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Synthesis and Evaluation of Lipophilic Aza-C-glycosides as Inhibitors of Glucosylceramide Metabolism

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The structure–activity relationship of lipophilic aza-C-glycosides as inhibitors of the three enzymes of glucosylceramide metabolism is investigated. A library of β-aza-C-glycosides was synthesized with variations in *N*-alkylation and the linker length/type to the lipophilic moiety. A cross-metathesis reaction was used to prepare a second library of α-aza-C-glycosides with D-*gluco*, L-*ido* and D-*xylo* iminosugar cores possessing analogous linker variations. Evaluation of both libraries did not reveal a potent or selective inhibitor of glucosylceramide synthase. However, β-aza-C-glycoside **43** was found to be a selective inhibitor of β-glucosidase 2. The α-aza-C-glycosides – especially with a D-*xylo* core (e.g. **80**) – proved to be very potent and selective inhibitors of glucocerebrosidase.

Introduction

The first synthesis[1] of carbohydrate analogues with a nitrogen atom in the ring – so-called iminosugars or azasugars – and their concurrent discovery as natural products in microorganisms[2,3] were reported during the 1960s. The continuously increasing amount of research on iminosugars since then can mainly be attributed to the subsequent discovery of their ability to inhibit glycoprocessing enzymes[4–6] combined with major advances in the field of glycobiology.[7] Recently, attention has focused on their ability to stabilize certain deficient glycosidases, associated with lysosomal storage disorders, during folding and transport as so-called pharmacological chaperones.[8] However, a recurring problem in the development of iminosugars as inhibitors or chaperones of these enzymes is their lack of specificity. The countless complex carbohydrate structures and conjugates involved in human physiological processes are composed of a relatively limited selection of monosaccharide building blocks. Therefore, an iminosugar inhibitor that only mimics one monosaccharide subunit of the complex substrate of the target enzyme will often inhibit additional carbohydrate-processing enzymes that also create or cleave a glycosidic bond with this monosaccharide. A way to achieve selectivity for a specific enzyme is to add structural elements to the iminosugar that resemble the anomeric substituent/aglycon of the enzyme glycoside substrate or transition state. This should result in additional interactions with the aglycon binding site and as a consequence more selective binding. However, a true iminosugar mimic of the glycoside substrate would result in a labile N,O-acetal function, making it unsuitable as a potential drug or probe in biological research. Replacing the oxygen atom of the iminosugar's pseudo-anomeric centre for a methylene group results in a stable mimic of the target glycoside or transition state. This class of iminosugars is called the aza-C-glycosides. The first piperidine-based aza-C-glycoside to be discovered was α-homonojirimycin (**1**) that was synthesized in 1987[9] and later also discovered as a natural product[10] (Figure 1).

Since then many synthetic strategies have been developed for the synthesis of aza-C-glycosides.[8,11,12] Most of these can be roughly divided into two general categories depending on the disconnection(s) made in the retrosynthetic analysis. Disconnecting C1–N and C5–N results in approaches that use a final intramolecular cyclization to construct the aza-C-glycoside (Figure 1, **A**–**C**). A convenient method for cyclization that uses the ability of amines to form imines with carbonyl compounds is the reductive amination. Both a double-reductive amination of a C-1/C-5 diketone (**A**)[13,14] or a single-reductive amination of a C-1/

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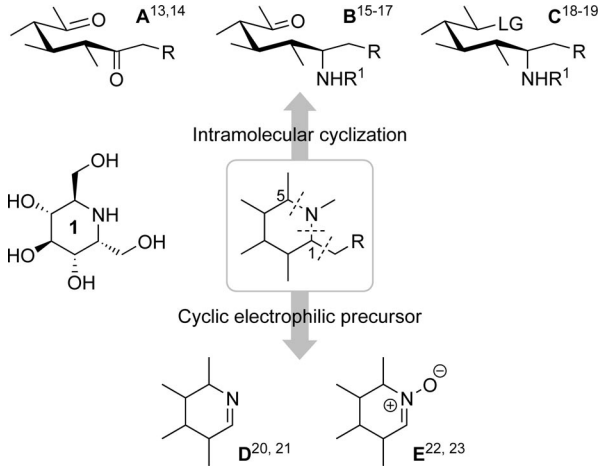


Figure 1. α-Homonojirimycin (**1**) and examples of strategies (**A**–**E**) for the synthesis of aza-C-glycosides.

C-5 amino ketone penultimate (**B**)[15–17] has proven to be a popular method for the preparation of aza-C-glycosides. Another method to achieve cyclization is to activate, with a suitable leaving group, the C-1 or C-5 position of an intermediate with an amine function on the opposing carbon centre (**C**).[18,19] Alternatively, a disconnection made at C-1–CH_2R results in approaches that use a cyclic electrophilic precursor (Figure 1, **D**–**E**). For example, in this category organometal additions[20] and Ugi multicomponent reactions[21] have been used on cyclic imines to produce aza-C-glycosides (**D**). Carbohydrate-derived cyclic nitrones have also been used. Aza-C-glycosides were constructed from these by 1,3-dipolar cycloadditions or nucleophilic additions (**E**).[22,23]

We recently reported three β-aza-C-glycoside derivatives (**3**–**5**) based on lipophilic iminosugar **2** (Figure 2). Iminosugar **2** is the lead compound in an ongoing study in which we aim to develop selective inhibitors of the enzymes involved in glucosylceramide metabolism.[24–28] Glucosylceramide is a β-D-glucoside of the lipid ceramide and belongs to the family of glycosphingolipids (GSLs) that are membrane components in eukaryotes and involved in many (patho)physiological processes.[29–31] The biosynthesis of glucosylceramide occurs on the cytosolic leaflet of the Golgi apparatus by the membrane-bound enzyme glucosylceramide synthase (GCS). Catabolism of glucosylceramide occurs in the lysosomes by glucocerebrosidase (GBA1). A second catabolic pathway for glucosylceramide, the membrane-bound β-glucosidase 2 (GBA2), is located at or close to the cell surface.[32,33] Selective inhibitors of these enzymes can be used to probe the diverse functions of GSLs, but also have potential as therapeutics for diseases associated with abnormal GSL metabolism such as lysosomal sphingolipidoses and type-2 diabetes.[26,31,34] Lead compound **2** is a potent inhibitor of GCS (IC_{50} = 150 nM), GBA1 (IC_{50} = 200 nM) and GBA2 (IC_{50} = 1 nM). It also inhibits several intestinal glycosidases (IC_{50} = 0.4–35 μM). The β-aza-C-glycosides (**3**–**5**) are part of a series of derivatives of **2** that vary in the position of the hydrophobic adamant-1-ylmethoxy moiety on the 1-deoxynojirimycin ring and the functionalization of the endocyclic nitrogen atom. The main message from that library of compounds was that changing the position of the hydrophobic moiety in **2** abolished all GCS inhibitory activity except for β-aza-C-glucoside **3** (GCS: IC_{50} = 9 μM).[28] Additionally, the *N*-butylated (**5**) derivative of **3**, but not its *N*-methylated (**4**) counterpart, also inhibits GCS with modest activity. Expanding on these findings, the here reported study consisted of the synthesis and evaluation of two libraries of lipophilic aza-C-glycosides based on compound **3**. This enabled the further investigation of the structure–activity relationship of this class of compounds as inhibitors of GCS, GBA1 and GBA2.

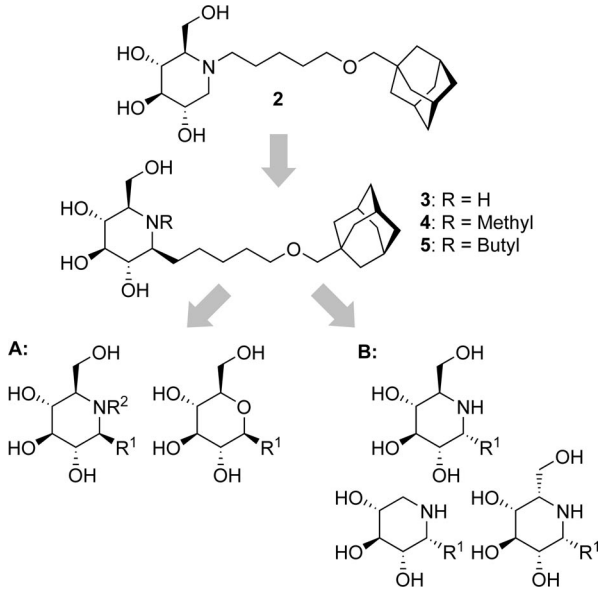
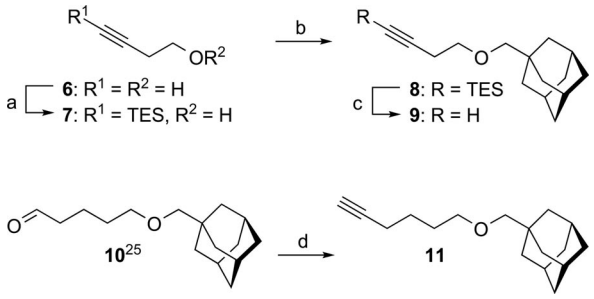


Figure 2. Lead compound **2**, β-aza-C-glycosides **3**–**5** and the here reported libraries **A**/**B**. R^1 = adamant-1-ylmethoxy–spacer; R^2 = H or *N*-alkylated.

The first library (**A**; Figure 2) consists of derivatives of **3** that retain the pseudo β-orientation [(*S*)-C-1] of the hydrophobic moiety, but vary in the length and the saturation of the pentyl spacer. The influence of the nitrogen atom on inhibition is also further investigated with C-glycoside derivatives and additional *N*-alkylated derivatives. For the second library (**B**) the C-1 stereochemistry was altered to pseudo-α [(*R*)-C-1)]. For this library the iminosugar core was varied to also encompass L-*ido* and D-*xylo* substitution patterns. This variation is based on our recently reported finding that epimerization of the C-5 position in **2** is a suitable strategy to obtain more selective inhibitors of GCS.[26] Additionally, analogous spacer variations to library **A** were prepared for all three α-aza-C-glycoside cores. Both libraries were evaluated in an enzyme assay for inhibitory activity against GCS, GBA1, GBA2. The library entries were also evaluated as inhibitors of the three intestinal glycosidases (sucrase, lactase and maltase) that are not associated with glucosylceramide metabolism, but which are known to be inhibited by **2**.

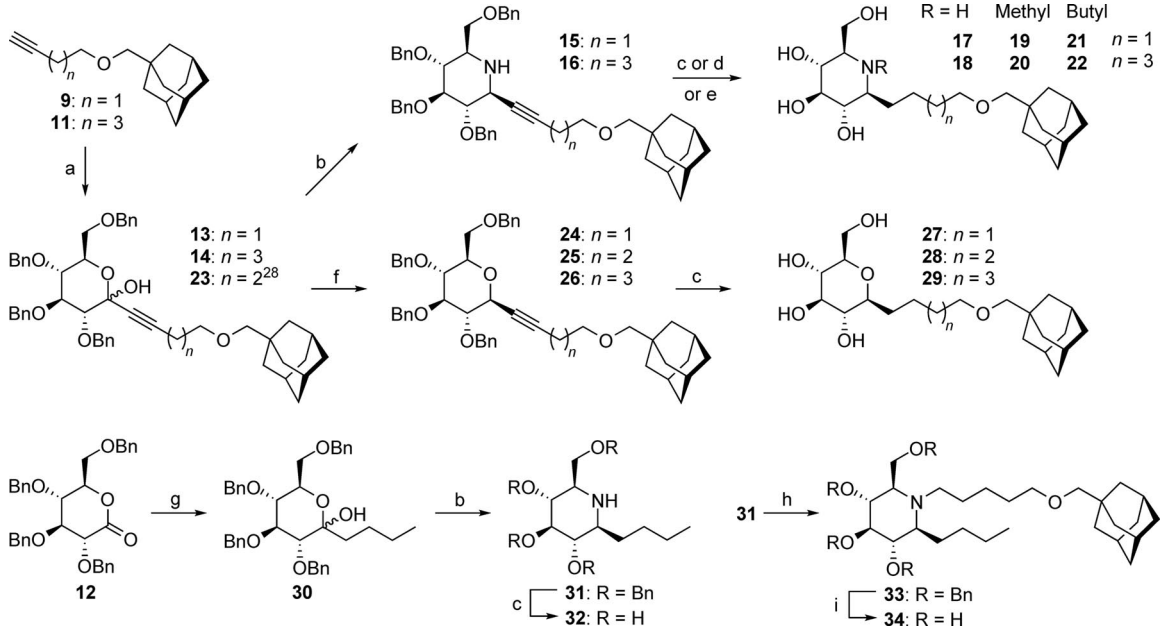
Results and Discussion

The entries of the first library of β-(aza)-C-glycosides with D-*gluco* stereochemistry could be synthesized by the route described previously[28] for **3**–**5** or via synthetic intermediates from this route. Alkyne **9** was synthesized from but-3-yn-1-ol (**6**) by the previously reported three-step protocol (Scheme 1). The synthesis of alkyne **11** was also attempted by this route but this proved low-yielding. The intermediate triflate proved susceptible to side reactions[35] and only produced approximately 30% of the desired triethylsilyl (TES) protected intermediate of **11** upon reaction with adamantylmethanol. An alternative higher yielding route for the synthesis of **11** was found in treating known aldehyde **10**[25] with the Bestmann–Ohira reagent[36,37] to produce **11** in 87% yield. Alkynes **9** and **11** were deprotonated to the acetylenic anion and condensed with 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone (**12**) to yield **13** and **14** (Scheme 2).[38] Next, ketoses **13** and **14** were transformed into **15** and **16** by a tandem reduction/Swern oxidation/double reductive amination reaction sequence.[28]

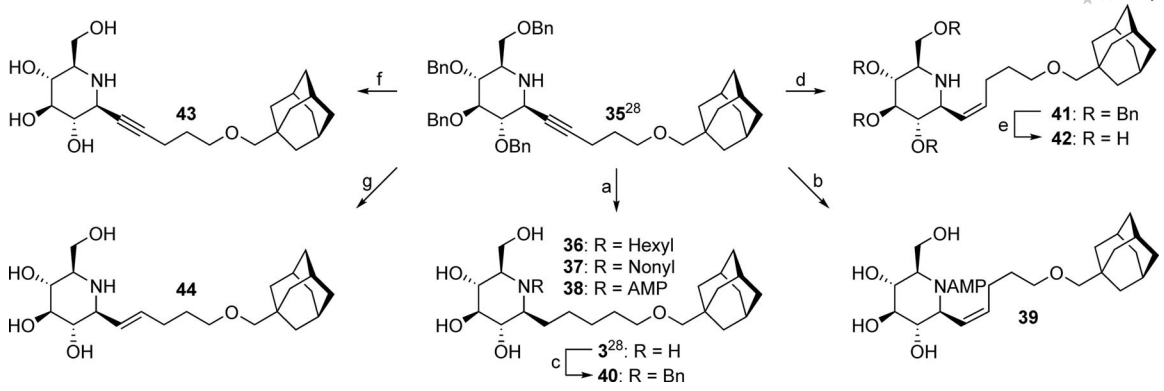


Scheme 1. Reagents and conditions: (a) i: BuLi, THF, –68 °C, 1 h; ii: TESCl, –68 °C to room temp., 20 h; iii: 2 M HCl, 48 h, 71%. (b) i: Tf_2O, Et_3N, DCM, –40 °C, 1 h; ii: adamantylmethanol, K_2CO_3, DCM, reflux, 3 d, 84%. (c) 4 equiv. NaOMe, THF/MeOH (2:1), 90 °C, 20 h, 87%. (d) Bestmann–Ohira reagent, K_2CO_3, MeOH, 0 °C → room temp., 16 h, 87%.

