73.2, 74.8, 75.5, and 75.7 (CH_2Bn), 68.5 (CH_2OBn), 59.8 (C-8), 29.9 (C-11); MS (ESI): calc. for $C_{38}H_{40}O_6$ 592.3, found *m*/*z* 615.3 $(M + Na)^+$.

(5*S*,7*R*,8*R*,9*S*,10*R*)-8,9,10-Tris-benzyloxy-7-benzyloxymethyl-1,6-dioxa-spiro[4.5]decane (9). Compound **7** (47 mg, 81 μmol) was dissolved in anhydrous EtOAc (3 mL) and platinum(IV) oxide (10 mg) was added. The mixture was degassed three times after which hydrogen gas was introduced. The mixture was stirred for 5 h when TLC analysis (25% EtOAc–light petroleum ether) revealed a completed conversion. The mixture was purged with nitrogen gas, filtered over Hyflo® and concentrated. Silica gel chromatography (10% EtOAc–light petroleum ether) of the residue yielded **9** as a colourless syrup (40 mg, 69 μmol, 85%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.33–7.20 (m, 20H, CH_{arom}), 4.54, 4.58, 4.71, 4.87, 4.93 and 4.99 (6d, 8H, CH_2 Bn), 4.07 (br t, 1H, *J* 9.5 Hz, H-9), 4.04 (m, 1H, CH_2OBn), 3.84–3.91 (m, 2H, H-2 and CH_2OBn), 3.67–3.79 (m, 3H, H-2,7,8), 3.58 (d, 1H, *J* 9.5 Hz, H-10), 1.86–1.97 (m, 4H, 2 × H-3 and 2 × H-4); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.0, 138.1, 138.3 and 138.7 (C_q Bn), 127.5–128.4 (CH_{arom}), 107.4 (C-5), 71.2, 78.5, 80.0 and 84.5 (C-7,8,9,10), 75.5, 75.6 and 76.4 (CH_2 Bn), 68.7 (CH_2OBn), 68.1 (C-8), 33.4 (C-4), 24.0 (C-3); MS (ESI): calc. for $C_{37}H_{40}O_6$ 580.3, found *m*/*z* 603.4 $(M + Na)^+$.

3-Buten-1-yl (4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy)-α-D-*gluco*-oct-1-eno-3-ulopyranoside (10). Prepared from **2** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (223 mg, 0.36 mmol, 68%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.22–7.30 (m, 20H, CH_{arom}), 5.92 (dd, 1H, *J* 11.0 and 17.5 Hz, H-2), 5.75 (dd, 1H, *J* 7.3 and 17.5 Hz, CH Bu), 5.56 (dd, 1H, *J* 1.5 and 17.5 Hz, H-1), 5.26 (dd, 1H, *J* 2.2 and 11.0 Hz, H-1), 5.06 (d, 1H, *J* 15.3 Hz, CH_2 Bu), 4.97 (d, 1H, *J* 5.1 Hz, CH_2 Bu), 4.54, 4.60, 4.64, 485, and 4.87 (5d, 8H, CH_2 Bn), 4.15 (br t, 1H, *J* 8.8 Hz, H-5), 3.71 (br t, 1H, *J* 8.8 Hz, H-6), 3.62–3.81 (m, 2H, CH_2 Bu), 3.42–3.52 (m, 3H, H-7 and 2 × H-8), 3.35 (d, 1H, *J* 9.5 Hz, H-4), 2.36 (dd, 2H, *J* 7.3 and 13.9 Hz, CH_2 Bu); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.3, 138.5 and 138.9 (C_q Bn), 135.6 (C-2), 135.1 (CH Bu), 127.6–128.4 (CH_{arom}), 118.5 (C-1), 116.5 (CH_2 Bu), 99.5 (C-3), 71.8, 78.6, 83.0 and 84.5 (C-4,5,6,7), 73.4, 75.0, 75.5 and 75.7 (CH_2 Bn), 68.9 (C-8), 61.2 (CH_2 Bu), 34.2 (CH_2 Bu); MS (ESI): calc. for $C_{40}H_{44}O_6$ 620.3, found *m*/*z* 643.4 $(M + Na)^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris-benzyloxy-2-benzyloxymethyl-1,7-dioxa-spiro[5.5]undec-10-ene (11). Obtained from **10** by RCM according to the general procedure (method A) as a colourless syrup (188 mg, 0.32 mmol, 88%); $[\alpha]_D$ +40.4 (*c* 1 in CH_2Cl_2); δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.06–7.68 (m, 20H, CH_{arom}), 6.10 (dd, 1H, *J* 4.7 and 9.9 Hz, H-10), 5.53 (dd, 1H, *J* 1.6 and 10.1 Hz, H-11), 4.51, 4.62, 4.69, 4.78, 4.83 and 4.93 (6d, 8H, CH_2 Bn), 4.06 (br t, 1H, *J* 9.3 Hz, H-4), 3.88 (ddd, 1H, *J* 1.9, 3.6 and 10.3 Hz, H-2), 3.86 (m, 1H, H-8), 3.75 (dd, 1H, *J* 3.8 and 10.8 Hz, CH_2OBn), 3.65 (br t, 1H, *J* 9.9 and 9.0 Hz, H-3), 3.64 (dd, 1H, *J* 1.6 and 10.6 Hz, CH_2OBn), 3.48 (br d, 1H, *J* 9.6 Hz, H-5), 2.43 (m, 1H, H-9), 1.89 (m, 1H, H-9); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.0, 138.2, 138, 3 and 138.8 (C_q Bn), 130.3 (C-10), 127.6–128.6 (C-11 and CH_{arom}), 95.6 (C-6), 71.0, 78.2, 82.9 and 83.2 (C-2,3,4,5), 73.4, 74.9, 75.3 and 75.7 (CH_2Bn), 68.8 (CH_2OBn), 58.1 (C-8), 24.2 (C-9); MS (ESI): calc. for $C_{38}H_{40}O_6$ 592.3, found *m*/*z* 615.3 $(M + Na)^+$, 631.4 $(M + K)^+$.