The double-reductive amination solely yielded the β-aza-C-D-glucoside stereoisomer in both cases. This indicates that the intramolecular cyclization probably occurs exclusively by axial hydride addition onto cyclic imines (C-1=N/C-5=N) that are in equilibrium with a bis(hemiaminal) intermediate.[13,14,39] Compounds **15** and **16** were deprotected by Pd-catalyzed hydrogenolysis to produce β-aza-C-glycosides **17** and **18**. Reductive amination of **15** and **16** with formaldehyde or butyraldehyde and hydrogenolysis of the crude intermediate produced the *N*-methylated (**19** and **20**) and *N*-butylated (**21** and **22**) derivatives, which together with **17** and **18** completed the butyl/hexyl spacer-length variations based on **3**–**5** (i.e. pentyl spacer length). Reductive elimination of ketoses **13**, **14** and previously reported **23**[28] with boron trifluoride–diethyl ether/triethylsilane and subsequent Pd/C-catalyzed hydrogenolysis of the intermediates **24**, **25** and **26** produced the β-C-glycosides **27**, **28** and **29**. The synthesis of two β-butyl-aza-C-glycoside derivatives started with the addition of butyllithium to lactone **12** and subsequent transformation of ketose **30** into



Scheme 2. Reagents and conditions: (a) i: BuLi, THF, –50 °C, 1 h; ii: **12**, –50 °C, 2 h, **13**: 60%, **14**: 86%. (b) i: $NaBH_4$, MeOH/DCM (5:1), 2 h; ii: DMSO, $(COCl)_2$, DCM, –75 °C, 2 h; iii: Et_3N, –75 °C → room temp., 0.5 h; iv: $NaBH_3CN$, NH_4HCO_2, 3 Å molecular sieves, MeOH/DCM (5:1), 0 °C → room temp., 20 h, **15**: 53%; **16**: 59%; **31**: 67% 3 steps. (c) Pd/C, H_2, EtOH, HCl, 20 h, **17**: 90%, **18**: 75%, **27**: 81%, **28**: 89%, **29**: 90%, **32**: 97%. (d) i: Pd/C (Degussa), H_2, formaldehyde, *n*-propanol, 1 h; ii: Pd/C, H_2, EtOH, HCl, 20 h, **19**: 89%, **20**: 69%. (e) i: butyraldehyde, $NaBH_3CN$, EtOH/AcOH (3:1), 20 h; ii: Pd/C, H_2 4 bar, EtOH, HCl, 20 h, **21**: 60%, **22**: 66%. (f) $BF_3{\cdot}Et_2O$, Et_3SiH, CH_3CN, –30 °C, 1.5 h, **24**: 89%, **25**: 79%, **26**: 60%. (g) BuLi, THF, –50 °C, 2 h, 72%. (h) **10**, $NaBH_3CN$, Na_2SO_4, CH_3CN/MeOH (5:1), 75 °C, 18 h, 79%. (i) Pd/C, H_2 4 bar, EtOH, HCl, 20 h, 85%.

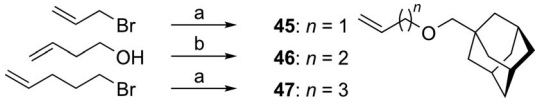


Scheme 3. Reagents and conditions: (a) i: aldehyde, $NaBH_3CN$, EtOH/AcOH (3:1), 20 h; ii: Pd/C, H_2 4 bar, EtOH, HCl, 20 h, **36**: 71%, **37**: 63%, **38**: 79%. (b) i: **10**, $NaBH_3CN$, EtOH/AcOH (3:1), 20 h; ii: Pd/C, H_2, EtOH, HCl, 20 h, 41%. (c) BnBr, K_2CO_3, DMF, 85 °C, 18 h, 71%. (d) Lindlar cat., H_2, EtOAc, 18 h, 74%. (e) Na, NH_3, –60 °C, 1 h, 67%. (f) Na, NH_3, –60 °C, 0.5 h, 24%. (g) Li, NH_3, –60 °C, 3 h, 70%. AMP = 5-(adamant-1-ylmethoxy)pentyl.

iminosugar **31** (Scheme 2). Straight deprotection of **31** produced library entry **32**. Reductive amination of **31** with aldehyde **10** and deprotection gave **34**, which is an analogue of **5** with the C-1/N substituents inverted.

Manipulation of previously reported **35**[28] provided the final two classes of derivatives for the first library (Scheme 3). Reductive amination of **35** with hexanal, nonanal or aldehyde **10** and subsequent deprotection gave **36**, **37** and **38**, respectively. During the synthesis of **38**, palladium-catalyzed hydrogenolysis of the alkyne function in the crude reductive amination product at atmospheric H_2 pressure proceeded sluggishly and gave a separable approximately 1:1 mixture of **38** and (*Z*)-alkene **39**. Alkylation of **3** with benzyl bromide under the agency of potassium carbonate at 85 °C in DMF produced the final *N*-alkylated derivative **40**. Hydrogenolysis of **35** in the presence of Lindlar's catalyst and subsequent Birch reduction of intermediate **41** produced (*Z*)-alkene **42**. A Birch reduction of **35** with sodium for 30 min achieved complete debenzylation but only minor reduction of the alkyne function to yield alkyne derivative **43**. A Birch reduction of **35** with lithium for 3 h was able to reduce the alkyne function to give (*E*)-alkene derivative **44**.

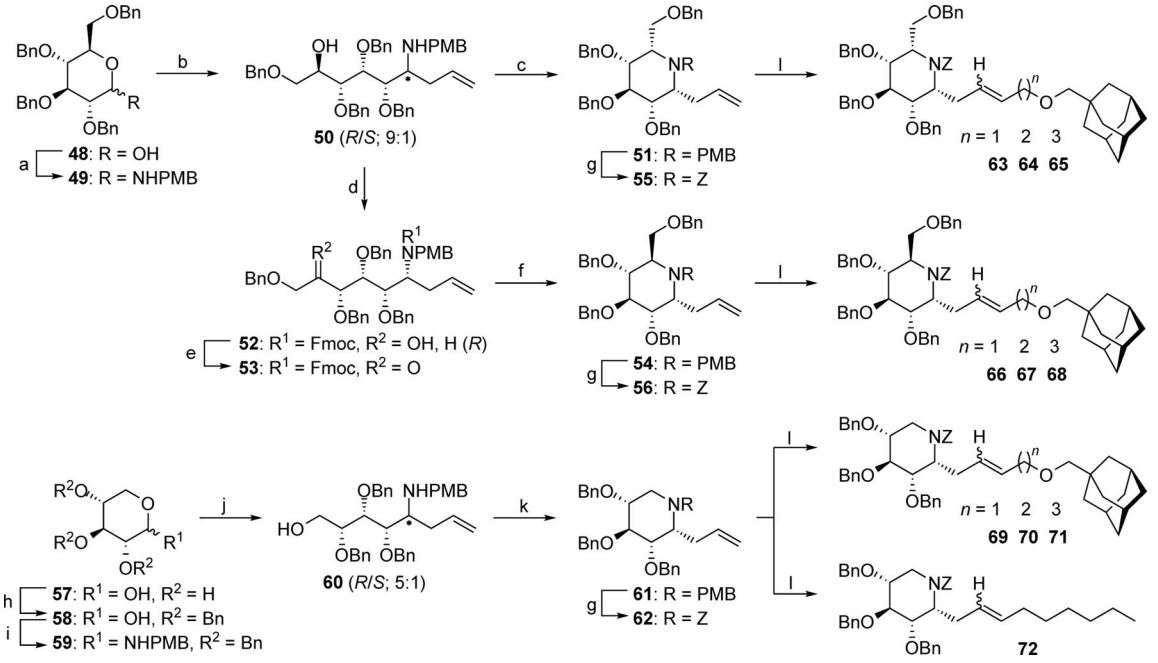
For the preparation of the second library, the adamant-1-ylmethoxy-functionalized α-aza-C-glycosides, a cross-metathesis reaction approach was chosen.[40,41] In this way the three distinct spacer lengths can be prepared by using three appropriate adamant-1-ylmethoxy-functionalized terminal alkenes in combination with the same iminosugar cross-metathesis partner. Additionally, unsaturated spacer derivatives can be generated by a Birch reduction of the cross-metathesis products. Positioning of this alkene function at the same site as in library one entries **42** and **44** is not possible, because Compain and Martin have previously reported that α-vinyl-aza-C-glycosides are not suitable for cross-metathesis.[41] Therefore D-*gluco*, L-*ido* and D-*xylo* α-allyl-aza-C-glycosides were selected as cross-metathesis partner (Scheme 5).



Scheme 4. Reagents and conditions: (a) adamantylmethanol, NaH, DMF, 16 h, **45**: 80%, **47**: 53%. (b) i: Tf_2O, Et_3N, DCM, –40 °C → 0 °C, 1 h; ii: adamantylmethanol, K_2CO_3, DCM, 50 °C, 20 h, 99%.

The adamant-1-ylmethoxy-functionalized alkenes **45** and **47** could be prepared by a Williamson etherification of adamantylmethanol with allyl bromide and 5-bromopent-4-ene (Scheme 4). Alkene **46** could be prepared by substitution of the triflate of 3-buten-1-ol with adamantylmethanol. The synthesis of the α-allyl-aza-C-glycosides started with a Grignard reaction of allylmagnesium bromide on the anomeric *p*-methoxybenzyl aminoglycoside **49**, which in turn was prepared from commercially available **48** (Scheme 5). The Grignard reaction produced (*R*)-**50**, which can be rationalized by taking into account an O-2/NPMB-chelated Felkin–Anh-type intermediate (see ref.[42]).[18,42] Selective mesylation of the 5-OH group in **50** and subsequent S_N2-like cyclization with a Walden inversion at C-5 produced L-*ido* compound **51**. Intermediate **50** could be transformed into D-*gluco* α-allyl-aza-C-glycoside **54** by a procedure adapted from Nicotra and co-workers. This procedure consisted of Fmoc protection of **50** to **52**, oxidation of the 5-hydroxy group in **52** to **53** and finally removal of the Fmoc group and cyclization to **54** by a reductive amination.[15] Compain and Martin have previously shown that the cross-metathesis reaction is incompatible with certain endocyclic tertiary amines similar to **51** and **54**.[41] The *p*-methoxybenzylamines in **51**, **54** were therefore oxidatively cleaved with ammonium cerium(IV) nitrate and protected as a benzyloxy carbamate (**55** and **66**) to make them suitable for cross-metathesis. Starting from the D-xylose (**57**) derived **58**, the D-*xylo* α-allyl-aza-C-glycoside **62** was synthesized by a similar sequence of reactions as described for **55**. Except now amino alcohol **60**, obtained from a stereoselective[43] Grignard reaction on **59**, was cyclized to **61** by an intramolecular Mitsunobu reaction.[44,45]

Initial attempts at cross-metathesis between α-allyl-aza-C-glycosides **55**, **56**, **62** and adamant-1-ylmethoxy alkenes **45**–



Scheme 5. Reagents and conditions: (a) NH_2PMB, *p*TsOH, Na_2SO_4, toluene, reflux, 18 h, used crude. (b) AllylMgBr, Et_2O, 0 °C → room temp., 16 h, 93%. (c) MsCl, pyridine, 0 °C → room temp., 4 h; ii: 90 °C, 16 h, 78%. (d) FmocCl, aq. $NaHCO_3$, DCM, 16 h, 91%. (e) Dess–Martin periodinane, DCM, 0 °C, 6 h, 98%. (f) i: piperidine, DMF, 0 °C, 0.5 h; ii: $NaCNBH_3$, AcOH, Na_2SO_4, MeOH, –35 °C → –20 °C, 16 h, 81%. (g) i: CAN, THF/H_2O (5:1), 0 °C, 3 h; ii: ZCl, aq. $NaHCO_3$, dioxane, 20 h, **55**: 75%, **56**: 65%, **62**: 87%. (h) i: BnBr, NaH, DMF, 0 °C → room temp., 20 h; ii: 1 M HCl/AcOH (1:2.2), 105 °C, 4 h, 55%. (i) NH_2PMB, CSA, Na_2SO_4, toluene, reflux, 2.5 h, used crude. (j) AllylMgBr, THF, 0 °C → room temp., 16 h, 97%. (k) PPh_3, DEAD, DCM, 20 h, 88%. (l) **45**, **46**, **47** or non-1-ene, 25 mol-% Grubbs' 1st generation catalyst, DCM, 45 °C, 24 h, 65–88%.

47 by using Grubbs' generation 2 catalyst showed little conversion of the aza-C-glycoside metathesis partners. Cross-metathesis of **55**, **56** and **62** with a threefold excess of **45**, **46** and **47** under the agency of 25 mol-% of Grubbs' generation 1 catalyst proved more productive. By using these conditions, the nine penultimates (**63**–**71**) were obtained in moderate to good yields (65–88%) as (*E*)/(*Z*) mixtures varying from 2:1 to 5:1 (Scheme 5). As a reference compound in the enzyme assay the potent GBA1 inhibitor **82** (Table 1), reported by Compain and co-workers,[46] was synthesized from **62** by cross-metathesis with oct-1-ene to produce **72**. Deprotection of all the cross-metathesis products by Pd/C-catalyzed hydrogenation at 4 bar gave library entries **73**–**82** (for structures see Table 1). The final entries for the second library were made by a Birch reduction of protected cross-metathesis products **64**, **67**, **70** and **72** to provide double-bond-containing α-aza-C-glycosides **83**–**86**. In the case of **86** this solely provided the (*E*) isomer, but for **83**, **84** and **85** it gave an inseparable mixture of (*E*)/(*Z*) isomers. These mixtures were tested as such in the enzyme assay.[47,48]

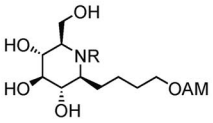
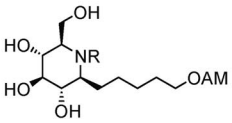
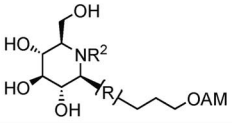
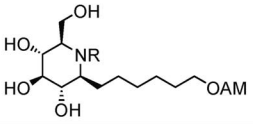
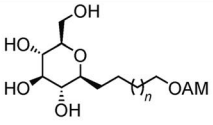
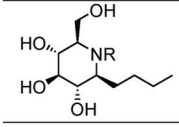
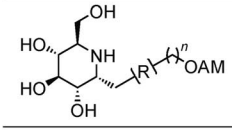
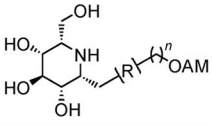
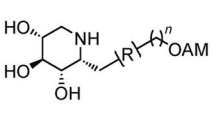
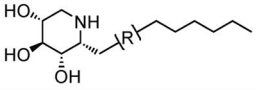
Biological Evaluation

The inhibitory potency and selectivity of the two libraries of lipophilic aza-C-glycosides A (**17**–**22**; **27**–**29**; **32**, **34**; **36**–**40**; **42**–**44**) and B (**73**–**86**) were assessed by evaluating the compounds in assays for the three enzymes involved in glucosylceramide metabolism; glucosylceramide synthase (GCS), glucocerebrosidase (GBA1) and β-glucosidase 2 (GBA2). To further establish the selectivity profile of the library entries they were also tested in inhibition assays for the intestinal glycosidases sucrase, lactase and maltase. As an unwanted side-effect most 1-deoxynojirymycin-based inhibitors of glucosylceramide metabolism also inhibit these glycosidases.

In our previous study[28] the hydrophobic moiety of lead compound **2** was translocated to produce β-aza-C-glycoside **3**. When comparing the structures of **2** and **3** this translocation lengthens the carbon chain connecting the endocyclic nitrogen atom and the adamant-1-ylmethoxy group from five to six atoms. The influence of this change on the SAR could be assessed with derivatives **17** and **18**. The assay results for the first library show that neither shortening (**17**) nor lengthening (**18**) this carbon chain by one carbon atom improves inhibition of GCS, but instead abolishes it (Table 1). Evidently, the carbon chain length of **3** is already optimal for GCS inhibition. Altering the saturation of the pentyl spacer of **3** into the (*Z*)-alkene **42**, alkyne **43** or (*E*)-alkene **44** derivatives also prevented GCS inhibition. When compared to **3**, **42** is a more selective inhibitor of GBA1, and both **43** and **44** are more selective for GBA2.

The β-C-glycoside derivatives **27**, **28** and **29** did not inhibit any of the tested enzymes to a significant extent. When combined with the fact[24] that derivatives of **2** with an endocyclic amide are also inactive as inhibitors of glucosylceramide metabolism this strongly suggests that a basic nitrogen function is essential for inhibition. The previously reported observation, that GCS is inhibited by the *N*-butyl-

Table 1. Enzyme inhibition assay results for α- and β-(aza)-C-glycosides (apparent IC_{50} values in μM).[a]

Compound		R (R^2) =	*n* =	GCS	GBA1	GBA2	Sucrase	Lactase	Maltase
	**17**:	H		> 10	5	0.2	260	180	500
	19:	Methyl		> 10	50	0.3	1000	1000	> 1000
	20:	Butyl		> 10	100	25	> 1000	> 1000	> 1000
	**3**:	H		9	3	0.04	> 100	> 100	> 100
	4:	Methyl		> 100	25	0.6	> 100	> 100	> 100
	5:	Butyl		25	40	10	> 100	> 100	> 100
	36:	Hexyl		> 10	10	1	1000	350	>1000
	37:	Nonyl		> 10	35	1	180	450	500
	38:	AMP		> 10	4	1	180	450	500
	40:	Benzyl		> 10	12	> 1000	> 1000	1000	> 1000
	**42**:	*Z*-C=C (H)		> 10	0.4	4	180	35	500
	43:	C≡C (H)		> 10	20	0.075	100	180	1000
	44:	*E*-C=C (H)		> 10	3	0.150	150	75	1000
	39:	*Z*-C=C (AMP)		> 10	10	5	600	500	> 1000
	**18**:	H		> 10	1	1	350	500	700
	21:	Methyl		> 10	7	1	160	> 1000	1000
	22:	Butyl		> 10	2	2	300	> 1000	> 1000
	**27**:		1	> 10	> 1000	> 1000	> 1000	> 1000	> 1000
	28:		2	> 10	> 1000	> 1000	> 1000	> 1000	> 1000
	29:		3	> 10	240	> 1000	> 1000	> 1000	> 1000
	**32**:	H		> 10	350	100	200	550	> 1000
	34:	AMP		> 10	130	40	> 1000	> 1000	> 1000
	**76**:	C–C	1	> 10	0.35	< 0.3	8	12	18
	77:	C–C	2	> 10	0.07	< 0.3	8	7	20
	84:	*E*/*Z*-C=C	2	> 10	0.25	0.020	2	18	3
	78:	C–C	3	> 10	0.07	< 0.3	10	85	37
	**73**:	C–C	1	> 10	2	8	> 1000	30	> 1000
	74:	C–C	2	> 10	5.5	100	> 1000	3	> 1000
	83:	*E*/*Z*-C=C	2	> 10	3	10	> 1000	18	> 1000
	75:	C–C	3	> 10	6	100	> 1000	40	> 1000
	**79**:	C–C	1	> 10	0.002	100	> 1000	3	> 1000
	80:	C–C	2	> 10	0.001	10	> 1000	20	> 1000
	85:	*E*/*Z*-C=C	2	> 10	0.001	20	> 1000	3	> 1000
	81:	C–C	3	> 10	0.002	90	> 1000	15	> 1000
	**82**:	C–C		> 10	0.001	250	> 1000	5	> 1000
	86:	*E*-C=C		> 10	0.002	> 1000	> 1000	10	> 1000

[a] AM = adamant-1-ylmethyl; AMP = 5-(adamant-1-ylmethoxy)pentyl.

ated **5** and not *N*-methylated **4**, is not reproduced for the lengthened or shortened *N*-alkylated derivatives **19**, **20** and **21**, **22**. Compound **19** is a relatively selective inhibitor of GBA2. Also the synthesized derivatives of **3** with alternate/lengthened *N*-alkyl moieties **36**–**40**, all lost the ability to inhibit GCS and showed no improvement of GBA1 or GBA2 inhibition. These findings indicate that the secondary endocyclic nitrogen atom of **3** plays an important part in the ability of **3** to inhibit GCS, GBA1 and GBA2. The only derivative from the first library that still very modestly inhibits GCS is **34** (15% at 10 μM) – the C-1/N-substituent-inverted derivative of **5**. The related entry, **32**, did not significantly inhibit any of the enzymes in the assay. Compound **32** is a β-aza-C-glycoside derivative of the known clinically used GCS inhibitor *N*-butyl-1-deoxynojirimycin (GCS: IC_{50} = 50 μM in this assay). This reconfirms the observation

from our previous study[28] that relocating the hydrophobic moiety from the nitrogen atom to C-1 does not lead to more potent GCS inhibitors.

Almost all the entries of the second library of lipophilic α-aza-C-glycosides showed very modest inhibition of GCS (≤20% at 10 μM) with none being as potent as **3** (Table 1). These results corroborate an earlier study by Boucheron and co-workers that showed that *N*-alkylated α-aza-C-glycosides are poor inhibitors of GCS.[49] The three different iminosugar cores did, however, have a distinct effect on GBA2 inhibition. The D-*gluco* derivatives (**76**–**78**, **84**) in general were >25-fold more potent GBA2 inhibitors than the L-*ido* (**73**–**75**, **83**) or D-*xylo* (**79**–**81**, **82**, **85**, **86**) derivatives. For GBA1 inhibition the effect of the iminosugar core was even more pronounced. The D-*xylo* α-aza-C-glycosides were all 1–2 nM inhibitors of GBA1 as opposed to the L-*ido* derivatives that were 2–6 μM inhibitors of the same enzyme. D-*xylo* analogue **85** is an (*E*)/(*Z*) mixture, and these isomers should be tested separately to fully elucidate their relative contributions to GBA1 inhibition. In general, the unsaturated pentyl spacer derivatives (**83**, **84** and **85**) did not show a significantly different inhibition profile for the tested enzymes compared to their saturated counterparts (**74**, **77** and **80**). However, introduction of an (*E*)-alkene into the known[46] potent GBA1 inhibitor **82** to give **86** does reduce inhibition of GCS and GBA2 to make it more selective.

Conclusions

The syntheses and biological evaluation of two libraries of lipophilic aza-C-glycosides is reported. The structures of the library entries are based on the previously reported β-aza-C-glycosides **3**.[28] The aim was to investigate the structure–activity relationship of this class of iminosugars as inhibitors of three enzymes, GCS, GBA1 and GBA2, involved in glucosylceramide metabolism.

The first library consisted of β-aza-C-glycosides and showed that for GCS inhibition an aliphatic pentyl-spacer length between C-1 and the adamant-1-ylmethoxy group combined with a secondary endocyclic nitrogen atom is optimal in this library. β-C-Glycoside derivatives showed the importance of a basic endocyclic nitrogen atom for inhibition of the here evaluated glycosidases and the glycosyltransferase GCS. From this first library the alkyne-containing **43** was found to be a potent and selective inhibitor of GBA2 and the (*Z*)-alkene-containing **42** a selective inhibitor of GBA1.

The second library of α-aza-C-glycosides did not contain a potent inhibitor of GCS, which indicates that a pseudo-β orientation of the hydrophobic moiety is necessary for potent inhibition of GCS. The type of iminosugar core in the α-aza-C-glycosides proved to exert a pronounced influence on inhibition of GBA1 and GBA2. The D-*gluco* iminosugar core proved most suitable for GBA2 inhibition, and the D-*xylo* core is optimal for GBA1 inhibition. All D-*xylo* analogues (**79**–**81**, **82**, **85**, **86**) were very potent and selective GBA1 inhibitors. Iminosugar **82** has already been reported by Compain, Martin and co-workers. Their study showed that **82** holds potential as a pharmacological chaperone for improving the activity of a deficient variant of GBA1 in N370S fibroblasts from patients with the lysosomal storage disorder, Gaucher disease.[46] Therefore, it might prove interesting to also evaluate the novel derivatives (**79**–**81**, **85**, **86**) presented here to this end.

Experimental Section

General Methods: All solvents and reagents were obtained commercially and used as received unless stated otherwise. Reactions were executed at ambient temperatures unless stated otherwise. All moisture-sensitive reactions were performed under argon. Residual water was removed from starting compounds by repeated coevaporation. All solvents were removed by evaporation under reduced pressure. Reaction grade acetonitrile, dimethyl sulfoxide, 2-propanol and methanol were stored over 3 Å molecular sieves. Other reaction grade solvents were stored over 4 Å molecular sieves. THF was distilled prior to use from $LiAlH_4$. Ethanol was purged of acetaldehyde contamination by distillation from zinc/KOH. DCM was distilled prior to use from P_2O_5. R_f values were determined from TLC analysis by using DC-Fertigfolien (Schleicher & Schuell, F1500, LS254) with detection by spraying with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$ (10 g/L) in 10% sulfuric acid or a solution of phosphomolybdic acid hydrate (7.5 wt.-% in ethanol) followed by charring at ca. 150 °C. Visualization of all deprotected iminosugar compounds during TLC analysis was accomplished by exposure to iodine vapour. Column chromatography was performed on silica gel (40–63 μm). Iminosugars (**43**, **73**–**86**) were purified with an automated HPLC system fitted with a semi-preperative C_{18} column (21 mm diameter × 150 mm length, 5 μm particle size, 25 mL/min). Isocratic or gradient elution was performed with eluent A: 0.1% aq. TFA and eluent B: CH_3CN. Iminosugar samples were dissolved in a mixture of 0.1% aq. TFA/*t*BuOH/CH_3CN (3:1:1, v/v/v, 2 mL) with optional MeOH for full solvation of the compound. The solution was filtered through a 5 μm filter and injected onto the column in 500 μL portions for preparative runs. Compound detection was carried out by a charged aerosol detector (Esa Corona, sensitivity setting: 100 pA). Appropriate fractions were collected, concentrated, coevaporated with water (2×) and lyophilized. ^1H and ^{13}C APT NMR spectra were recorded with a Bruker DMX 600 (600/150 MHz), Bruker DMX 500 (500/125 MHz), Bruker AV 400 (400/100 MHz), or Bruker AC 200 (200/50 MHz) spectrometer in $CDCl_3$ or MeOD. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard (^1H NMR in $CDCl_3$) or the signal of the deuterated solvent. Coupling constants (J) are given in Hz. Where indicated, NMR peak assignments were made by using COSY and HSQC experiments. All presented ^{13}C APT spectra are proton-decoupled. High-resolution mass spectra were recorded by direct injection (2 μL of a 2 μM solution in water/acetonitrile; 50:50; v/v and 0.1% formic acid) with a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electrospray ion source in positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 250 °C) with resolution R = 60000 at m/z = 400 (range m/z = 150–2000) and dioctyl phthalate (m/z = 391.28428) as a "lock mass". Optical rotations were measured with a Propol automatic polarimeter (sodium D-line, λ = 589 nm). ATR-

IR spectra were recorded with a Shimadzu FTIR-8300 fitted with a single-bounce Durasample IR diamond crystal ATR-element and are reported in cm^{-1}.

Enzyme Assays: The enzyme assays used for determining the inhibition of activity of glucosylceramide synthase (GCS), glucocerebrosidase (GBA1), β-glucosidase 2 (GBA2), sucrase, lactase and maltase were carried out as described previously.[28]

General Procedure A. Addition of Acetylenic Anions of 9 and 11 to Gluconolactone (12): A dry solution of the acetylene in THF (0.1 M) was cooled to –50 °C, and BuLi (1.2 equiv., 1.6 M in toluene) was added slowly to the solution. After stirring at –50 °C for 1 h, a dry solution of **12**[38] (2 equiv.) in THF (0.33 M) was slowly added, and the reaction mixture was stirred at –50 °C for 2 h. The reaction mixture was quenched (satd. aq. NH_4Cl), warmed to room temp. and poured into satd. aq. NH_4Cl. The aqueous layer was extracted with Et_2O (3×), and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography to provide the ketose product.

General Procedure B. Transformation of Ketose 13, 14 and 23 into β-C-Glycosides by Reductive Elimination: Triethylsilane (5 equiv.) and $BF_3{\cdot}O(Et)_2$ (6 equiv.) were successively added to a cooled (–30 °C) solution of the ketose in anhydrous acetonitrile (0.1 M). After stirring at –30 °C for 1.5 h, TLC analysis showed complete disappearance of the starting material. The reaction mixture was quenched by addition of aq. Na_2CO_3 (6× reaction volume, 10 wt.-%) and subsequently extracted with Et_2O (3×). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography to provide the β-C-glycoside.

General Procedure C. Transformation of Ketose 13 and 14 into β-Aza-C-glycosides: Reduction of Ketal: A dry solution of the ketose in MeOH/DCM (0.1 M, 5:1, v/v) was cooled to 0 °C and $NaBH_4$ (5 equiv.) was added. After stirring at 0 °C for 2 h, TLC analysis indicated full conversion to a slower running product. The reaction was quenched by addition of acetone and additional stirring (15 min). The reaction mixture was concentrated, transferred into satd. aq. NH_4Cl and extracted with EtOAc (3×). The combined organic phases were dried ($MgSO_4$) and concentrated to provide the glucitol derivative, which was used without further purification in the Swern oxidation [R_f(diol) ≈ 0.4 in EtOAc/toluene; 1:3].

Swern Oxidation of Diol: A solution of oxalyl chloride (4 equiv.) in DCM (1 M) was cooled to –78 °C. After dropwise addition of a solution of DMSO (5 equiv.) in DCM (2 M) over 10 min, the reaction mixture was stirred for 40 min, while being kept below –70 °C. Next, a dry solution of the glucitol intermediate in DCM (0.5 M) was added dropwise to the reaction mixture over a 15 min period, while keeping the reaction mixture below –70 °C. After stirring the reaction mixture below –65 °C for 2 h, Et_3N (12 equiv.) was added dropwise over a 10 min period, while keeping the reaction mixture below –65 °C. After addition, the reaction mixture was warmed to –5 °C over 2 h [R_f(diketone) ≈ 0.80 in EtOAc/toluene, 1:3].

Double-Reductive Amination: The Swern reaction mixture was concentrated at a moderate temperature (ca. 30 °C) with simultaneous coevaporation of toluene (3×). The residue was dissolved in a mixture of MeOH/DCM (0.02 M, relative to starting compound, 5:1, v/v), and NH_4HCO_2 (20 equiv.) was added. The mixture was cooled to 0 °C and stirred until all NH_4HCO_2 had dissolved. Activated 3 Å molecular sieves (10 g/mmol) was added, and the reaction mixture was stirred for 15 min, after which $NaBH_3CN$ (4 equiv.) was added. The reaction mixture was kept at 0 °C for 1 h, after which the cooling source was removed, and the reaction mixture was stirred for an additional 20 h. After removal of the molecular sieves with the aid of a glass microfibre filter, the filtrate was concentrated, dissolved in EtOAc and washed with satd. aq. $NaHCO_3$. The aqueous phase was back-extracted with EtOAc (3×), and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography to provide the β-aza-C-glycoside product (R_f ≈ 0.5 in EtOAc/toluene, 1:3).

General Method D. *N*-Alkylation of β-Aza-C-glycosides by Reductive Amination: A dry mixture of the tetrabenzylated iminosugar, the aldehyde (10 equiv.) and Na_2SO_4 (10 equiv.) in a mixture of EtOH/AcOH (0.1 M, 3:1, v/v) was charged with $NaBH_3CN$ (4 equiv.). The reaction mixture was stirred for 20 h and subsequently concentrated by coevaporation with toluene. The residue was dissolved EtOAc, poured into satd. aq. $NaHCO_3$ and extracted with EtOAc (3×). The combined organic layers were dried (Na_2SO_4) and concentrated. The crude *N*-alkylated iminosugar was used in the Pd/C-catalyzed hydrogenolysis.