3-Buten-1-yl (5,6,7,9-tetra-*O*-benzyl-1,2,3-trideoxy)-α-D-*gluco*-non-1-eno-4-ulopyranose (12). Prepared from **3** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (181 mg, 0.29 mmol, 69%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.22–7.31 (m, 20H, CH_{arom}), 5.80 (m, 2H, H-2 and CH Bu), 5.01–5.12 (m, 4H, 2 × H-1 and CH_2 Bu), 4.53, 4.58, 4.65, 4.70, 4.85 and 4.91 (6d, 8H, CH_2 Bn), 4.12 (br t, 1H, *J* 9.5 Hz, H-6), 3.48–3.78 (m, 7H, H-5,7,8 and 2 × H-9 and CH_2 Bu), 2.64 (m, 2H, 2 × H-3), 2.39 (m, 2H, CH_2 Bu); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.8 (C_q Bn), 135.0 (C-2), 133.7 (CH Bu), 127.5–128.4 (CH_{arom}), 118.0 (CH_2 Bu), 116.7 (C-1), 101.5 (C-4), 72.0, 78.8, 81.3 and 83.4 (C-5,6,7,8), 73.2, 74.8, 75.0 and 75.4 (CH_2 Bn), 68.9 (C-9), 60.0 (CH_2 Bu), 38.0 (C-3), 34.4 (CH_2 Bu); MS (ESI): calc. for $C_{41}H_{46}O_6$ 634.3, found *m*/*z* 657.5 $(M + Na)^+$.

4-Penten-1-yl (5,6,7,9-tetra-*O*-benzyl-1,2,3-trideoxy)-α-D-*gluco*-non-1-eno-4-ulopyranose (13). Prepared from **3** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (638 mg, 0.98 mmol, 80%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.47–7.52 (m, 20H, CH_{arom}), 5.94–6.11 (m, 2H, H-2 and CH Pent), 4.76, 4.85, 4.86, 4.95, 5.11, 5.13 and 5.15 (7d, 8H, CH_2 Bn), 4.38 (br t, 1H, *J* 9.5 Hz, H-6), 3.71–4.01 (m, 7H, H-5,7,8 and 2 × H-9 and CH_2 Pent), 2.86 (m, 2H, CH_2 Pent), 2.35 (m, 2H, 2 × H-3), 1.94–2.00 (m, 2H, CH_2 pent); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.4, 138.7 and 138.9 (C_q Bn), 138.3 (CH Pent), 134.0 (C-2), 127.6–128.5 (CH_{arom}), 118.0 (C-1), 115.0 (CH_2 Pent), 101.6 (C-4), 72.1, 78.9, 81.4 and 83.6 (C-5,6,7,8), 73.4, 74.8, 75.1 and 75.5 (CH_2 Bn), 69.0 (C-9), 59.8 (CH_2 Pent), 38.1 (C-3), 30.6 (CH_2 Pent), 29.1 (CH_2 Pent); MS (ESI): calc. for $C_{42}H_{48}O_6$ 648.3, found *m*/*z* 671.3 $(M + Na)^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris-benzyloxy-2-benzyloxymethyl-1,7-dioxa-spiro[5.6]dodec-10-ene (14). Obtained from **12** by RCM according to the general procedure (method A) as a colourless syrup (128 mg, 0.21 mmol, 95%); $[\alpha]_D$ +47.4 (*c* 1 in CH_2Cl_2); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.19–7.32 (m, 20H, CH_{arom}), 5.69 (m, 1H, H-11), 5.52 (m, 1H, H-10), 4.52, 4.55, 4.61, 4.70, 4.86 and 4.92 (6d, 8H, CH_2 Bn), 4.07 (br t, 1H, *J* 9.5 Hz, H-4), 3.69–3.90 (m, 5H, H-2 and 2 × H-8 and CH_2OBn), 3.63 (br t, 1H, *J* 9.5 Hz, H-3), 3.33 (d, 1H, *J* 9.5 Hz, H-5), 2.75 (d, 2H, *J* 16.1 Hz, H-12), 2.19–2.42 (m, 3H, H-12 and 2 × H-9); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.7 (C_q Bn), 129.7 (C-11), 127.6–128.7 (CH_{arom}), 124.7 (C-10), 101.4 (C-6), 71.5, 78.7, 83.6 and 84.7 (C-2,3,4,5), 73.3, 74.9, and 75.6 (CH_2 Bn), 68.7 (CH_2OBn), 61.8 (C-8), 36.3 (C-9), 31.3 (C-12); MS (ESI): calc. for $C_{39}H_{42}O_6$ 606.3, found *m*/*z* 629.4 $(M + Na)^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris-benzyloxy-2-benzyloxymethyl-1,7-dioxa-spiro[5.7]tridec-11-ene (15). Obtained from **13** by RCM according to the general procedure (method A) as a greenish syrup (319 mg, 0.51 mmol, 90%); $[\alpha]_D$+15.8 (*c* 1 in $CHCl_3$); δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.30–7.41 (m, 20H, CH_{arom}), 5.89 (m, 2H, H-11,12), 4.68, 4.72, 4.78, 4.86, 5.00, 5.05 and 5.09 (7d, 8H, CH_2 Bn), 4.19 (br t, 1H, *J* 8.8 Hz, H-4), 4.05 (d, 1H, *J* 11.7 Hz, CH_2OBn), 3.59–3.84 (m, 5H, H-2,3 and 2 × H-8 and CH_2OBn), 3.57 (d, 1H, *J* 9.5 Hz, H-5), 2.79 (dd, 1H, *J* 5.8 and 13.9 Hz, H-13), 2.04–2.45 (m, 4H, 2 × H-9 and 2 × H-10); δ_C (50 MHz; $CDCl_3$; Me_4Si) 137.8, 137.9, 138.1 and 138.6 (C_q Bn), 131.2 (C-12), 127.3–128.2 (CH_{arom}), 126.3 (C-11), 102.0 (C-6), 72.0, 78.4, 83.5 and 84.7 (C-2,3,4,5), 73.1, 74.8, and 75.4 (CH_2 Bn), 68.4 (CH_2OBn), 59.2 (C-8), 35.0 (C-13), 30.7 (C-10), 23.7 (C-9); MS (ESI): calc. for $C_{40}H_{44}O_6$ 620.3, found *m*/*z* 643.4 $(M + Na)^+$.

5,6,7-Tri-*O*-benzyl-1,2,3-trideoxy-α-L-*fuco*-non-1-eno-4-ulopyranose (16). Prepared from 5,6,7-tri-*O*-benzyl-L-fuco-1,5-lactone[16] by Grignard addition, according to the general procedure. Colourless syrup (1.42 g, 2.99 mmol, 87%); δ_H (200

MHz; $CDCl_3$; Me_4Si) 7.22–7.39 (m, 15H, CH_{arom}), 5.82–5.94 (m, 1H, H-2), 5.16 (dd, 2H, *J* 4.4 and 5.8 Hz, 2 × H-1), 4.73 (m, 3H, CH_2 Bn), 4.70, 4.98 and 4.99 (3d, each 1H, CH_2 Bn), 3.78–4.05 (m, 3H, H-5,6,8), 3.66 (d, 1H, *J* 1.5 Hz, H-7), 2.75 (s, 1H, OH), 2.35–2.55 (m, 2H, 2 × H-3), 1.14 (d, 3H, *J* 6.6 Hz, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.4 (C_q Bn), 132.9 (C-1), 127.5–128.9 (CH_{arom}), 119.0 (C-2), 98.0 (C-4), 77.5, 78.0 and 81.4 (C-5,6,7), 72.5, 74.4 and 75.3 (CH_2 Bn), 67.1 (C-8), 43.2 (C-3), 16.9 (CH_3); MS (ESI): calc. for $C_{30}H_{34}O_5$ 474.2, found *m*/*z* 497.2 $(M + Na)^+$.

Allyl (5,6,7-tri-*O*-benzyl-1,2,3-trideoxy)-α-L-*fuco*-non-1-eno-4-ulopyranose (17). Prepared from **16** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (1.07 g, 2.08 mmol, 70%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.26–7.44 (m, 15H, CH_{arom}), 5.84–6.00 (m, 2H, H-2 and CH allyl), 5.26 and 5.34 (2d, 2H, *J* 1.5 and 16.8 Hz, CH_2 allyl), 5.12 and 5.17 (2d, 2H, *J* 1.5 and 10.2 Hz, 2 × H-1), 4.71, 4.74 and 5.00 (3d, each 1H, CH_2 Bn), 4.78 and 5.04 (m, 3H, CH_2 Bn), 3.99–4.18 (m, 3H, H-5,6,8), 3.80 (dd, 2H, *J* 6.6 and 13.1 Hz, CH_2 allyl), 3.71 (d, 1H, *J* 2.2 Hz, H-7), 2.66 (m, 2H, H-3), 1.20 (d, 3H, *J* 5.8 Hz, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.9 and 139.2 (C_q Bn), 135.5 (C-1), 134.2 (CH_2 allyl), 127.0–128.8 (CH_{arom}), 117.5 (C-2), 116.2 (CH allyl), 102.1 (C-4), 78.0, 78.2 and 81.2 (C-5,6,7), 72.7, 74.5 and 75.1 (CH_2 Bn), 67.5 (C-8), 61.6 (CH_2 allyl), 39.0 (C-3), 16.9 (CH_3); MS (ESI): calc. for $C_{33}H_{38}O_5$ 514.3, found *m*/*z* 537.4 $(M + Na)^+$.

(2*S*,3*R*,4*R*,5*S*,6*R*)-3,4,5-Tris-benzyloxy-2-methyl-1,7-dioxa-spiro[5.5]undec-9-ene (18). Obtained from **17** by RCM according to the general procedure (method B) as a greenish syrup (0.90 g, 1.85 mmol, 90%); $[\alpha]_D$ −51.4 (*c* 1 in $CHCl_3$); δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.30–7.24 (m, 15H, CH_{arom}), 5.66 (s, 2H, H-9,10), 4.71, 4.99 and 5.00 (3d, each 1H, CH_2 Bn), 4.77 (s, 3H, CH_2 Bn), 4.04–4.19 (m, 3H, H-2,4,5), 3.80 (dd, 2H, *J* 10.2 and 15.3 Hz, H-8), 3.69 (d, 1H, *J* 1.5 Hz, H-3), 2.57 (m, 1H, H-11), 1.82 (m, 1H, H-11), 1.16 (d, 3H, *J* 6.6 Hz, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.2, 138.7 and 138.8 (C_q Bn), 127.6–128.7 (CH_{arom}), 121.7 and 123.8 (C-9,10), 97.6 (C-6), 78.1, 78.5 and 80.9 (C-3,4,5), 72.7, 74.6 and 75.9 (CH_2 Bn), 67.1 (C-2), 60.3 (C-8), 30.4 (C-11), 16.9 (CH_3); MS (ESI): calc. for $C_{31}H_{34}O_5$ 486.2, found *m*/*z* 509.3 $(M + Na)^+$.

5,6,7-Tri-*O*-benzyl-1,2,3-trideoxy-α-L-*rhamno*-non-1-eno-4-ulopyranose (19). Prepared from 5,6,7-tri-*O*-benzyl-L-rhamno-1,5-lactone[18] by Grignard addition, according to the general procedure. Colourless syrup (1.49 g, 3.14 mmol, 90%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.51–7.59 (m, CH_{arom}), 6.00–6.12 (m, 1H, H-2), 4.88–5.45 (m, 8H, 2 × H-1 and CH_2 Bn), 4.38 (d, 1H, *J* 9.5 Hz, H-6), 3.89–4.20 (m, 3H, H-5,7,8), 3.05 (s, 1H, OH), 2.93 (dd, 1H, *J* 5.1 and 13.9 Hz, H-3), 2.54 (dd, 1H, *J* 9.5 and 13.2 Hz, H-3), 1.56 (d, 3H, *J* 5.8 Hz, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.8, 138.9 (C_q Bn), 132.7 (C-1), 127.7–128.7 (CH_{arom}), 120.6 (C-2), 98.0 (C-4), 68.8, 77.7, 80.7 and 81.9 (C-5,6,7,8), 72.7, 74.8 and 75.3 (CH_2 Bn), 42.8 (C-3), 18.3 (CH_3); MS (ESI): calc. for $C_{30}H_{34}O_5$ 474.2, found *m*/*z* 497.3 $(M + Na)^+$.

Allyl (5,6,7-tri-*O*-benzyl-1,2,3-trideoxy)-α-L-*rhamno*-non-1-eno-4-ulopyranose (20). Prepared from **19** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (1.43 g, 2.78 mmol, 89%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.50–7.65 (m, 15H, CH_{arom}), 5.83–6.20 (m, 2H, H-2 and CH allyl), 5.49 (d, 1H, *J* 16.8 Hz, H-1), 5.17 (d, 1H, CH_2 Bn), 4.90–5.39 (m, 7H, H-1, CH_2 allyl and Bn), 4.79 (d, 1H, CH_2 Bn), 4.39 (d, 1H, *J* 8.8 Hz, H-6), 4.20 (br s, 2H, 2 × H-10), 4.015 (d, 1H, *J* 2.9 Hz, H-5), 3.83–4.00 (m, 2H, H-7,8), 3.07 (dd, 1H, *J* 7.3 and 15.3 Hz, H-3), 2.76 (dd, 1H, *J* 5.8 and 15.3 Hz, H-3), 1.57 (d, 3H, *J* 5.1 Hz, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.7, 138.8 and 139.0 (C_q Bn), 134.4 (CH_2 allyl), 132.7 (C-1), 127.6–128.5 (CH_{arom}), 118.6 (C-2), 116.3 (CH allyl), 102.4 (C-4), 69.4, 76.4, 80.4 and 82.0 (C-5,6,7,8), 72.6, 74.9, 75.1 and 75.4 (CH_2 Bn), 61.0 (CH_2 allyl), 36.4 (C-3), 18.2 (CH_3); MS (ESI): calc. for $C_{33}H_{38}O_5$ 514.3, found *m*/*z* 537.4 $(M + Na)^+$.