General Method E. Oxidative Cleavage of the PMB Group and Reprotection as Benzyloxy Carbamate: A solution of the PMB-protected amine in THF (0.5 M) was slowly added to a cooled (0 °C) solution of ammonium cerium(IV) nitrate (4 equiv.) in H_2O/THF (0.05 M, 1:5, v/v). The resulting suspension was stirred at 0 °C for 3 h, after which it was diluted with EtOAc (3× reaction volume) and washed with satd. aq. $NaHCO_3$ (3× reaction volume). The aqueous phase was back-extracted with EtOAc (2×). The combined organic phases were concentrated. The residue was suspended in a mixture of dioxane/satd. aq. $NaHCO_3$ (0.1 M, 2:1, v/v) after which benzyloxy chloroformate (2 equiv.) was added. The reaction mixture was stirred for 20 h. The mixture was diluted with water and extracted with Et_2O (2×). The combined organic phases were dried (Na_2SO_4) and concentrated. To facilitate the separation of the product from *p*-anisaldehyde during column chromatography, the crude benzyloxy carbamate was dissolved in MeOH (0.2 M), cooled to 0 °C and treated with sodium borohydride (3 equiv.). After 15 min, the reaction was quenched by slow addition of acetone. The mixture was acidified to pH = 2 with 1 M aq. HCl, diluted with water (3× reaction volume) and extracted with Et_2O (3×). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography to afford the benzyloxy carbamate protected iminosugar.

General Procedure F. Cross Metathesis: The iminosugar cross metathesis partner was coevaporated with DCE (3×). Next, the second alkene cross-metathesis partner (3 equiv.) was added, and together they were dissolved in DCM (0.067 M, relative to iminosugar). Alkenes **45**, **46** and **47** are not coevaporated because **46** and **47** are volatile. The solution was degassed by sonication under an argon flow for 10 min. Grubbs' first generation catalyst (25 mol-%) was added, and the reaction mixture was refluxed at 45 °C for 24 h. The reaction mixture was concentrated and exposed to air at room temp. for 48 h. The residue was purified by by silica gel column chromatography to afford the cross-metathesis product. In cases were the product was difficult to isolate from residual iminosugar cross-metathesis partner or catalyst breakdown products, the residue was purified once and then used impure in general procedure G or general procedure H (in a Parr apparatus).

General Procedure G. Birch Reduction: A dry (100 mL) three-neck roundbottom flask was cooled to –60 °C, and ammonia gas (through a CaO-filled drying column) was passed through it until 20–30 mL of ammonia had condensed. The ammonia gasflow was stopped, and sodium (50–100 mg, rinsed beforehand with heptane)

was added to the liquid ammonia. After stirring the dark blue mixture at –60 °C for 1 min, a solution of the benzylated iminosugar (50–200 mg) in *t*BuOH/THF (0.5 mL/ 2 mL) was added. The reaction mixture was stirred at –60 °C for 1–2 h, and additional sodium was added if the blue colour of the mixture disappeared. The reaction was quenched by slow addition of satd. aq. NH_4HCO_2 (1 mL). The ammonia was evaporated, and the resulting residue was coevaporated with dioxane. The solid residue was redissolved in MeOH and concentrated in the presence of Celite. The Celite/compound mixture was purified by silica gel column chromatography to afford the deprotected iminosugar.

General Procedure H. Pd/C-Catalyzed Hydrogenolysis at Atmospheric H_2 Pressure: A solution of the compound (ca. 50–250 μmol) in "acetaldehyde-free" EtOH (4 mL) was acidified to pH ≈ 2 with 1 M aq. HCl. Argon was passed through the solution for 5 min, after which a catalytic amount of Pd/C (ca. 50 mg, 10 wt.-% Pd on C) was added. Hydrogen was passed through the reaction mixture for 15 min, and the reaction mixture was stirred under atmospheric hydrogen pressure for 20 h. The Pd/C was removed by filtration through a glass microfibre filter, followed by thorough rinsing of the filter cake with MeOH. The filtrate was concentrated by coevaporation with toluene. In the case of incomplete reduction, hydrogenolysis was repeated after workup and coevaporation (3×) with "acetaldehyde-free" EtOH, at atmospheric pressure in the presence of Pd/C (ca. 50 mg) and Pd black (ca. 5 mg) or at higher H_2 pressure in a Parr apparatus.

Pd/C-Catalyzed Hydrogenolysis in a Parr Apparatus: A solution of the compound (ca. 50–250 μmol) in "acetaldehyde-free" EtOH (50 mL) was acidified to pH ≈ 2 with 1 M aq. HCl. Argon was passed through the solution for 5 min, after which a catalytic amount of Pd/C (50 mg, 10 wt.-% Pd on C) was added. The reaction vessel was placed under vacuum and subsequently ventilated with hydrogen gas. This cycle was repeated one more time, after which the vessel was placed under 4 bar of hydrogen gas and mechanically shaken for 20 h. Workup was the same as described in general procedure H.

4-(Triethylsilyl)but-3-yn-1-ol (7): A dry and cooled (–68 °C) solution of but-3-yn-1-ol (**6**; 3.11 g, 44.3 mmol) in THF (50 mL) was charged with BuLi (60.9 mL, 97.5 mmol, 1.6 M in toluene) and stirred at –68 °C for 1 h. Triethylsilyl chloride (22.5 mL, 132.9 mmol) was added dropwise to the reaction mixture, and the mixture was stirred at –68 °C for 1 h, after which cooling was ceased and the solution was stirred for 18 h. 2 M aq. HCl (200 mL) was added, and the reaction mixture was stirred for 48 h [R_f(intermediate disilyl compound) = 0.80 (EtOAc/PE, 1:2)]. The mixture was extracted with Et_2O (2 × 200 mL), and the combined organic layers were washed with water (2 × 200 mL). The organic phase was dried ($MgSO_4$), concentrated, and the resulting residue was purified by silica gel column chromatography (0% → 30% EtOAc in PE) to provide product **7** (5.82 g, 31.5 mmol) in 71% yield as a colourless oil. R_f = 0.10 (EtOAc/PE, 1:9). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.72 (t, J = 5.8 Hz, 2 H, OCH_2-1 butynyl), 2.53 (t, J = 6.6 Hz, 2 H, CH_2-2 butynyl), 1.82 (br. s, 1 H, OH), 0.99 (t, J = 8.0 Hz, 9 H, 3× CH_3 $SiEt_3$), 0.58 (q, J = 8.0 Hz, 6 H, 3× CH_2SiEt_3) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3323, 2953, 2876, 2174, 1458, 1414, 1236, 1018, 1004, 972, 889, 721 cm^{-1}. MS (ESI): found 185.2 $[M + H]^+$, calcd. for $[C_{10}H_2OSi + H]^+$ 185.1.

[4-(Adamant-1-ylmethoxy)but-1-ynyl]triethylsilane (8): A dry solution of **7** (2.21 g, 12.0 mmol) in DCM (120 mL) was cooled to –40 °C followed by addition of Et_3N (1.66 mL, 12.0 mmol). Next, Tf_2O (2.42 mL, 14.4 mmol) was added dropwise, and the reaction mixture was stirred at –40 °C for 1 h. Cooling was ceased, and the reaction mixture was concentrated at room temp. by means of a nitrogen flow. The residue was purified by silica gel column chromatography (isocratic 10% EtOAc in PE), and the product-containing fractions were concentrated under a nitrogen flow at room temp. to provide the intermediate triflate. [R_f = 0.67 (EtOAc/PE, 1:9)]. The triflate (ca. 12 mmol) was dissolved in DCM (80 mL), to which adamantylmethanol (9.98 g, 60 mmol) and K_2CO_3 (8.17 g, 60 mmol) were successively added. The reaction mixture was refluxed (ca. 55 °C) for 3 d, after which the solids were removed by filtration, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (0% → 20% EtOAc in PE) to provide **8** (3.37 g, 10.1 mmol) in 84% yield as a colourless oil. R_f = 0.83 (EtOAc/PE, 1:9). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.52 (t, J = 7.1 Hz, 2 H, OCH_2-4 butynyl), 3.02 (s, 2 H, OCH_2-Ada), 2.49 (t, J = 7.1 Hz, 2 H, CH_2-3 butynyl), 1.95 (s, 3 H, 3× CH Ada), 1.79-1.57 (m, 6 H, 3× CH_2 Ada), 1.53 (d, J = 2.7 Hz, 6 H, 3× CH_2 Ada), 0.98 (t, J = 7.8 Hz, 9 H, 3× CH_3 $SiEt_3$), 0.57 (q, J = 7.7 Hz, 6 H, 3× CH_2 $SiEt_3$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 105.5 (C_q-2 butynyl), 82.6 (C_q-1 butynyl), 82.2 (OCH_2-Ada), 70.2 (OCH_2-4 butynyl), 39.9 (CH_2 Ada), 37.5 (CH_2 Ada), 34.3 (C_q Ada), 28.6 (CH Ada), 21.4 (CH_2-3 butynyl), 7.6 (CH_3 $SiEt_3$), 4.7 (CH_2 $SiEt_3$) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2901, 2874, 2849, 2175, 1456, 1236, 1157, 1111, 1003, 723 cm^{-1}. HRMS: found 333.2609 $[M + H]^+$, calcd. for $[C_{21}H_{36}OSi + H]^+$ 333.2608.

4-(Adamant-1-ylmethoxy)but-1-yne (9): A dry solution of **8** (3.37 g, 10.1 mmol) in a mixture of THF (50 mL) and MeOH (25 mL) was charged with NaOMe (2.86 g, 52.95 mmol) and refluxed at 90 °C for 20 h. The reaction was quenched (water, 0.5 mL) and the mixture concentrated. The residue was dissolved in EtOAc (200 mL) and washed with water (2 × 200 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography (2% → 10% acetone in PE) to provide **9** (1.92 g, 8.80 mmol) in 87% yield as a colourless oil. R_f = 0.70 (EtOAc/PE, 1:9). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.53 (t, J = 7.2 Hz, 2 H, OCH_2-4 butynyl) 3.01 (s, 2 H, OCH_2-Ada), 2.43 (td, J = 2.7, 7.2 Hz, 2 H, CH_2-3 butynyl), 1.97 (br. s, 3 H, 3× CH Ada), 1.94 (t, J = 2.6 Hz, 1 H, CH-1 butynyl), 1.78–1.57 (m, 6 H, 3× CH_2 Ada), 1.53 (d, J = 2.8 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 82.1, (OCH_2-Ada), 81.6 (C_q butynyl), 69.8 (OCH_2-4 butynyl), 69.2 (C_q butynyl), 39.8 (CH_2 Ada), 37.3 (CH_2 Ada), 34.2 (C_q Ada), 28.4 (CH Ada), 19.8 (CH_2-3 butynyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3312, 2899, 2847, 1450, 1362, 1157, 1103, 1070 cm^{-1}. MS (ESI): found 219.9 $[M + H]^+$, calcd. for $[C_{15}H_{22}O + H]^+$ 219.2.

6-(Adamant-1-ylmethoxy)hex-1-yne (11): (1-Diazo-2-oxopropyl)-di-*O*-methyl phosponate (1.44 g, 7.5 mmol)[50,51] and K_2CO_3 (1.38 g, 10.0 mmol) were added to a cooled (0 °C) solution of **10**[25] (1.25 g, 5.0 mmol) in methanol (25 mL). After 30 min, the reaction mixture was warmed to room temp. and stirred for an additional 16 h. The reaction mixture was transferred into satd. aq. NH_4Cl (20 mL) and extracted with Et_2O (4 × 50 mL). The combined organic phases were washed with satd. aq. NaCl (50 mL), dried ($MgSO_4$) and concentrated. The crude product was purified by silica gel column chromatography (0% → 6% EtOAc in PE) to furnish **11** (1.07 g, 4.34 mmol) in 87% yield as a colourless oil. R_f = 0.6 (PE/acetone, 19:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.40 (t, J = 6.0 Hz, 2 H, OCH_2-6 hex-1-yn), 2.95 (s, 2 H, OCH_2-Ada), 2.28–2.17 (m, 2 H, CH_2-3 hexynyl), 1.96 (br. s, 3 H, 3× CH Ada), 1.94 (t, J = 2.6 Hz, 1 H, CH-1 hexynyl), 1.78–1.57 (m, 10 H, 3× CH_2 Ada, 2× CH_2 hexynyl), 1.53 (d, J = 2.8 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 84.3 (C_q hexynyl), 82.0 (OCH_2-Ada), 70.9 (OCH_2-6 hexynyl), 68.6 (C_q hexynyl), 39.9 (CH_2 Ada), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 28.8 (CH_2-5 hexynyl), 28.5 (CH Ada), 25.5

(CH_2-4 hexynyl), 18.3 (CH_2-3 hexynyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3311, 2899, 2847, 1452, 1360, 1157, 1113, 1056, 625 cm^{-1}. HRMS: found 247.2058 $[M + H]^+$, calcd. for $[C_{17}H_{26}O + H]^+$ 247.2056.

α/β-Mixture of 1-*C*-[4-(Adamant-1-ylmethoxy)but-1-ynyl]-2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (13): Compound **9** (1.0 g, 4.58 mmol) was subjected to general procedure A to produce **13** (2.09 g, 2.76 mmol) in 60% yield after silica gel column purification (0% → 5% acetone in toluene). R_f = 0.46 (toluene/acetone, 19:1). ^1H NMR (300 MHz, $CDCl_3$, α/β mixture): δ = 7.42–7.09 (m, 20 H, H_{Ar} Bn), 5.07–4.43 (m, 8 H, 4× CH_2 Bn), 4.06–3.56 (m, 6 H, 2-H, 3-H, 4-H, 5-H, CH_2-6), 3.55–3.44 (m, 2 H, OCH_2-4 butynyl), 3.01–2.90 (m, 2 H, OCH_2-Ada), 2.56–2.43 (m, 2 H, CH_2-3 butynyl), 1.91 (br. s, 3 H, 3× CH Ada), 1.74–1.54 (m, 6 H, 3× CH_2 Ada), 1.48 (s, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, α/β mixture): δ = 138.5, 138.46, 138.42, 138.3, 137.93, 137.91, 137.8 (C_q Bn α/β), 128.1, 128.0, 127.86, 127.81, 127.7, 127.6, 127.5, 127.4, 127.2 (CH_{Ar} Bn α/β), 95.3, 91.4, 86.2, 84.1, 84.0, 83.5, 82.9, 82.3, 81.9, 81.8 (OCH_2-Ada), 80.3, 78.0, 77.5, 77.3, 77.0, 76.8, 76.7, 76.4, 75.6, 75.5, 75.4, 74.9, 74.7, 74.4, 73.8, 73.2, 71.5, 69.2, 69.0 (OCH_2-4 butynyl), 68.3, 39.4 (CH_2 Ada), 36.9 (CH_2 Ada), 33.8 (C_q Ada), 28.0 (CH Ada), 19.8, 19.7 (CH_2-3 butynyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3321, 3032, 2905, 2847, 1496, 1454, 1367, 1209, 1146, 1103, 1045, 1028, 1007, 986, 951, 910, 808, 754, 742 cm^{-1}. $[\alpha]_D^{20}$ = 36.1 (*c* = 4.6, $CHCl_3$). HRMS: found 774.4367 $[M + NH_4]^+$, calcd. for $[C_{49}H_{56}O_7 + NH_4]^+$ 774.4364.