(2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-Tris-benzyloxy-2-methyl-1,7-dioxa-spiro[5.5]undec-9-ene (21). Obtained from **20** by RCM according to the general procedure (method B) as a greenish syrup (1.35 g, 2.78 mmol, 85%); $[\alpha]_D$ −27.2 (*c* 1 in $CHCl_3$); δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.31–7.43 (m, 15H, CH_{arom}), 5.68 (s, 2H, H-9,10), 4.66. 4.68, 4.80, 4.94 and 5.02 (5d, 6H, CH_2 Bn), 4.00–4.12 (m, 3H, H-2,3,4), 3.79 (d, 1H, *J* 2.2 Hz, H-5), 3.66 (dd, 2H, *J* 7.3 and 16.1 Hz, H-8), 2.25 (m, 1H, H-11), 2.01 (m, 1H, H-11), 1.35 (d, 3H, *J* 5.0 Hz, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 137.3, 137.6 and 137.8 (C_q Bn), 126.9–130.0 (CH_{arom}), 121.6 and 123.9 (C-9,10), 97.4 (C-6), 78.7, 80.3 and 81.5 (C-3,4,5), 72.6, 74.9 and 75.2 (CH_2 Bn), 68.9 (C-2), 59.6 (C-8), 32.2 (C-11), 17.9 (CH_3); MS (ESI): calc. for $C_{31}H_{34}O_5$ 486.2, found *m*/*z* 509.3 $(M + Na)^+$.

1,2-Dideoxy-4,5;7,8-di-*O*-isopropylidene-α-D-*manno*-oct-1-eno-3-ulofuranose (22). Prepared from 2,3;5,6-di-*O*-isopropylidene-D-manno-1,4-lactone[19] by Grignard addition, according to the general procedure. Colourless syrup (1.34 g, 4.7 mmol, 45%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 5.89 (dd, 1H, *J* 10.9 and 17.5 Hz, H-2), 5.41 (dd, 1H, *J* 1.5 and 17.5 Hz, H-1), 5.20 (dd, 1H, *J* 1.5 and 10.9 Hz, H-1), 4.72 (dd, 1H, *J* 2.9 and 5.1 Hz, H-5), 4.34 (d, 1H, *J* 5.8 Hz, H-4), 4.25 (m, 1H, H-7), 4.02 (dd, 1H, *J* 3.6 and 7.3 Hz, H-8), 3.86–3.97 (m, 3H, H-6,8 and OH), 1.17, 1.23, 1.31 and 1.32 (4s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 136.2 (C-2), 117.0 (C-1), 112.4 (C-3), 104.1 and 108.7 (C_q), 73.1, 78.9, 80.1 and 86.5 (C-4,5,6,7), 66.2 (C-8), 24.1, 25.0, 25.6 and 26.5 (CH_3); MS (ESI): calc. for $C_{14}H_{22}O_6$ 286.1, found *m*/*z* 309.1 $(M + Na)^+$.

Allyl (1,2-dideoxy-4,5;7,8-di-*O*-isopropylidene)-α-D-*manno*-oct-1-eno-3-ulofuranose (23). Prepared from **22** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (0.73 g, 2.24 mmol, 66%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 5.52–5.72 (m, 2H, H-2 and CH allyl), 5.31 (dd, 1H, *J*.2.2 and 21.9 Hz, H-1), 5.16 (dd, 1H, *J* 2.2 and 16.1 Hz, H-1), 4.98 (br t, 2H, CH_2 allyl), 4.67 (dd, 1H, *J* 3.6 and 5.8 Hz, H-5), 4.37 (d, 1H, *J* 5.8 Hz, H-4), 4.25 (dd, 1H, *J* 6.6 and 13.1 Hz, H-8), 3.82–3.99 (m, 3H, H-6,7,8), 3.64 (m, 2H, CH_2 allyl), 1.14, 1.21, 1.26 and 1.28 (4s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 134.4 (CH allyl), 132.6 (C-2), 118.8 (C-1), 115.9 (CH_2 allyl), 112.3 (C-3), 107.8 and 108.7 (C_q), 72.9, 79.1, 79.9 and 86.3 (C-4,5,6,7), 66.6 (C-8), 62.4 (CH_2 allyl), 24.3, 25.0, 25.6 and 26.5 (CH_3); MS (ESI): calc. for $C_{17}H_{26}O_6$ 326.2, found *m*/*z* 349.0 $(M + Na)^+$.

(2*R*,3*S*,4*S*,5*S*)-3,4-Dihydroxy-3,4-*O*-isopropylidene-2-({(*R*)-1,2-dihydroxy-1,2-*O*-isopropylidene}ethyl)-1,6-dioxa-spiro-[4.4]non-8-ene (24). Obtained from **23** by RCM according to the general procedure (method B) as a greenish syrup (0.63 g, 2.11 mmol, 95%); $[\alpha]_D$ −10.4 (*c* 1 in $CHCl_3$); δ_H (600 MHz; $CDCl_3$; Me_4Si) 6.17 (d, 1H, *J* 6.0 Hz, H-9), 5.73 (m, 1H, H-8), 4.76 (dd, 1H, *J* 4.1 and 5.4 Hz, H-3), 4.58 (d, 1H, *J* 14.0 Hz, H-7), 4.48 (d, 1H, *J* 13.9 Hz, H-7), 4.46 (d, 1H, *J* 5.9 Hz, H-4), 4.23 (m, 1H, CH Et), 3.95 (t, 1H, *J* 8.7 Hz, CH_2 Et), 3.86–3.90 (m, 2H, H-2 and CH_2 Et), 1.21, 1.24, 1.32 and 1.38 (4s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 132.6 (C-9), 124.5 (C-8), 119.2 (C-5), 108.8 and 112.4 (C_q), 72.9, 79.9 and 85.7 (C-2,3,4 and CH Et), 74.6 (C-7), 66.8 (CH_2 Et), 24.3, 25.0, 25.7 and 26.7 (CH_3); MS (ESI): calc. for $C_{15}H_{22}O_6$ 298.1, found *m*/*z* 321.0 $(M + Na)^+$, 337.2 $(M + K)^+$.