α/β-Mixture of 1-*C*-[6-(Adamant-1-ylmethoxy)hex-1-ynyl]-2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (14): Compound **11** (493 mg, 2.0 mmol) was subjected to general procedure A to produce **14** (1.35 g, 1.72 mmol) in 86% yield after silica gel column purification (0% → 5% acetone in toluene). R_f = 0.50 (toluene/acetone, 19:1). ^1H NMR (200 MHz, $CDCl_3$, α/β mixture): δ = 7.44–7.08 (m, 20 H, H_{Ar} Bn), 5.07–4.45 (m, 8 H, 4× CH_2 Bn), 3.96–3.25 (m, 8 H, CH_2-6 hexenyl, 2-H, 3-H, 4-H, 5-H, CH_2-6), 2.92, 2.91 (s, 2 H, OCH_2-Ada α/β), 2.36–2.21 (m, 2 H, CH_2-3 hexenyl), 1.93 (br. s, 3 H, 3× CH Ada), 1.76–1.54 (m, 10 H, 3× CH_2 Ada, 2× CH_2 hexenyl), 1.50 (d, *J* = 2.0 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, α/β mixture): δ = 138.7, 138.7, 138.6, 138.1, 138.1, 138.0, 138.0 (C_q Bn α/β), 128.3, 128.2, 128.1, 127.99, 127.97, 127.94, 127.92, 127.87, 127.85, 127.7, 127.6, 127.5, 127.4, 127.3 (CH_{Ar} Bn α/β), 95.6, 91.6 (C-1 α/β), 89.1, 84.8 (C_q hexenyl α/β), 84.4, 84.3, 83.7, 82.5, 81.8 (OCH_2-Ada), 79.9, 77.8, 77.4, 77.1, 76.4, 75.6, 75.6, 75.0, 74.8, 74.4, 73.8, 73.6, 73.4, 73.2, 73.2, 71.5, 70.8, 70.7, 68.5, 39.6 (CH_2 Ada), 37.1 (CH_2 Ada), 34.0 (C_q Ada), 28.8, 28.7 (CH_2 hexenyl α/β), 28.2 (CH Ada), 25.1, 24.9 (CH_2 hexenyl α/β), 18.5 (CH_2-3 hexenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3362, 3032, 2902, 2849, 1497, 1453, 1360, 1211, 1067, 1027, 910, 733, 695 cm^{-1}. $[\alpha]_D^{20}$ = 33.4 (*c* = 2.2, $CHCl_3$). HRMS: found 802.4681 $[M + NH_4]^+$, calcd. for $[C_{51}H_{60}O_7 + NH_4]^+$ 802.4677.

(1*S*)-1-*C*-[4-(Adamant-1-ylmethoxy)but-1-ynyl]-2,3,4,6-tetra-*O*-benzyl-1-deoxynojirimycin (15): Compound **13** (371 mg, 0.49 mmol) was subjected to general procedure C to give **15** (191 mg, 0.26 mmol) as a colourless oil in 53% yield after silica gel column chromatography (0% → 20% EtOAc in toluene). R_f = 0.19 (toluene/EtOAc, 9:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.39–7.16 (m, 20 H, H_{Ar} Bn), 5.02 (d, *J* = 10.5 Hz, 1 H, C*H*H Bn), 4.91 (d, *J* = 10.8 Hz, 1 H, C*H*H Bn), 4.83 (d, *J* = 11.0 Hz, 1 H, C*H*H Bn), 4.81 (m, 2 H, 2× CH*H* Bn), 4.49–4.42 (m, 3 H, CH_2 Bn, CH*H* Bn), 3.68 (dd, *J* = 2.4, 9.0 Hz, 1 H, 6a-H), 3.54–3.48 (m, 4 H, 3-H, 6b-H, OCH_2-4 butynyl), 3.44–3.43 (m, 2 H, 1-H, 2-H), 3.37 (dd, *J* = 9.4, 9.4 Hz, 1 H, 4-H), 2.95 (s, 2 H, OCH_2-Ada), 2.77–2.73 (m, 1 H, 5-H), 2.47 (t, *J* = 7.3 Hz, 2 H, CH_2-3 butynyl), 1.93 (br. s, 3 H, 3× CH Ada), 1.65 (dd, *J* = 12.0, 43.7 Hz, 6 H, 3× CH_2 Ada), 1.49 (d, *J* = 2.4 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.9, 138.6, 138.4, 138.1 (4× C_q Bn), 128.65, 128.62, 128.5, 128.4, 128.2, 128.17, 128.12, 128.0, 127.97, 127.95, 127.8 (CH_{Ar} Bn), 87.0 (C-3), 84.6 (C-2), 82.2 (OCH_2-Ada), 81.3 (C_q butynyl), 80.1 (C-4), 76.0, 75.7, 75.3, 73.6 (4× CH_2 Bn), 70.3 (C-6), 70.0 (CH_2-4 butynyl), 58.9 (C-5), 51.9 (C-1), 39.8 (CH_2 Ada), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 28.4 (CH Ada), 20.2 (CH_2-3 butynyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2901, 2847, 1454, 1360, 1151, 1096, 1070, 1028, 1007, 735, 696 cm^{-1}. $[\alpha]_D^{20}$ = 6.8 (*c* = 0.8, $CHCl_3$). HRMS: found 740.4309 $[M + H]^+$, calcd. for $[C_{49}H_{57}NO_5 + H]^+$ 740.4310.

(1*S*)-1-*C*-[6-(Adamant-1-ylmethoxy)hex-1-ynyl]-2,3,4,6-tetra-*O*-benzyl-1-deoxynojirimycin (16): Compound **14** (0.40 g, 0.51 mmol) was subjected to general procedure C to give **16** (234 mg, 0.30 mmol) as a colourless oil in 59% yield after silica gel column chromatography (0% → 20% EtOAc in toluene). R_f = 0.6 (toluene/acetone, 9:1). ^1H NMR (400 MHz, C_6D_6): δ = 7.23–7.05 (m, 20 H, H_{Ar} Bn), 5.20 (d, *J* = 11.0 Hz, 1 H, C*H*H Bn), 4.97–4.93 (m, 2 H, CH*H* Bn, C*H*H Bn), 4.88 (d, *J* = 11.4 Hz, 1 H, C*H*H Bn), 4.81 (d, *J* = 11.3 Hz, 1 H, CH*H* Bn), 4.47 (d, *J* = 11.4 Hz, 1 H, CH*H* Bn), 4.25 (d, *J* = 11.9 Hz, 1 H, C*H*H Bn), 4.19 (d, *J* = 11.9 Hz, 1 H, CH*H* Bn), 3.65 (dd, *J* = 2.4, 8.9 Hz, 1 H, 6a-H), 3.59–3.48 (m, 4 H, 1-H, 2-H, 3-H, 6b-H), 3.45 (dd, *J* = 9.1, 9.1 Hz, 1 H, 4-H), 3.21 (t, *J* = 5.9 Hz, 2 H, CH_2-6 hexenyl), 2.87 (s, 2 H, OCH_2-Ada), 2.76 (ddd, *J* = 2.4, 6.2, 9.0 Hz, 1 H, 5-H), 2.08 (t, *J* = 6.5 Hz, 2 H, CH_2-3 hexenyl), 1.94 (s, 3 H, 3× CH Ada), 1.73–1.50 (m, 16 H, 6× CH_2 Ada, 2× CH_2 hexenyl) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 140.2, 140.0, 139.8, 139.1 (4× C_q Bn), 129.0, 128.8, 128.7, 128.5, 128.3, 128.2, 128.0, 127.9 (CH_{Ar} Bn), 87.9 (C-3), 85.6 (C-2), 84.2 (C_q hexenyl), 82.6 (OCH_2-Ada), 80.9 (C-4), 80.9 (C_q hexenyl), 76.0, 75.8, 75.4, 73.9 (4× CH_2 Bn), 71.4 (CH_2-6 hexenyl), 71.0 (C-6), 59.8 (C-5), 52.9 (C-1), 40.5 (CH_2 Ada), 38.0 (CH_2 Ada), 34.7 (C_q Ada), 29.7 (CH_2 hexenyl), 29.2 (CH Ada), 26.3 (CH_2 hexenyl), 19.3 (C-3 hexenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3031, 2901, 2848, 1497, 1452, 1359, 1209, 1071, 1027, 1007, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = 6.2 (*c* = 1.0, $CHCl_3$). HRMS: found 768.4623 $[M + H]^+$, calcd. for $[C_{51}H_{61}NO_5 + H]^+$ 768.4623.

(1*S*)-1-*C*-[4-(Adamant-1-ylmethoxy)butyl]-1-deoxynojirimycin (17): Compound **15** (66 mg, 89 μmol) was subjected to hydrogenolysis at atmospheric H_2 (see general procedure H) to produce **17** (30 mg, 79 μmol) as a colourless oil in 90% yield after purification (silica gel: 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.22 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.92 (dd, *J* = 3.1, 10.8 Hz, 1 H, 6a-H), 3.50 (dd, *J* = 7.8, 10.8 Hz, 1 H, 6b-H), 3.41 (t, *J* = 6.2 Hz, 2 H, OCH_2-4 butyl), 3.20 (dd, *J* = 8.9, 8.9 Hz, 1 H, 3-H), 3.11 (dd, *J* = 9.3, 9.3 Hz, 1 H, 4-H), 2.99 (dd, *J* = 9.2, 9.2 Hz, 1 H, 2-H), 2.97 (s, 2 H, OCH_2-Ada), 2.56 (ddd, *J* = 3.1, 7.8, 9.9 Hz, 1 H, 5-H), 2.43 (td, *J* = 2.8, 9.2 Hz, 1 H, 1-H), 1.94 (s, 3 H, 3× CH Ada), 1.93–1.89 (m, 1 H, C*H*H-1 butyl), 1.72 (dd, *J* = 11.9, 44.4 Hz, 6 H, 3× CH_2 Ada), 1.65–1.52 (m, 3 H, C*H*H-2 butyl, CH_2-3 butyl), 1.56 (d, *J* = 2.1 Hz, 6 H, 3× CH_2 Ada), 1.45–1.28 (m, 2 H, CH*H*-1 butyl, CH*H*-2 butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 80.7 (C-3), 76.7 (C-2), 73.7 (C-4), 72.6 (CH_2-4 butyl), 63.7 (C-6), 62.6 (C-5), 60.9 (C-1), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 32.9 (CH_2-1 butyl), 31.1 (CH_2-3 butyl), 29.9 (CH Ada), 23.7 (CH_2-2 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3356, 2899, 2847, 1448, 1092, 999 cm^{-1}. $[\alpha]_D^{20}$ = 3.3 (*c* = 0.3, MeOH). HRMS: found 384.2746 $[M + H]^+$, calcd. for $[C_{21}H_{37}NO_5 + H]^+$ 384.2744.

(1*S*)-1-*C*-[6-(Adamant-1-ylmethoxy)hexyl]-1-deoxynojirimycin (18): Compound **16** (75 mg, 98 μmol) was subjected to hydrogenolysis at atmospheric H_2 (see general procedure H) to produce **18** (30 mg,

73 μmol) as a colourless oil in 75% yield after purification (silica gel: 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.24 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 3.92 (dd, J = 3.0, 11.1 Hz, 1 H, 6a-H), 3.62 (dd, J = 6.8, 11.1 Hz, 1 H, 6b-H), 3.38 (t, J = 6.4 Hz, 2 H, CH_2-6 hexyl), 3.28–3.20 (m, 2 H, 3-H, 4-H), 3.12–3.06 (m, 1 H, 2-H), 2.96 (s, 2 H, OCH_2-Ada), 2.71–2.64 (m, 1 H, 1-H), 2.61–2.54 (m, 1 H, 5-H), 1.94 (br. s, 4 H, 3× CH Ada, C*H*H-1 hexyl), 1.72 (dd, J = 12.1, 32.0 Hz, 6 H, 3× CH_2 Ada), 1.59–1.51 (m, 8 H, 3× CH_2 Ada, CH_2 hexyl), 1.39 (m, 7 H, 3× CH_2 hexyl, CH*H*-1 hexyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 80.2 (C-3), 75.9 (C-2), 72.8 (CH_2-6 hexyl), 72.6 (C-4), 62.5 (C-5), 62.5 (C-6), 60.9 (C-1), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 32.6 (CH_2-1 hexyl), 30.9 (CH_2 hexyl), 30.8 (CH_2-5 hexyl), 29.9 (CH Ada), 27.4 (CH_2 hexyl), 26.9 (CH_2 hexyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3344, 2901, 2849, 1606, 1452, 1360, 1156, 1095, 753 cm^{-1}. $[\alpha]_D^{20}$ = –6.5 (c = 1.0, MeOH). HRMS: found 412.3056 $[M + H]^+$, calcd. for $[C_{23}H_{41}NO_5 + H]^+$ 412.3057.

(1*S*)-1-*C*-[4-(Adamant-1-ylmethoxy)butyl]-1-deoxy-*N*-methylnojirimycin (19): Argon was passed through a solution of compound **15** (62 mg, 84 μmol) and formaldehyde (1 mL, 37 wt.-% in water) in *n*-propanol (4 mL) for 5 min, after which a catalytic amount of Pd/C (Degussa type, 50 mg, 5 wt.-% Pd on C) was added. Hydrogen was passed through the reaction mixture for 15 min. After stirring the reaction mixture under atmospheric hydrogen pressure for 2 h, the Pd/C was removed by filtration through a glass microfibre filter, followed by thorough rinsing with MeOH [R_f(intermediate) = 0.73 (EtOAc/PE, 1:3)]. The filtrate was concentrated, and the resulting residue was subjected to Pd/C-catalyzed hydrogenolysis at atmospheric H_2 (see general procedure H). The crude product was purified by silica gel column chromatography (0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH) to give **19** (30 mg, 75 μmol) as a colourless oil in 89% yield. R_f = 0.35 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.92 (dd, J = 3.0, 11.8 Hz, 1 H, 6a-H), 3.83 (dd, J = 3.9, 11.9 Hz, 1 H, 6b-H), 3.40 (t, J = 6.3 Hz, 2 H, CH_2-4 butyl), 3.39 (dd, J = 9.1, 10.0 Hz, 1 H, 4-H), 3.23 (dd, J = 9.4, 9.4 Hz, 1 H, 2-H), 3.17 (dd, J = 9.1, 9.4 Hz, 1 H, 3-H), 2.98 (s, 2 H, OCH_2-Ada), 2.32 (s, 3 H, NCH_3), 2.12–2.07 (m, 2 H, 1-H, 5-H), 1.94 (s, 3 H, 3× CH Ada), 1.82–1.66 (m, 8 H, 3× CH_2 Ada, CH_2-1 butyl), 1.60–1.54 (m, 8 H, 3× CH_2 Ada, CH_2-3 butyl), 1.51–1.43 (m, 2 H, CH_2-2 butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 80.6 (C-3), 72.9 (C-2), 72.7 (CH_2-4 butyl), 71.0 (C-4), 70.0 (C-5), 68.1 (C-1), 60.4 (C-6), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 36.3 (NCH_3), 35.3 (C_q Ada), 31.2 (CH_2-3 butyl), 29.9 (CH Ada), 29.7 (CH_2-1 butyl), 22.5 (CH_2-2 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3358, 2900, 2848, 1652, 1452, 1362, 1158, 1095, 1014 cm^{-1}. $[\alpha]_D^{20}$ = 2.6 (c = 0.3, MeOH). HRMS: found 398.2898 $[M + H]^+$, calcd. for $[C_{22}H_{39}NO_5 + H]^+$ 398.2901.

(1*S*)-1-*C*-[6-(Adamant-1-ylmethoxy)hexyl]-1-deoxy-*N*-methylnojirimycin (20): Argon was passed through a solution of compound **16** (76 mg, 99 μmol) and formaldehyde (1 mL, 37 wt.-% in water) in *n*-propanol (4 mL) for 5 min, after which a catalytic amount of Pd/C (Degussa type, 50 mg, 5 wt.-% Pd on C) was added. Hydrogen was passed through the reaction mixture for 15 min. After stirring the reaction mixture under atmospheric hydrogen pressure for 2 h, the Pd/C was removed by filtration through a glass microfibre filter, followed by thorough rinsing with MeOH [R_f(intermediate) = 0.75 (EtOAc/PE, 1:3)]. The filtrate was concentrated, and the resulting residue was subjected to Pd/C-catalyzed hydrogenolysis at atmospheric H_2 (see general procedure H). The crude product was purified by silica gel column chromatography (0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH) to give **20** (29 mg, 68 μmol) as a colourless oil in 69% yield. R_f = 0.36 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (400 MHz, MeOD + $CDCl_3$): δ = 3.94 (s, 2 H, CH_2-6), 3.48 (dd, J = 9.4, 9.4 Hz, 1 H, 4-H), 3.38 (t, J = 6.4 Hz, 2 H, CH_2-6 hexyl), 3.34–3.25 (m, 2 H, 2-H, 3-H), 2.97 (s, 2 H, OCH_2-Ada), 2.56 (s, 3 H, NCH_3), 2.50–2.42 (s, 2 H, 1-H, 5-H), 1.95 (s, 3 H, 3× CH Ada), 1.80–1.65 (m, 8 H, 3× CH_2 Ada, CH_2 hexyl), 1.60–1.54 (m, 8 H, 3× CH_2 Ada, CH_2-5 hexyl), 1.50–1.32 (m, 6 H, 3× CH_2 hexyl) ppm. ^{13}C NMR (100 MHz, MeOD + $CDCl_3$): δ = 81.1 (OCH_2-Ada), 77.7 (C-3), 70.8 (CH_2-6 hexyl), 70.5 (C-2), 67.9 (C-4), 67.8 (C-5), 66.3 (C-1), 57.0 (C-6), 38.9 (CH_2 Ada), 36.4 (CH_2 Ada), 34.3 (NCH_3), 33.2 (C_q Ada), 28.9 (CH_2 hexyl), 28.7 (CH_2 hexyl), 27.7 (CH Ada, CH_2 hexyl), 25.3 (CH_2 hexyl), 24.7 (CH_2 hexyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3324, 2902, 2849, 1637, 1452, 1362, 1158, 1102, 1025, 753 cm^{-1}. $[\alpha]_D^{20}$ = –1.6 (c = 1.0, MeOH). HRMS: found 426.3212 $[M + H]^+$, calcd. for $[C_{24}H_{43}NO_5 + H]^+$ 426.3214.

(1*S*)-1-*C*-[4-(Adamant-1-ylmethoxy)butyl]-*N*-butyl-1-deoxynojirimycin (21): Compound **15** (62 mg, 83 μmol) was *N*-butylated (see general procedure D), and the crude intermediate (R_f = 0.80 in EtOAc/PE, 1:3) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **21** (22 mg, 50 μmol) as a colourless oil in 60% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.45 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.87 (dd, J = 3.1, 11.8 Hz, 1 H, 6a-H), 3.84 (dd, J = 2.7, 11.8 Hz, 1 H, 6b-H), 3.41 (t, J = 6.1 Hz, 2 H, CH_2-4 butyl), 3.34 (dd, J = 9.3, 9.3 Hz, 1 H, 4-H), 3.18 (dd, J = 9.3, 9.3 Hz, 1 H, 2-H), 3.11 (dd, J = 9.1, 9.1 Hz, 1 H, 3-H), 2.98 (s, 2 H, OCH_2-Ada), 2.88–2.81 (m, 1 H, NC*H*H butyl), 2.75–2.68 (m, 1 H, NCH*H* butyl), 2.39 (dt, J = 3.6, 7.6 Hz, 1 H, 1-H), 2.33 (dt, J = 2.8, 9.7 Hz, 1 H, 5-H), 1.95 (s, 3 H, 3× CH Ada), 1.72 (dd, J = 11.6, 46.1 Hz, 8 H, 3× CH_2 Ada, CH_2-1 butyl), 1.62–1.33 (m, 12 H, 3× CH_2 Ada, 2× CH_2 butyl, CH_2 N-butyl), 1.30–1.24 (m, 2 H, CH_2CH_3 N-butyl), 0.96 (t, J = 7.3 Hz, 3 H, CH_3 N-butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 80.6 (C-3), 73.0 (C-2), 72.7 (CH_2-4 butyl), 71.6 (C-4), 65.8 (C-5), 63.7 (C-1), 60.0 (C-6), 47.3 (NCH_2 butyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 31.5 (CH_2-3 butyl), 29.9 (CH Ada), 29.0 (CH_2-1 butyl), 25.4 (CH_2 N-butyl), 21.8 (CH_2-CH_3 N-butyl), 21.6 (CH_2-2 butyl), 14.6 (CH_3 N-butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3366, 2903, 2849, 1636, 1454, 1343, 1158, 1103 cm^{-1}. $[\alpha]_D^{20}$ = –1.0 (c = 0.1, MeOH). HRMS: found 440.3368 $[M + H]^+$, calcd. for $[C_{25}H_{45}NO_5 + H]^+$ 440.3370.

(1*S*)-1-*C*-[6-(Adamant-1-ylmethoxy)hexyl]-*N*-butyl-1-deoxynojirimycin (22): Compound **16** (77 mg, 100 μmol) was *N*-butylated (see general procedure D), and the crude intermediate (R_f = 0.77 in EtOAc/PE, 1:3) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **22** (31 mg, 66 μmol) as a colourless oil in 66% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.45 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 3.98 (d, J = 12.0 Hz, 1 H, 6a-H), 3.88 (d, J = 12.0 Hz, 1 H, 6b-H), 3.53–3.43 (m, 1 H, 4-H), 3.38 (t, J = 6.1 Hz, 2 H, CH_2-5 hexyl), 3.34–3.29 (m, 1 H, 2-H), 3.28–3.20 (m, 1 H, 3-H), 3.16–3.09 (m, 1 H, NC*H*H butyl), 3.01–2.93 (m, 3 H, NCH*H* butyl, OCH_2-Ada), 2.80–2.68 (m, 2H. 1-H, 5-H), 1.94 (s, 3 H, 3× CH Ada), 1.88–1.21 (m, 26 H, 6× CH_2 Ada, 5× CH_2 hexyl, 2× CH_2 N-butyl), 0.98 (t, J = 7.2 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 79.5 (C-3), 72.7 (CH_2-6 hexyl), 72.6 (C-2), 70.1 (C-4), 66.7 (C-5), 65.1 (C-1), 58.4 (C-6), 48.5 (NCH_2 butyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 31.0 (CH_2), 30.8 (2× CH_2), 29.9 (CH Ada), 29.2 (CH_2), 27.4 (CH_2), 26.1 (CH_2), 21.4 (CH_2-CH_3 N-butyl), 14.3 (CH_3 N-butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3364, 2902, 2847, 1720 1453, 1366, 1258, 1011, 926 cm^{-1}. $[\alpha]_D^{20}$ =

–1.0 (*c* = 0.2, MeOH). HRMS: found 468.3679 $[M + H]^+$, calcd. for $[C_{27}H_{50}NO_5 + H]^+$ 468.3684.

4-(Adamant-1-ylmethoxy)-1-*C*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)but-1-yne (24): Compound **13** (100 mg, 132 μmol) was subjected to general procedure B to produce **24** (86 mg, 116 μmol) in 89% yield after silica gel column purification (0% → 5% acetone in toluene). R_f = 0.50 (toluene/EtOAc, 9:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.09 (m, 20 H, H, H_{Ar} Bn), 5.02 (d, *J* = 10.5 Hz, 1 H, C*H*H Bn), 4.91 (d, *J* = 10.9 Hz, 1 H, C*H*H Bn), 4.83–4.77 (m, 3 H, CH_2 Bn, CH*H* Bn), 4.60 (d, *J* = 12.2 Hz, 1 H, C*H*H Bn), 4.54–4.49 (m, 2 H, 2× CH*H* Bn), 4.03 (dt, *J* = 2.0, 9.0 Hz, 1 H, 1-H), 3.73 (dd, *J* = 1.6, 10.7 Hz, 1 H, 6a-H), 3.67 (dd, *J* = 4.4, 10.8 Hz, 1 H, 6b-H), 3.64–3.55 (m, 3 H, 2-H, 3-H, 4-H), 3.50 (t, *J* = 7.3 Hz, 2 H, CH_2-4 butenyl), 3.42 (ddd, *J* = 1.8, 4.2, 9.1 Hz, 1 H, 5-H), 2.97-2.93 (m, 2 H, OCH_2-Ada), 2.51 (td, *J* = 1.8, 7.3 Hz, 2 H, CH_2-3 butenyl), 1.92 (s, 3 H, 3× CH Ada), 1.65 (dd, *J* = 11.9, 45.5 Hz, 6 H, 3× CH_2 Ada), 1.49 (d, *J* = 2.4 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (151 MHz, CDCl3): δ = 138.7, 138.3, 138.2, 138.2 (4× C_q Bn), 128.6, 128.6, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8 (CH_{Ar} Bn), 86.2 (C-3), 84.1 (C_q butynyl), 82.7 (C-2), 82.2 (OCH_2-Ada), 79.1 (C-5), 78.4 (C_q butynyl), 77.9 (C-4), 75.9, 75.6, 75.3, 73.7 (4× CH_2 Bn), 70.3 (C-1), 69.8 (CH_2-4 butynyl), 69.0 (C-6), 39.8 (CH_2 Ada), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 28.4 (CH Ada), 20.3 (CH_2-3 butynyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3036, 2901, 2849, 1734, 1497, 1452, 1360, 1209, 1094, 1063, 1028, 1003, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = –1.7 (*c* = 0.6, $CHCl_3$). HRMS: found 758.4416 $[M + NH_4]^+$, calcd. for $[C_{49}H_{56}O_6 + NH_4]^+$ 758.4415.

5-(Adamant-1-ylmethoxy)-1-*C*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)pent-1-yne (25): Compound **23** (250 mg, 337 μmol) was subjected to general procedure B to produce **25** (201 mg, 266 μmol) in 79% yield after silica gel column purification (0% → 5% acetone in toluene). R_f = 0.55 (toluene/EtOAc, 9:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40–7.08 (m, 20 H, H_{Ar} Bn), 5.07–4.46 (m, 8 H, 4× CH_2 Bn), 4.05 (d, *J* = 8.6 Hz, 1 H, 1-H), 3.78–3.53 (m, 6 H, 2-H, 3-H, 4-H, 5-H, CH_2-6), 3.41 (t, *J* = 6.0 Hz, 2 H, CH_2-5 pentenyl), 2.90 (s, 2 H, OCH_2-Ada), 2.35 (td, *J* = 1.6, 7.1 Hz, 2 H, CH_2-3 pentenyl), 1.93 (s, 3 H, 3× H Ada), 1.84–1.55 (m, 8 H, 3× CH_2 Ada, CH_2-4 pentenyl), 1.49 (d, *J* = 2.7 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.7, 138.3, 138.2, 138.1 (4× C_q Bn), 128.5, 128.4, 128.29, 128.23, 128.04, 128.02, 127.9, 127.8, 127.7 (CH_{Ar} Bn), 86.7 (C_q pentynyl), 86.1 (C-3), 82.7 (C-2), 81.9 (OCH_2-Ada), 79.0 (C-5), 77.8 (C-4), 77.4 (C_q pentynyl), 75.8, 75.4, 75.1, 73.6 (4× CH_2 Bn), 70.3 (C-1), 69.9 (CH_2-5 pentynyl), 68.9 (C-6), 39.8 (CH_2 Ada), 37.3 (CH_2 Ada), 34.1 (C_q Ada), 28.7 (CH_2-4 pentynyl), 28.3 (CH Ada), 15.9 (CH_2-3 pentynyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3033, 2901, 2848, 1724, 1452, 1361, 1269, 1090, 1065, 1026, 735, 696 cm^{-1}. $[\alpha]_D^{20}$ = 3.5 (*c* = 0.4, $CHCl_3$). HRMS: found 772.4572 $[M + NH_4]^+$, calcd. for $[C_{50}H_{58}O_6 + NH_4]^+$ 772.4572.

6-(Adamant-1-ylmethoxy)-1-*C*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)hex-1-yne (26): Compound **14** (428 mg, 0.56 mmol) was subjected to general procedure B to produce **26** (257 mg, 0.33 mmol) in 60% yield after silica gel column purification (0% → 5% acetone in toluene). R_f = 0.65 (toluene/EtOAc, 9:1). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.12–6.69 (m, 20 H, H_{Ar} Bn), 4.77 (d, *J* = 11.0 Hz, 1 H, CHH Bn), 4.62–4.41 (m, 4 H, CH_2 Bn, CH*H* Bn, C*H*H Bn), 4.25 (d, *J* = 11.3 Hz, 1 H, CH*H* Bn), 4.15 (d, *J* = 12.1 Hz, 1 H, C*H*H Bn), 4.04 (d, *J* = 12.1 Hz, 1 H, CH*H* Bn), 3.76 (dt, *J* = 1.8, 9.3 Hz, 1 H, 1-H), 3.42 (dd, *J* = 8.9, 9.6 Hz, 1 H, 4-H), 3.36–3.27 (m, 3 H, 2-H, CH_2-6), 3.22 (dd, *J* = 8.8, 8.9 Hz, 1 H, 3-H), 2.96 (dt, *J* = 2.7, 10.1 Hz, 1 H, 5-H), 2.86 (t, *J* = 5.8 Hz, 2 H, CH_2-6 hexynyl), 2.52 (s, 2 H, OCH_2-Ada), 1.78 (td, *J* = 1.4, 6.5 Hz, 2 H, CH_2-3 hexynyl), 1.60 (s, 3 H, CH Ada), 1.38–1.18 (m, 16 H, 6× CH_2 Ada, 2× CH_2 hexenyl) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 139.4, 139.1, 139.0, 138.8 (4× C_q Bn), 128.5, 128.48, 128.46, 128.42, 128.2, 128.1, 127.96, 127.93, 127.8, 127.7, 127.65, 127.62, 127.54, 127.50 (CH_{Ar} Bn), 86.4 (C_q hexynyl), 86.3 (C-3), 83.2 (C-2), 82.0 (OCH_2-Ada), 79.3 (C-5), 78.6 (C_q pentynyl), 78.1 (C-4), 75.4, 75.2, 74.9, 73.5 (4× CH_2 Bn), 70.9 (CH_2-6 hexynyl), 70.6 (C-1), 69.3 (C-6), 40.0 (CH_2 Ada), 37.5 (CH_2 Ada), 34.2 (C_q Ada), 29.1 (CH_2 hexynyl), 28.6 (CH Ada), 25.6 (CH_2 hexynyl), 18.8 (CH_2-3 hexynyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3031, 2901, 2848, 1497, 1453, 1360, 1294, 1210, 1155, 1091, 1064, 1027, 1005, 910, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = 2.6 (*c* = 1.0, $CHCl_3$). HRMS: found 786.4730 $[M + NH_4]^+$, calcd. for $[C_{51}H_{60}O_6 + NH_4]^+$ 786.4728.

1-(Adamant-1-ylmethoxy)-4-*C*-(β-D-glucopyranosyl)butane (27): Compound **24** (86 mg, 116 μmol) was subjected to Pd/C-catalyzed hydrogenolysis at atmospheric H_2 (see general procedure H). The resulting residue was purified by silica gel column chromatography (0% → 15% MeOH in $CHCl_3$ with 0.5% NH_4OH) to give **27** (36 mg, 94 μmol) as a colourless oil in 81% yield. R_f = 0.29 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 3.83 (dd, *J* = 2.3, 11.8 Hz, 1 H, 6a-H), 3.63 (dd, *J* = 5.7, 11.8 Hz, 1 H, 6b-H), 3.39 (t, *J* = 6.3 Hz, 2 H, CH_2-4 butyl), 3.30 (dd, *J* = 8.8, 9.2 Hz, 1 H, 3-H), 3.25 (dd, *J* = 9.2, 9.4 Hz, 1 H, 4-H), 3.18 (ddd, *J* = 2.3, 5.6, 9.4 Hz, 1 H, 5-H), 3.15–3.09 (m, 1 H, 1-H), 3.04 (dd, *J* = 8.8, 9.3 Hz, 1 H, 2-H), 2.97 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3× CH Ada), 1.91–1.83 (m, 1 H, C*H*H-1 butyl), 1.72 (dd, *J* = 11.8, 44.2 Hz, 6 H, 3× CH_2 Ada), 1.66–1.52 (m, 9 H, 3× CH_2 Ada, CH_2-3 butyl, C*H*H butyl), 1.48–1.39 (m, 2 H, CH*H*-1 butyl, CH*H* butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 81.7 (C-5), 81.0 (C-1), 80.0 (C-3), 75.6 (C-2), 72.9 (CH_2-6 hexyl), 72.2 (C-4), 63.3 (C-6), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 32.9 (CH_2-1 butyl), 30.9 (CH_2-3 butyl), 29.9 (CH Ada), 23.3 (CH_2 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3365, 2901, 2848, 1593, 1453, 1342, 1092, 1013 cm^{-1}. $[\alpha]_D^{20}$ = –1.0 (*c* = 0.2, MeOH). HRMS: found 385.2586 $[M + H]^+$, calcd. for $[C_{21}H_{36}O_6 + H]^+$ 385.2585.