1,2,3-Trideoxy-5,6;8,9-di-*O*-isopropylidene-α-D-*manno*-non-1-eno-4-ulofuranose (25). Prepared from 2,3;5,6-di-*O*-isopropylidene-D-manno-1,4-lactone[19] by Grignard addition, according

to the general procedure. Colourless syrup (1.65 g, 5.50 mmol, 95%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 5.75–5.96 (m, 1H, H-2), 5.23 (dd, 2H, *J* 10.2 and 17.5 Hz, 2 × H-1), 4.84 (dd, 1H, *J* 3.7 and 4.8 Hz, H-6), 4.49 (d, 1H, *J* 6.6 Hz, H-5), 4.37 (m, 2H, H-8,9), 3.97–4.20 (m, 3H, H-7,9 and OH), 2.52 (d, 2H, *J* 6.6 Hz, 2 × H-3), 1.34, 1.38, 1.45 and 1.49 (4s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 123.4 (C-2), 119.0 (C-1), 112.2 (C-4), 105.1 and 108.7 (C_q), 73.0, 78.6, 79.9 and 84.8 (C-5,6,7,8), 66.3 (C-9), 39.6 (C-3), 24.1, 24.9, 25.5 and 26.5 (CH_3); MS (ESI): calc. for $C_{15}H_{24}O_6$ 300.2, found *m*/*z* 323.2 $(M + Na)^+$.

Allyl (1,2,3-trideoxy-5,6;8,9-di-*O*-isopropylidene)-α-D-*manno*-non-1-eno-4-ulofuranose (26). Prepared from **25** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (0.60 g, 1.76 mmol, 54%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 5.64–5.84 (m, 2H, H-2 and CH allyl), 5.19 (m, 1H, H-1), 4.97–5.10 (m, 3H, H-1 and CH_2 allyl), 4.71 (dd, 1H, *J* 4.0 and 5.8 Hz, H-6), 4.38 (d, 1H, *J* 5.8 Hz, H-5), 4.24–4.30 (m, 1H, H-9), 3.94–4.03 (dd, 1H, *J* 6.2 and 8.4 Hz, H-8), 3.79–3.90 (m, 3H, H-9 and CH_2 allyl), 3.72 (dd, 1H, *J* 3.7 and 7.7 Hz, H-7), 2.51 (d, 2H, *J* 7.7 Hz, 2 × H-3), 1.23, 1.27, 1.34 and 1.38 (4s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 134.3 (CH allyl), 132.1 (C-2), 117.6 (C-1), 116.1 (CH_2 allyl), 112.2 (C-4), 108.7 and 108.9 (C_q), 72.8, 79.2, 79.8 and 84.6 (C-5,6,7,8), 66.7 (C-9), 61.3 (CH_2 allyl), 34.2 (C-3), 24.3, 25.0, 25.7 and 26.6 (CH_3); MS (ESI): calc. for $C_{18}H_{28}O_6$ 340.2, found *m*/*z* 363.2 $(M + Na)^+$.

(2*R*,3*S*,4*S*,5*S*)-3,4-Dihydroxy-3,4-*O*-isopropylidene-2-({(*R*)-1,2-dihydroxy-1,2-*O*-isopropylidene}ethyl)-1,6-dioxa-spiro[4.5]-dec-8-ene (27). Obtained from **26** by RCM according to the general procedure (method A) as a colourless syrup (0.48 g, 1.54 mmol, 87%); $[\alpha]_D$ +58.2 (*c* 1 in $CHCl_3$); δ_H (300 MHz; $CDCl_3$; Me_4Si) 5.72 (br s, 2H, H-8,9), 4.82 (dd, 1H, *J* 3.6 and 5.8 Hz, H-3), 4.43 (d, 1H, *J* 5.8 Hz, H-4), 4.35–4.40 (m, 1H, CH_2 Et), 3.95–4.18 (m, 4H, 2 × H-7 and CH and CH_2 Et), 3.85 (dd, 1H, *J* 3.7 and 8.0 Hz, H-2), 2.50 (dd, 1H, *J* 1.5 and 19 Hz, H-10), 2.12 (dd, 1H, *J* 2.2 and 17.5 Hz, H-10), 1.33, 1.36, 1.44 and 1.46 (4s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 124.2 (C-8), 121.6 (C-9), 108.9 and 112.1 (C_q), 104.6 (C-5), 72.8, 79.3, 79.8 and 85.5 (C-2,3,4 and CH Et), 67.0 (CH_2 Et), 59.8 (C-7), 28.6 (C-10), 24.4, 24.9, 25.7 and 26.6 (CH_3); MS (ESI): calc. for $C_{16}H_{24}O_6$ 312.2, found *m*/*z* 335.2 $(M + Na)^+$.

3-Buten-1yl (1,2,3-trideoxy-5,6;8,9-di-*O*-isopropylidene)-α-D-*manno*-non-1-eno-4-ulofuranose (28). Prepared from **25** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (0.30 g, 0.85 mmol, 42%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 5.68–5.81 (m, 2H, H-2 and CH Bu), 5.00–5.19 (m, 4H, 2 × H-1 and CH_2 Bu), 4.79 (dd, 1H, *J* 4.4 and 5.8 Hz, H-6), 4.43 (d, 1H, *J* 5.8 Hz, H-5), 4.32–4.39 (m, 1H, H-8), 4.10 (dd, 1H, *J* 6.6 and 8.8 Hz, H-9), 3.97 (dd, 1H, *J* 4.4 and 8.8 Hz, H-9), 3.80 (dd, 1H, *J* 3.7 and 8.0 Hz, H-7), 3.47 (br t, 2H, *J* 6.6 Hz, CH_2 Bu), 2.56–2.61 (m, 2H, 2 × H-3), 2.50 (dd, 2H, *J* 6.6 and 13.1 Hz, CH_2 Bu), 1.32, 1.37, 1.45 and 1.47 (4s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 135.3 (CH Bu), 132.3 (C-2), 117.6 (C-1), 116.4 (CH_2 Bu), 112.3 (C-4), 108.7 and 109.0 (C_q), 72.9, 79.0, 79.9 and 84.6 (C-5,6,7,8), 66.9 (C-9), 59.6 (CH_2 Bu), 34.1 (C-3), 34.0 (CH_2 Bu), 24.4, 25.1, 25.8 and 26.7 (CH_3); MS (ESI): calc. for $C_{19}H_{30}O_6$ 354.2, found *m*/*z* 377.2 $(M + Na)^+$.

(2*R*,3*S*,4*S*,5*S*)-3,4-Dihydroxy-3,4-*O*-isopropylidene-2-({(*R*)-1,2-dihydroxy-1,2-*O*-isopropylidene}ethyl)-1,6-dioxa-spiro[4.6]-undec-9-ene (29). Obtained from **28** by RCM according to the general procedure (method B) as a greenish syrup (0.27 g, 0.83 mmol, 99%); $[\alpha]_D$ +9.2 (*c* 1 in $CHCl_3$); δ_H (600 MHz; $CDCl_3$; Me_4Si) 5.65 (m, 1H, H-9), 5.53 (m, 1H, H-10), 4.74 (dd, 1H, *J* 3.8 and 5.9 Hz, H-3), 4.36 (d, 1H, *J* 5.9 Hz, H-4), 4.29–4.32 (m, 1H, CH Et), 4.03 (dd, 1H, *J* 6.3 and 8.7 Hz, CH_2 Et), 3.94 (dd, 1H, *J* 4.3 and 8.7 Hz, CH_2 Et), 3.89 (dd, 1H, *J* 2.2 and 12.0 Hz, H-7), 3.75 (dd, 1H, *J* 3.8 and 8.2 Hz, H-2), 3.55 (dd, 1H, *J* 3.7 and 12.3 Hz, H-7), 2.66 (dd, 1H, *J* 6.5 and 16.3 Hz, H-11), 2.46 (dd, 1H, *J* 5.3 and 16.3 Hz, H-11), 2.38–2.43 (m, 1H, H-8), 2.17 (br d, 1H, *J* 17.2 Hz, H-8), 1.26, 1.31, 1.38 and 1.42 (4s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 130.0 (C-10), 124.3 (C-9), 112.3 (C_q), 108.9 (C-5), 72.9, 78.6, 79.9 and 85.4 (C-2,3,4 and CH Et), 67.1 (CH_2 Et), 60.4 (C-7), 31.8 (C-11), 31.1 (C-8), 24.3, 25.0, 25.7 and 26.7 (CH_3); MS (ESI): calc. for $C_{17}H_{26}O_6$ 326.2, found *m*/*z* 349.1 $(M + Na)^+$.

(1*R*,3*R*,4*R*,5*S*,6*R*)-4,5-Bis-benzyloxy-3-hydroxy-3-vinyl-2,7-dioxa-bicyclo[4.4.0]dec-9-ene (32). Bicyclic methyl glycoside **30**[22] (630 mg, 1.7 mmol) was dissolved in acetic acid (20 ml) and 3 M sulfuric acid (2.4 ml). The mixture was stirred at 80 °C for 6 h, then allowed to cool to room temperature and diluted with ethyl acetate (30 ml). The organic phase was washed with sat. $NaHCO_3$ until pH 7, dried, filtered and concentrated. The residue was purified by silica gel chromatography (15% EtOAc–light petroleum ether). The purified lactol was dissolved in dimethylsulfoxide–acetic anhydride 2 : 1 v/v (6 ml) and stirred for 17 h, when TLC analysis (25% EtOAc–light petroleum ether) revealed complete consumption of the starting material. The mixture was concentrated, dissolved in ethyl acetate and extracted with sat. $NaHCO_3$. Organics were dried, filtered and concentrated to leave a brown syrup (300 mg, 0.8 mmol, 50%), which was subjected to a Grignard reaction with vinylmagnesium bromide as described in the general procedure to give **32** as a colourless syrup (117 mg, 0.30 mmol, 21%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.26–7.31 (m, 10H, CH_{arom}), 5.89 (dd, 1H, *J* 10.2 and 17 Hz, CH vinyl), 5.68–5.77 (m, 2H, H-9,10), 5.59 (dd, 1H, *J* 1.5 and 16.8 Hz, CH_2 vinyl), 5.28 (dd, 1H, *J* 1.5 and 10.2 Hz, CH_2 vinyl), 4.61, 4.77, 4.82 and 4.98 (4d, each 1H, CH_2 Bn), 4.48 (m, 1H, H-1), 4.25 (br s, 2H, 2 × H-8), 3.89 (dd, 1H, *J* 8.8 and 9.5 Hz, H-5), 3.43 (d, 1H, *J* 8.8 Hz, H-4), 3.33 (dd, 1H, *J* 8.8 and 9.5 Hz, H-6); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.8 (CH vinyl), 127.7–128.7 (C-9 and CH_{arom}), 126.1 (C-10), 117.0 (CH_2 vinyl), 96.2 (C-3), 65.1, 78.8, 80.5 and 82.7 (C-1,4,5,6), 74.9 and 75.8 (CH_2 Bn), 66.0 (C-8); MS (ESI): calc. for $C_{24}H_{26}O_5$ 394.2, found *m*/*z* 417.3 $(M + Na)^+$.

(1*R*,3*R*,4*R*,5*S*,6*R*)-3-Allyloxy-4,5-bis-benzyloxy-3-vinyl-2,7-dioxa-bicyclo[4.4.0]dec-9-ene (33). Prepared from **32** by K-10-mediated glycosidation according to the general procedure. Colourless syrup (65 mg, 0.15 mmol, 50%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.22–7.40 (m, 10H, CH_{arom}), 5.73–6.00 (m, 2H, CH vinyl and allyl), 5.52 (dd, 1H, *J* 2.2 and 17.5 Hz, CH_2 allyl), 5.27 (dd, 1H, *J* 1.5 and 16.8 Hz, CH_2 vinyl), 5.26 (dd, 1H, *J* 2.2 and 11.0 Hz, CH_2 allyl), 5.12 (dd, 1H, *J* 1.5 and 10.2 Hz, CH_2 vinyl), 4.62, 4.78, 4.91 and 4.96 (4d, each 1H, CH_2 Bn), 4.26 (br s, 2H, 2 × H-8), 4.18 (m, 1H, H-1), 4.06 (dd, 1H, *J* 8.8 and 9.5 Hz, H-5), 3.94 (m, 2H, CH_2 allyl), 3.35 (d, 1H, *J* 8.8 Hz, H-4), 3.31 (dd, 1H, *J* 8.8 and 9.5 Hz, H-6); MS (ESI): calc. for $C_{27}H_{30}O_5$ 434.2, found *m*/*z* 457.2 $(M + Na)^+$.