1-(Adamant-1-ylmethoxy)-5-*C*-(β-D-glucopyranosyl)pentane (28): Compound **25** (95 mg, 126 μmol) was subjected to Pd/C-catalyzed hydrogenolysis at atmospheric H_2 (see general procedure H). The resulting residue was purified by silica gel column chromatography (0% → 15% MeOH in $CHCl_3$ with 0.5% NH_4OH) to give **28** (45 mg, 112 μmol) as a colourless oil in 89% yield. R_f = 0.32 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 3.83 (dd, *J* = 2.3, 11.8 Hz, 1 H, 6a-H), 3.63 (dd, *J* = 5.7, 11.9 Hz, 1 H, 6b-H), 3.38 (t, *J* = 6.5 Hz, 2 H, CH_2-5 pentyl), 3.31–3.28 (dd, *J* = 8.8, 9.1 Hz, 1 H, 3-H), 3.25 (dd, *J* = 9.1, 9.4 Hz, 1 H, 4-H), 3.17 (ddd, *J* = 2.3, 5.7, 9.4 Hz, 1 H, 5-H), 3.15–3.09 (m, 1 H, 1-H), 3.04 (dd, *J* = 8.8, 9.3 Hz, 1 H, 2-H), 2.97 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3× CH Ada), 1.90–1.82 (m, 1 H, C*H*H-1 pentyl), 1.72 (dd, *J* = 11.7, 44.9 Hz, 6 H, 3× CH_2 Ada), 1.65–1.51 (m, 9 H, 3× CH_2 Ada, CH_2-4 pentyl, C*H*H pentyl), 1.45–1.31 (m, 4 H, CH*H*-1 pentyl, CH_2 pentyl, CH*H* pentyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 81.7 (C-5), 81.0 (C-1), 80.0 (C-3), 75.6 (C-2), 72.8 (CH_2-5 pentyl), 72.1 (C-4), 63.3 (C-6), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 33.0 (CH_2-1 pentyl), 30.8 (CH_2-4 pentyl), 29.9 (CH Ada), 27.6 (CH_2 pentyl), 26.5 (CH_2 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3362, 2902, 2849, 1453, 1362, 1091, 1016 cm^{-1}. $[\alpha]_D^{20}$ = –12.0 (*c* = 0.2, MeOH). HRMS: found 399.2739 $[M + H]^+$, calcd. for $[C_{22}H_{38}O_6 + H]^+$ 399.2741.

1-(Adamant-1-ylmethoxy)-6-*C*-(β-D-glucopyranosyl)hexane (29): Compound **26** (75 mg, 97 μmol) was subjected to Pd/C-catalyzed hydrogenolysis at atmospheric H_2 (see general procedure H). The

resulting residue was purified by silica gel column chromatography (0% → 15% MeOH in $CHCl_3$ with 0.5% NH_4OH) to give **29** (36 mg, 87 μmol) as a colourless oil in 90% yield. R_f = 0.33 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.83 (dd, J = 2.4, 11.9 Hz, 1 H, 6a-H), 3.63 (dd, J = 5.7, 11.9 Hz, 1 H, 6b-H), 3.37 (t, J = 6.5 Hz, 2 H, CH_2-6 hexyl), 3.32–3.28 (dd, J = 8.7, 9.2 Hz, 1 H, 3-H), 3.25 (dd, J = 9.2, 9.4 Hz, 1 H, 4-H), 3.18 (ddd, J = 2.4, 5.7, 9.4 Hz, 1 H, 5-H), 3.14–3.09 (m, 1 H, 1-H), 3.04 (dd, J = 8.7, 9.4 Hz, 1 H, 2-H), 2.96 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3× CH Ada), 1.88–1.81 (m, 1 H, C*H*H-1 hexyl), 1.72 (dd, J = 11.7, 44.9 Hz, 6 H), 1.60–1.53 (m, 9 H, 3× CH_2 Ada, CH_2-5 hexyl, C*H*H hexyl), 1.45–1.29 (m, 6 H, CH*H*-1 hexyl, 2× CH_2 hexyl, CH*H* hexyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 81.7 (C-5), 81.0 (C-1), 80.0 (C-3), 75.6 (C-2), 72.9 (CH_2-6 hexyl), 72.2 (C-4), 63.3 (C-6), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 33.0 (CH_2-1 hexyl), 30.9 (CH_2 hexyl), 30.8 (CH_2-5 hexyl), 29.9 (CH Ada), 27.5 (CH_2 hexyl), 26.6 (CH_2 hexyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3361, 2901, 2849, 1453, 1361, 1092, 1012 cm^{-1}. $[\alpha]_D^{20}$ = –9.2 (c = 1.0, MeOH). HRMS: found 413.2896 $[M + H]^+$, calcd. for $[C_{23}H_{40}O_6 + H]^+$ 413.2898.

α/β-Mixture of 2,3,4,6-Tetra-*O*-benzyl-1-*C*-butyl-D-glucopyranose (30): A solution of **12** (1.02 g, 1.9 mmol) in THF (3 mL) was added to a cooled (–50 °C) solution of BuLi (0.59 mL, 0.95 mmol, 1.6 M in toluene) in THF (10 mL). The reaction mixture was stirred at –50 °C for 2 h. The reaction mixture was quenched (satd. aq. NH_4Cl), warmed to room temp. and poured into satd. aq. NH_4Cl (150 mL). The aqueous layer was extracted with Et_2O (3×150 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography (5% → 20% EtOAc in PE) to give **30** (409 mg, 0.69 mmol) in 72% yield as colourless oil. R_f = 0.45 (EtOAc/PE, 1:3). ^1H NMR (200 MHz, $CDCl_3$, α/β mixture): δ = 7.41–7.15 (m, 20 H, H_{Ar} Bn), 4.96–4.41 (m, 9 H, 2× CH_2 Bn, 6a-H), 4.12–3.57 (m, 4 H, 3-H, 4-H, 5-H, 6b-H), 3.43 (d, J = 9.2 Hz, 1 H, 2-H), 2.57 (s, 1 H, OH-1), 1.70–1.50 (m, 2 H, CH_2 butyl), 1.49–1.13 (m, 4 H, 2× CH_2 butyl), 0.86 (t, J = 6.8 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, α/β mixture): δ = 138.9, 138.7, 138.5, 138.2 (4× C_q Bn), 128.6, 128.5, 128.3, 128.2, 128.14, 128.12, 127.99, 127.94, 127.8, 127.7 (CH_{Ar} Bn), 98.6 (C_q-1), 84.1, 81.6, 76.6 (C-2, C-3, C-4), 75.8, 75.6, 75.1, 73.5 (2× CH_2 Bn), 71.8 (C-5), 69.0 (C-6), 38.6 (CH_2 butyl), 24.9 (CH_2 butyl), 23.0 (CH_2 butyl), 14.3 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3032, 2911, 2860, 1460, 1350, 1360, 1211, 1008, 736, 694 cm^{-1}. $[\alpha]_D^{20}$ = 0.7 (c = 2.9, $CHCl_3$). HRMS: found 596.3140 $[M + H]^+$, calcd. for $[C_{38}H_{44}O_6 + H]^+$ 596.3138.

(1*S*)-2,3,4,6-Tetra-*O*-benzyl-1-*C*-butyl-1-deoxynojirimycin (31): Compound **30** (600 mg, 1.0 mmol) was subjected to general procedure procedure C to give **31** (387 mg, 0.67 mmol) as a colourless oil in 67% yield after silica gel column chromatography (0% → 20% EtOAc in toluene). R_f(diol) = 0.33, R_f(diketone) = 0.77, R_f(aza-C-glycoside) = 0.56 (toluene/EtOAc, 3:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.16 (m, 20 H, H_{Ar} Bn), 4.93–4.88 (m, 3 H, C*H*H Bn, CH_2 Bn), 4.84 (d, J = 10.9 Hz, 1 H, C*H*H Bn), 4.64 (d, J = 10.9 Hz, 1 H, CH*H* Bn), 4.52–4.45 (m, 3 H, CH*H* Bn, CH_2 Bn), 3.71 (dd, J = 2.4, 9.0 Hz, 1 H, 6a-H), 3.60 (dd, J = 9.1, 9.3 Hz, 1 H, 3-H), 3.45 (dd, J = 7.1, 9.0 Hz, 1 H, 6b-H), 3.35 (dd, J = 9.1, 9.4 Hz, 1 H, 4-H), 3.14 (dd, J = 9.1, 9.3 Hz, 1 H, 2-H), 2.78 (ddd, J = 2.4, 7.1, 9.4 Hz, 1 H, 5-H), 2.57–2.53 (m, 1 H, 1-H), 1.88–1.81 (m, 1 H, C*H*H-2 butyl), 1.41–1.24 (m, 4 H, CH_2-1 butyl, CH*H*-2 butyl, CH_2-3 butyl), 0.89 (t, J = 6.9 Hz, 3 H, CH_3-4 butyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.9, 138.6, 138.4, 138.2 (4× C_q Bn), 128.6, 128.4, 128.28, 128.24, 128.0, 127.98, 127.95, 127.91, 127.7, 127.3 (CH_{Ar} Bn), 88.5 (C-3), 84.4 (C-2), 80.9 (C-4), 75.8, 75.6, 75.2, 73.5 (4× CH_2 Bn), 70.7 (C-6), 59.2, 59.2 (C-1, C-5), 31.8 (CH_2-2 butyl), 28.2, 23.1 (CH_2-1 butyl, CH_2-3 butyl), 14.2 (CH_3-4 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3032, 2924, 2862, 1458, 1358, 1312, 1211, 1072, 1026, 1003, 741, 694 cm^{-1}. $[\alpha]_D^{20}$ = 11.9 (c = 2.2, $CHCl_3$). HRMS: found 580.3417 $[M + H]^+$, calcd. for $[C_{38}H_{45}NO_4 + H]^+$ 580.3421.

(1*S*)-1-*C*-Butyl-1-deoxynojirimycin (32): Compound **31** (60 mg, 104 μmol) was subjected to hydrogenolysis at atmospheric H_2 (see general procedure H) to furnish **32** (23 mg, 100 μmol) as a colourless oil in 97% yield after purification (silica gel, 10% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.12 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 4.00–3.86 (m, 2 H, CH_2-6), 3.60–3.51 (m, 1 H, 4-H), 3.42–3.33 (m, 2 H, 2-H, 3-H), 3.09–3.00 (m, 1 H, 5-H), 3.00–2.94 (m, 1 H, 1-H), 2.05–1.95 (m, 1 H, C*H*H-1 butyl), 1.72–1.61 (m, 1 H, CH*H*-1 butyl), 1.60–1.46 (m, 2 H, CH_2-2 butyl), 1.46–1.33 (m, 2 H, CH_2-3 butyl), 0.97 (t, J = 7.0 Hz, 3 H, CH_3-4 butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 78.7 (C-3), 73.6 (C-2), 69.4 (C-4), 62.3 (C-5), 60.9 (C-1), 59.0 (C-6), 31.1 (CH_2-1 butyl), 29.1 (CH_2-2 butyl), 24.0 (CH_2-3 butyl), 14.3 (CH_3-4 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3331, 2959, 2932, 2870, 1636, 1436, 1380, 1098, 1014 cm^{-1}. $[\alpha]_D^{20}$ = –6.1 (c = 0.5, MeOH). HRMS: found 220.1545 $[M + H]^+$, calcd. for $[C_{10}H_{21}NO_4 + H]^+$ 220.1543.

(1*S*)-*N*-[5-(Adamant-1-ylmethoxy)pentyl]-2,3,4,6-tetra-*O*-benzyl-1-*C*-butyl-1-deoxynojirimycin (33): A solution of **31** (210 mg, 360 mmol) and **10**[25] (900 mg, 3.6 mmol) in acetonitrile/MeOH (1.8 mL, 5:1, v/v) was acidified to pH = 5–6 with AcOH (10 μL). Sodium sulfate (100 mg) and sodium cyanoborohydride (90 mg, 1.44 mmol) were added, and the reaction mixture was heated at 75 °C for 18 h. The mixture was diluted with satd. aq. $NaHCO_3$ (20 mL) and extracted with Et_2O (3×20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Purification by silica gel column chromatography (0% → 10% MeOH in $CHCl_3$ with 0.5% NH_4OH) gave **33** (230 mg, 283 mmol) as a colourless oil in 79% yield. R_f = 0.75 (EtOAc/PE, 1:3). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.36–7.15 (m, 20 H, H_{Ar} Bn), 4.95–4.79 (m, 4 H, 2× CH_2 Bn), 4.67–4.39 (m, 4 H, 2× CH_2 Bn), 4.01–3.26 (m, 8 H, 2-H, 3-H, 4-H, CH_2-6, CH_2-5 pentyl), 2.94 (m, 2 H, OCH_2-Ada), 2.78-2.45 (m, 4 H, NCH_2-1 pentyl, 1-H, 5-H), 1.95 (s, 3 H, 3× CH Ada), 1.78–1.07 (m, 24 H, 6× CH_2 Ada, 3× CH_2 butyl, 3× CH_2 pentyl), 0.89 (t, J = 6.9 Hz, 3 H) ppm. NMR (50 MHz, $CDCl_3$): δ = 139.1, 138.8, 138.2 (C_q Bn), 128.5, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6 (CH_{Ar} Bn), 88.7 (C-3), 82.1 (OCH_2-Ada), 80.6 (C2), 78.8 (C4), 75.3, 75.1, 73.5, 71.7 (4× CH_2 Bn), 67.7, 65.0 (C-6, CH_2-5 pentyl), 63.2, 62.5 (C1, C-5), 46.9 (NCH_2-1 pentyl), 39.9 (CH_2 Ada), 37.4 (CH_2 Ada), 34.3 (C_q Ada), 29.7, 29.6 (CH_2 pentyl/butyl), 28.5 (CH Ada), 27.2, 24.0, 23.5 (CH_2 pentyl/butyl), 14.5 (CH_3-4 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2900, 2847, 1450, 1358, 1065, 941, 841, 733, 694 cm^{-1}. $[\alpha]_D^{20}$ = –2.3 (c = 1.2, $CHCl_3$). HRMS: found 814.5406 $[M + H]^+$, calcd. for $[C_{54}H_{71}NO_5 + H]^+$ 814.5405.

(1*S*)-*N*-[5-(Adamant-1-ylmethoxy)pentyl]-1-*C*-butyl-1-deoxynojirimycin (34): Compound **33** (76 mg, 93 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **34** (36 mg, 79 μmol) as a colourless oil in 85% yield after purification (silica gel, 0% → 15% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.44 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.92 (dd, J = 2.7, 11.9 Hz, 1 H, 6a-H), 3.86 (dd, J = 2.5, 11.9 Hz, 1 H, 6b-H), 3.41–3.34 (m, 3 H, 4-H, CH_2-5 pentyl), 3.23 (dd, J = 9.4, 9.4 Hz, 1 H, 2-H), 3.16 (dd, J = 9.1, 9.1 Hz, 1 H, 3-H), 2.98–2.92 (m, 3 H, OCH_2-Ada, NC*H*H-1 pentyl), 2.83–2.73 (m, 1 H, NCH*H*-1 pentyl), 2.52 (d, J = 4.8 Hz, 1 H, 1-H), 2.47 (d, J = 8.1 Hz, 1 H, 5-H), 1.95 (s, 3 H, 3× CH Ada), 1.84–

1.66 (m, 7 H, 3× CH_2 Ada, C*H*H-1 butyl), 1.62–1.53 (m, 9 H, 3× CH_2 Ada, CH*H*-1 butyl, CH_2-4 pentyl), 1.45–1.29 (m, 8 H, CH_2-2 butyl, CH_2-3 butyl, CH_2-2 pentyl, CH_2-3 pentyl), 0.95 (t, J = 7.2 Hz, 3 H, CH_3-4 butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 80.2 (C-3), 72.9 (C-2), 72.4 (CH_2-5 pentyl), 71.1 (C-4), 66.1 (C-5), 64.2 (C-1), 59.4 (C-6), 48.0 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.6 (CH_2-4 pentyl), 29.9 (CH Ada), 28.9 (CH_2-1 butyl), 27.4 (CH_2-2 pentyl), 25.1, 24.5, 23.2 (3× CH_2 butyl, CH_2-3 pentyl), 14.6 (CH_3-4 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3348, 2901, 2847, 1450, 1366, 1234, 1096, 1003, 833 cm^{-1}. $[\alpha]_D^{20}$ = –1.5 (c = 0.2, MeOH). HRMS: found 454.3523 $[M + H]^+$, calcd. for $[C_{26}H_{48}NO_5 + H]^+$ 454.3527.