(1*R*,3*S*,4*R*,5*S*,6*R*)-4,5-Bis-benzyloxy-2,7-dioxa-bicyclo[4.4.0]-dec-9-enylspiro-3,2′-[2′,5′-dihydrofuran] (34). Obtained from **33** by RCM according to the general procedure (method B) as a greenish syrup (58 mg, 0.14 mmol, 95%); δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.20–7.29 (m, 10H, CH_{arom}), 6.26 (m, 1H, H-3′), 5.77 (m, 2H, H-9,10), 5.55 (m, 1H, H-4′), 4.77 (br s, 2H, 2 × H-5′), 4.59, 4.80 and 4.98 (3d, 4H, CH_2 Bn), 4.40 (m, 1H, H-1), 4.26 (m, 2H, 2 × H-8), 3.97 (br t, 1H, *J* 9.5 Hz, H-6), 3.61 (d, 1H, *J* 8.8 Hz, H-4), 3.33 (dd, 1H, *J* 8.8 and 9.5 Hz, H-5); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.1 and 138.9 (C_q Bn), 132.6 (C-3′), 126.1–128.1 (C-4′,9,10 and CH_{arom}), 112.8 (C-3), 78.9, 80.8 and 81.2 (C-4,5,6), 75.1 and 75.9 (CH_2 Bn), 66.1 (C-8), 66.0 (C-1); MS (ESI): calc. for $C_{25}H_{26}O_5$ 406.2, found *m*/*z* 429.1 $(M + Na)^+$.

3-*O*-(4′,5′,6′,8′-Tetra-*O*-benzyl-1′,2′-dideoxy-α-D-*gluco*-oct-1′-eno-3′-ulopyranosyl)-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranoside (36). K-10 mediated glycosidation, as described in the general procedure, of **2** (0.39 g, 0.68 mmol) with 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose[22] (**35**, 0.76 g, 4.09 mmol) afforded **36** as a colourless syrup (0.23 g, 0.31 mmol, 45%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.18–7.35 (m, 20H, CH_{arom}), 6.21 (m, 1H, H-5), 5.95 (dd, 1H, *J* 11.0 and 17.5 Hz, H-2′), 5.93 (dd, 1H, *J* 2.2 and 12.4 Hz, H-6), 5.64 (dd, 1H, *J* 2.2 and 17.5 Hz, H-6), 5.38 (d, 1H, *J* 2.9 Hz, H-1), 5.31–5.39 (m, 1H, H-1), 5.17 (dd, 1H, *J* 1.5 and 10.2 Hz, H-1), 4.52–4.91 (m, 10H, H-3,4 and CH_2 Bn), 4.26 (d, 1H, *J* 2.9 Hz, H-2), 4.07 (t, 1H, *J* 9.5 Hz, H-5′), 3.94 (m, 1H, H-8′), 3.63–3.82 (m, 2H, H-7′,8′), 3.53 (t, 1H, *J* 9.5 Hz, H-6′), 3.30 (d, 1H, *J* 9.5 Hz, H-4′), 1.18 and 1.47 (2s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 137.9 and 138.5 (C_q Bn), 133.2 and 135.0 (C-2′,5), 127.1–128.4 (CH_{arom}), 119.5 and 119.7 (C-1′,6), 111.2 (C_q), 104.7 (C-1), 100.5 (C-3′), 73.5, 75.2, 75.4 and 75.6 (CH_2 Bn), 72.5, 78.4, 78.6, 82.3, 82.5, 83.6 and 85.1 (C-2,3,4,4′,5′,6′,7′), 69.1 (C-8′), 26.0 and 26.7 (CH_3); MS (ESI): calc. for $C_{45}H_{50}O_9$ 734.3, found *m*/*z* 757.4 $(M + Na)^+$.

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosylspiro-1′-[(3′*S*,4′*R*,5′*R*,7′*R*)-4′,5′-dihydroxy-4′,5′-*O*-isopropylidene-2′,6′-dioxa-bicyclo[3.4.0]non-8′-ene] (37). Obtained from **36** by RCM according to the general procedure (method B) as a colourless syrup (85 mg, 0.12 mmol, 64%); $[\alpha]_D$+64.4 (*c* 1 in $CHCl_3$); δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.12–7.31 (m, 20H, CH_{arom}), 6.18 (dd, 1H, *J* 5.1 and 10.2 Hz, H-9′), 6.08 (d, 1H, *J* 3.6 Hz, H-1), 5.78 (d, 1H, *J* 10.2 Hz, H-8′), 4.69 (br s, 2H, CH_2 Bn), 4.47, 4.53, 4.60, 4.81, 4.83 and 4.91 (6d, each 1H, CH_2 Bn), 4.40 (m, 1H, H-5′), 4.29 (d, 1H, *J* 3.0 Hz, H-4′), 4.05 (t, 1H, *J* 8.8 Hz, H-3), 3.61–3.88 (m, 4H, H-1,7 and 2 × H-8), 3.71 (t, 1H, *J* 8.8 Hz, H-4), 3.51 (d, 1H, *J* 8.8 Hz, H-2), 1.32 and 1.52 (2s, each 3H, CH_3); δ_C (50 MHz; $CDCl_3$; Me_4Si) 137.9, 138.1 and 138.7 (C_q Bn), 127.7–128.3 (CH_{arom}), 125.4 and 132.2 (C-8′,9′), 111.3 (C_q), 105.7 (C-3′), 95.5 (C-1′), 73.4, 74.7, 74.9 and 75.5 (CH_2 Bn), 69.5, 71.8, 73.7, 77.8, 82.6 and 84.2 (C-1′,2,3,4,4′,5,5′), 68.3 (C-6), 26.1 and 26.8 (CH_3); MS (ESI): calc. for $C_{43}H_{46}O_9$ 706.3, found *m*/*z* 729.5 $(M + Na)^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris-benzyloxy-2-benzyloxymethyl-1,7-dioxa-spiro[5.5]undec-8-ene (38). To a stirred solution of **8** (330 mg, 0.56 mmol) in anhydrous ethanol (30 mL) were added Wilkinson's catalyst (129 mg, 0.13 mmol) and DBU (2 drops) under a nitrogen atmosphere. The mixture was heated to 60 °C for 1 h after which TLC analysis (25% EtOAc–light petroleum ether) revealed completed conversion. The mixture was allowed to cool to room temperature and concentrated. Silica gel chromatography (15% EtOAc–light petroleum ether) of the residue yielded **38** as a colourless syrup (296 mg, 0.50 mmol, 90%); $[\alpha]_D$+8.4 (*c* 1 in $CHCl_3$); δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.16–7.26 (m, 20H, CH_{arom}), 6.25 (d, 1H, *J* 6.2 Hz, H-8), 4.50, 4.55, 4.57, 4.60, 4.68 4.86, 4.91 and 4.92 (8d, each 1H, CH_2 Bn), 4.79 (m, 1H, H-9), 4.16 (t, 1H, *J* 9.1 Hz, H-4), 4.11–4.21 (m, 1H, CH_2OBn), 3.62–3.79 (m, 3H, H-2,3 and CH_2OBn), 3.40 (d, 1H, *J* 9.9 Hz, H-5), 1.49–2.05 (m, 4H, 2 × H-10 and 2 × H-11); δ_C (50 MHz; $CDCl_3$; Me_4Si) δ 139.6 (C-8), 137.7, 138.2 and 138.6 (C_q Bn), 127.5–128.4 (CH_{arom}), 102.3 (C-9), 97.6 (C-6), 71.8, 78.3, 82.6 and 83.0 (C-2,3,4,5), 73.1, 74.8, 75.5 and 75.6 (CH_2 Bn), 68.4 (CH_2OBn), 26.8 (C-11), 16.0 (C-10); MS (ESI): calc. for $C_{38}H_{40}O_6$ 592.3, found *m*/*z* 615.3 $(M + Na)^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*,8*R*,9*S*)-8-Allyl-3,4,5-tris-benzyloxy-2-benzyloxymethyl-1,7-dioxa-spiro[5.5]-undecan-9-ol (39). To a chilled (0 °C) solution of spiroketal **38** (370 mg, 0.63 mmol) in anhydrous dichloromethane (3 mL) was added dropwise a freshly prepared solution of 3,3-dimethyldioxirane (9 mL, 0.09 M, 0.8 mmol) in acetone.[25] After stirring the mixture for 10 min, TLC analysis (20% EtOAc–light petroleum ether) showed complete consumption of the starting material. The mixture was concentrated, redissolved in anhydrous toluene (5 mL) and concentrated again. The crude epoxide was dissolved in THF (5 mL), cooled to 0 °C under argon atmosphere, after which a solution of allylmagnesium chloride (0.58 mL, 2 M, 1.16 mmol) was added. After stirring for 15 min., TLC analysis (33% EtOAc/light petroleum ether) showed a nearly completed reaction. The reaction was quenched by addition of sat. NH_4Cl and extracted with diethyl ether. The organic layer was washed with sat. NH_4Cl, dried and concentrated. Silica gel chromatography (16 to 40% EtOAc–light petroleum ether) yielded compound **39** as a colourless syrup (246 mg, 0.37 mmol, 61%); δ_C (50 MHz; $CDCl_3$; Me_4Si) 137.7, 138.1 and 138.5 (C_q Bn), 134.8 (CH allyl), 127.4–128.2 (CH_{arom}), 117.1 (CH_2 allyl), 98.3 (C-6), 73.2, 74.8, 75.3 and 75.7 (CH_2 Bn), 68.7 (CH_2OBn), 65.9, 71.1, 77.9, 78.5, 82.9 and 83.7 (C-2,3,4,5,8,9), 37.4 (CH_2 allyl), 25.0 (C-11), 21.8 (C-10); MS (ESI): calc. for $C_{41}H_{46}O_7$ 650.3, found *m*/*z* 673.3 $(M + Na)^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*,8*R*,9*S*)-8-Allyl-9-allyloxy-3,4,5-tris-benzyloxy-2-benzyloxymethyl-1,7-dioxa-spiro[5.5]undecane (40). To a solution of compound **39** (246 mg, 0.38 mmol) in anhydrous *N,N*-dimethylformamide (3 mL) were added allyl bromide (50 µl, 0.57 mmol) and sodium hydride (20 mg, 60% dispersion in oil, 0.49 mmol). After stirring for 16 h, TLC analysis (33% EtOAc–light petroleum ether) showed complete disappearance of **39**. The excess sodium hydride was destroyed by addition of methanol (5 mL). The mixture was partitioned between diethyl ether and brine. The organic phase was extracted with brine, dried and concentrated. Purification was effected by silica gel chromatography (20% EtOAc–light petroleum ether) to afford **40** as a colourless syrup (242 mg, 0.35 mmol, 93%); δ_C (50 MHz; $CDCl_3$; Me_4Si) 138.2 and 138.7 (C_q Bn), 135.1 (CH allyl), 127.3–128.2 (CH_{arom}), 116.1 and 116.9 (CH_2 allyl), 98.6 (C-6), 73.1, 74.7, 75.3 and 75.5 (CH_2 Bn), 70.9, 72.9, 75.4, 78.6, 82.9 and 84.0 (C-2,3,4,5,8,9), 69.1 (CH_2 allyl), 68.8 (CH_2OBn), 37.6 (CH_2 allyl), 25.5 (C-11), 19.4 (C-10); MS (ESI): calc. for $C_{44}H_{50}O_7$ 690.3, found *m*/*z* 713.3 $(M + Na)^+$.

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosylspiro-3′-[(1′*R*,6′*S*)-2′,7′-dioxa-bicyclo[4.5.0]undec-9′-ene] (42). To a solution of diene **40** (240 mg, 0.35 mmol) in anhydrous dichloromethane (5 mL) was added Grubbs' catalyst **41**[27] (0.1 mg, 0.18 µmol) under argon atmosphere and the mixture was stirred at 40 °C for 2 h. TLC analysis (33% EtOAc–light petroleum ether) revealed a completed conversion, after which the mixture was concentrated and purified by silica gel chromatography (20% EtOAc–light petroleum ether) to give a colourless syrup of **42** (185 mg, 0.28 mmol, 80%); δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.16–7.31 (m, 20H, CH_{arom}), 5.76–5.86 (m, 2H, H-9′,10′), 4.88 (br s, 2H, CH_2 Bn), 4.51, 4.54, 4.60, 4.67, 4.84 and 4.89 (6d, each 1H, CH_2 Bn), 4.14 (d, 1H, *J* 4.9 and 14.7 Hz, H-8′), 4.04 (t, 1H, *J* 9.2 Hz, H-3), 3.84–4.01 (m, 1H, H-8′), 3.57–3.76 (m, 5H, H-1,4,5 and 2 × H-6), 3.33 (d, 1H, *J* 9.5 Hz, H-2), 2.61–2.69 (m, 1H, H-11′), 2.11–2.33 (m, 3H, H-4′,5′,11′), 1.42–1.83 (m, 2H, H-4′,5′); δ_C (50 MHz; $CDCl_3$; Me_4Si) 137.9, 138.1, 138.2 and 138.6 (C_q Bn), 131.7 and 131.9 (C-9′,10′), 127.4–128.8 (CH_{arom}), 98.6 (C-1), 73.2, 74.9 and 75.4 (CH_2 Bn), 70.7, 73.4, 78.6, 81.0, 83.3 and 83.7 (C-1′,2,3,4,5,6′), 68.9 (C-6), 67.1 (C-8′), 34.3 (C-11′), 27.5 (C-4′), 24.8 (C-5′); MS (ESI): calc. for $C_{42}H_{46}O_7$ 662.3, found *m*/*z* 685.3 $(M + Na)^+$.

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