(1*S*)-1-*C*-[5-(Adamant-1-ylmethoxy)pentyl]-1-deoxy-*N*-hexylnojirimycin (36): Compound **35**[28] (292 mg, 220 μmol) was *N*-alkylated (see general procedure D), and the crude intermediate was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **36** (75 mg, 156 μmol) as a colourless oil in 71% yield after purification (silica gel, 0% → 10% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.49 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 3.88 (dd, J = 3.1, 11.8 Hz, 1 H, 6a-H), 3.84 (dd, J = 2.8, 11.7 Hz, 1 H, 6b-H), 3.39 (t, J = 6.5 Hz, 2 H, CH_2-5 pentyl), 3.34 (dd, J = 9.3, 9.6 Hz, 1 H, 4-H), 3.18 (dd, J = 9.0, 9.2 Hz, 1 H, 2-H), 3.11 (dd, J = 9.0, 9.3 Hz, 1 H, 3-H), 2.97 (s, 2 H, OCH_2-Ada), 2.88–2.79 (m, 1 H, NC*H*H hexyl), 2.73–2.64 (m, 1 H, NCH*H* hexyl), 2.39 (dt, J = 3.5, 9.2 Hz, 1 H, 1-H), 2.33 (dt, J = 2.9, 9.6 Hz, 1 H, 5-H), 1.95 (s, 3 H, 3× CH Ada), 1.83–1.67 (m, 7 H, 3× CH_2 Ada, CH*H*-1 pentyl), 1.66–1.51 (m, 9 H, 3× CH_2 Ada, CH*H*-1 pentyl, CH_2-4 pentyl), 1.41–1.18 (m, 14 H, CH_2-2 pentyl, CH_2-3 pentyl, CH_2-4 pentyl, 4× CH_2 hexyl), 0.91 (t, J = 7.0 Hz, 3 H, CH_3 hexyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.1 (OCH_2-Ada), 80.6 (C-3), 73.1 (C-2), 72.6 (CH_2-5 pentyl), 71.7 (C-4), 65.9 (C-5), 63.8 (C-1), 60.1 (C-1), 47.7 (NCH_2 hexyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 33.1 (CH_2 hexyl), 30.8 (CH_2-4 pentyl), 29.9 (CH Ada), 29.2 (CH_2-1 pentyl), 28.4, 28.0, 24.6, 24.0, 23.4 (2× CH_2 pentyl, 3× CH_2 hexyl), 14.6 (CH_3 hexyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3366, 2903, 2849, 1592, 1454, 1358, 1157, 1098, 1012 cm^{-1}. $[\alpha]_D^{20}$ = –2.3 (c = 0.3, MeOH). HRMS: found 482.3835 $[M + H]^+$, calcd. for $[C_{28}H_{51}NO_5 + H]^+$ 482.3840.

(1*S*)-1-*C*-[5-(Adamant-1-ylmethoxy)pentyl]-1-deoxy-*N*-nonylnojirimycin (37): Compound **35**[28] (35 mg, 46 μmol) was *N*-alkylated (see general procedure D), and the crude intermediate was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **37** (15 mg, 29 μmol) as a colourless oil in 63% yield after purification (silica gel, 0% → 10% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.53 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 3.88 (dd, J = 3.2, 11.8 Hz, 1 H, 6a-H), 3.84 (dd, J = 2.9, 11.8 Hz, 1 H, 6b-H), 3.39 (t, J = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.35 (dd, J = 9.3, 9.3 Hz, 1 H, 4-H), 3.19 (dd, J = 9.3, 9.3 Hz, 1 H, 2-H), 3.13 (dd, J = 9.0, 9.0 Hz, 1 H, 3-H), 2.97 (s, 2 H, OCH_2-Ada), 2.89–2.80 (m, 1 H, NC*H*H nonyl), 2.74–2.66 (m, 1 H, NCH*H* nonyl), 2.42 (dt, J = 3.6, 7.6 Hz, 1 H, 1-H), 2.37 (dt, J = 2.8, 9.7 Hz, 1 H, 5-H), 1.95 (s, 3 H, 3× CH Ada), 1.83–1.66 (m, 7 H, 3× CH_2 Ada, CH*H*-1 pentyl), 1.66–1.55 (m, 9 H, 3× CH_2 Ada, CH*H*-1 pentyl, CH_2-4 pentyl), 1.49-1.36 (m, 6 H, 2× CH_2 pentyl, NCH_2CH_2 nonyl), 1.36–1.18 (m, 12 H, 6× CH_2 nonyl), 0.90 (t, J = 7.0 Hz, 3 H, CH_3 nonyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2, 80.5 (C-3), 73.1 (C-2), 72.6 (CH_2-5 pentyl), 71.6 (C-4), 66.0 (C-5), 64.0 (C-1), 60.1 (C-6), 47.8 (NCH_2 nonyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 33.2 (CH_2 nonyl), 30.9 (CH_2 nonyl), 30.8 (CH_2-4 pentyl), 30.7, 30.6 (2× CH_2 nonyl), 29.9 (CH Ada), 29.3 (CH_2-1 pentyl), 28.6, 28.0, 24.8, 23.9, 23.6 (2× CH_2 pentyl, 3× CH_2 nonyl), 14.6 (CH_3 nonyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3395, 2903, 2850, 1622, 1456, 1361, 1259, 1110, 1037 cm^{-1}. $[\alpha]_D^{20}$ = –3.0 (c = 0.2, MeOH). HRMS: found 524.4304 $[M + H]^+$, calcd. for $[C_{31}H_{58}NO_5 + H]^+$ 524.4310.

(1*S*)-1-*C*,*N*-Bis[5-(adamant-1-ylmethoxy)pentyl]-1-deoxynojirimycin (38): A solution of **35**[28] (271 mg, 0.36 mmol) and **10**[25] (900 mg, 3.6 mmol) in acetonitrile/MeOH (1.8 mL, 5:1, v/v) was acidified to pH = 5–6 with AcOH (10 μL). Sodium sulfate (100 mg) and sodium cyanoborohydride (90 mg, 1.44 mmol) were added, and the reaction mixture was heated at 75 °C for 18 h. The mixture was diluted with satd. aq. $NaHCO_3$ (20 mL) and extracted with Et_2O (3× 20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Half of the resulting crude residue was subjected to Pd/C-catalyzed hydrogenolysis at 4 bar H_2 (see general procedure H). The resulting crude product was purified by silica gel column chromatography (0% → 10% MeOH in $CHCl_3$ with 0.5% NH_4OH) to give **38** (90 mg, 142 mmol) as a colourless oil in 79% yield. R_f = 0.57 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 3.89 (dd, J = 2.9, 11.9 Hz, 1 H, 6a-H), 3.85 (dd, J = 2.5, 11.8 Hz, 1 H, 6b-H), 3.41–3.37 (m, 4 H, 2× CH_2-5 pentyl), 3.35 (dd, J = 8.8, 10.2 Hz, 1 H, 4-H), 3.19 (t, J = 9.3 Hz, 1 H, 2-H), 3.12 (t, J = 9.0 Hz, 1 H, 3-H), 2.97 (s, 4 H), 2.92–2.85 (m, 1 H, NCH*H*-1 pentyl), 2.75–2.66 (m, 1 H, NCH*H*-1 pentyl), 2.45–2.40 (m, 1 H, 1-H), 2.38–2.32 (m, 1 H, 5-H), 1.95 (s, 6 H, 6× CH Ada), 1.87–1.66 (m, 14 H, 6× CH_2 Ada, 2× CH*H*-1 pentyl), 1.66–1.53 (m, 18 H, 6× CH_2 Ada, 2× CH*H*-1 pentyl, 2× CH_2-4 pentyl), 1.52–1.26 (m, 8 H, 4× CH_2 pentyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2, 83.1 (2× OCH_2-Ada), 80.5 (C-3), 73.0 (C-2), 72.5, 72.4 (2× CH_2-5 pentyl), 71.4 (C-4), 65.9 (C-5), 63.7 (C-1), 59.8 (C-6), 47.8 (NCH_2-1 pentyl), 41.1, 41.0 (2× CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.8, 30.6 (2× CH_2-4 pentyl), 29.9 (CH Ada), 29.1 (CH_2 pentyl), 28.1 (CH_2 pentyl), 25.2 (CH_2 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3368, 2902, 2848, 1452, 1157, 1111 cm^{-1}. $[\alpha]_D^{20}$ = 0.9 (c = 0.2, MeOH). HRMS: found 632.4881 $[M + H]^+$, calcd. for $[C_{38}H_{65}NO_6 + H]^+$ 632.4885.

(1*S*)-1-*C*-[(*Z*)-5-(Adamant-1-ylmethoxy)pent-1-enyl]-*N*-[5-(adamant-1-ylmethoxy)pentyl]-1-deoxynojirimycin (39): The other half of the crude product residue from the reductive amination was subjected to Pd/C-catalyzed hydrogenolysis at atmospheric H_2 pressure (see general procedure H). This resulted in a product mixture of **38** and **39**. Purification by silica gel column chromatography produced **38** (60 mg, 95 mmol) in 53% and (*Z*)-alkene **39** (47 mg, 74 mmol) in 41% yield. R_f = 0.43 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 5.72 (dt, J = 7.5, 11.0 Hz, 1 H, =CH-2 pentenyl), 5.24 (dd, J = 9.9, 11.0 Hz, 1 H, =CH-1 pentenyl), 3.93 (dd, J = 2.2, 11.9 Hz, 1 H, 6a-H), 3.82 (dd, J = 2.4, 11.9 Hz, 1 H, 6b-H), 3.47–3.34 (m, 6 H, CH_2-5 pentyl, CH_2-5 pentenyl), 3.27 (t, J = 9.5 Hz, 1 H), 3.21 (t, J = 9.2 Hz, 1 H), 3.05 (t, J = 9.1 Hz, 1 H), 2.99–2.94 (m, 5 H, 2× OCH_2-Ada), 2.90–2.79 (m, 2 H, NCH_2-1 pentyl), 2.34 (dt, J = 2.4, 9.2 Hz, 1 H, 5-H), 2.32–2.27 (m, 1 H, C*H*H-3 pentenyl), 2.25–2.17 (m, 1 H, CH*H*-3 pentenyl), 1.95 (s, 6 H, 6× CH Ada), 1.73 (dd, J = 12.3, 46.5 Hz, 12 H, 6× CH_2 Ada), 1.66–1.52 (m, 16 H, 6× CH_2 Ada, CH_2-4 pentyl, CH_2-4 pentenyl), 1.48–1.17 (m, 4 H, CH_2-2 pentyl, CH_2-3 pentyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 135.6 (=CH-2 pentenyl), 130.1 (=CH-1 pentenyl), 83.1, 83.1 (2× OCH_2-Ada), 79.5 (C-3), 74.9 (C-2), 72.6, 72.3 (CH_2-5 pentenyl/pentyl), 71.7 (C-4), 64.9 (C-5), 63.0 (C-1), 59.3 (C-6), 49.0 (NCH_2-1 pentyl), 41.1, 41.1 (CH_2-Ada), 38.5 (CH_2-Ada), 35.3 (C_q Ada), 31.0 (CH_2-4 pentyl), 30.8 (CH_2-4 pentenyl), 29.9 (CH Ada), 26.6 (CH_2-3 pentenyl), 25.3 (C-3), 22.0 (C-2) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3362, 2901, 2848, 1452, 1157, 1109, 1011 cm^{-1}. $[\alpha]_D^{20}$ = 23.7 (c = 0.4, MeOH). HRMS: found 630.4725 $[M + H]^+$, calcd. for $[C_{38}H_{63}NO_6 + H]^+$ 630.4728.

(1*S*)-1-*C*-[5-(Adamant-1-ylmethoxy)pentyl]-*N*-benzyl-1-deoxynojirimycin (40): A suspension of **3**[28] (40 mg, 101 μmol), benzyl bromide (25 μL, 211 μmol) and K_2CO_3 (42 mg, 303 μmol) in DMF (0.5 mL) was heated at 85 °C for 18 h. The reaction mixture was filtered through a glass fibre filter and concentrated. The residue was purified by silica gel column chromatography (0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH) to give **40** (35 mg, 72 μmol) as a colourless oil in 71% yield. R_f = 0.67 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 7.43 (d, J = 7.4 Hz, 2 H, *o*-CH_{Ar} Bn), 7.30 (t, J = 7.7 Hz, 2 H, *m*-CH_{Ar} Bn), 7.20 (t, J = 7.4 Hz, 1 H, *p*-CH_{Ar} Bn), 3.95–3.87 (m, 3 H, 6a-H, CH_2 Bn), 3.82 (dd, J = 4.5, 11.6 Hz, 1 H, 6b-H), 3.53 (dd, J = 9.1, 9.8 Hz, 1 H, 4-H), 3.35 (dd, J = 9.0, 9.7 Hz, 1 H, 2-H), 3.26 (t, J = 6.6 Hz, 2 H,CH_2-5 pentyl), 3.24 (dd, J = 9.0, 9.1 Hz, 1 H, 3-H), 2.93 (s, 2 H, OCH_2-Ada), 2.61 (ddd, J = 4.0, 4.5, 9.8 Hz, 1 H, 5-H), 2.56 (ddd, J = 3.5, 6.3, 9.7 Hz, 1 H, 1-H), 1.96 (s, 3 H, 3× CH Ada), 1.80–1.67 (m, 7 H, 3× CH_2 Ada, CH*H*-1 pentyl), 1.60–1.54 (m, 7 H, 3× CH_2 Ada, CH*H*-1 pentyl), 1.45–1.28 (m, 4 H, CH_2-2, CH_2-4 pentyl), 1.10–1.02 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (151 MHz, MeOD): δ = 143.1 (C_q Bn), 129.3 (*m*-CH_{Ar} Bn), 129.0 (*o*-CH_{Ar} Bn), 127.6 (*p*-CH_{Ar} Bn), 83.1 (OCH_2-Ada), 80.8 (C-3), 73.1 (C-2), 72.8 (CH_2-5 pentyl), 72.1 (C-4), 68.2 (C-5), 67.1 (C-1), 62.4 (C-6), 52.4 (CH_2 Bn), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.7 (CH_2-4 pentyl), 30.1 (CH_2-1 pentyl), 29.9 (CH Ada), 27.6 (CH_2-2 pentyl), 26.4 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3368, 2901, 2848, 1700, 1454, 1285, 1094, 729, 699 cm^{-1}. $[\alpha]_D^{20}$ = –4.0 (c = 0.5, MeOH). HRMS: found 488.3365 $[M + H]^+$, calcd. for $[C_{29}H_{45}NO_5 + H]^+$ 488.3370.

(1*S*)-1-*C*-[(*Z*)-5-(Adamant-1-ylmethoxy)pent-1-enyl]-2,3,4,6-tetra-*O*-benzyl-1-deoxynojirimycin (41): A solution of **35**[28] (151 mg, 0.2 mmol) in EtOAc (2 mL) was charged with Lindlar catalyst (25 mg). Argon was passed through the reaction mixture for 5 min, and the mixture was subsequently exposed to atmospheric hydrogen pressure for 18 h. After 18 h, the conversion was ca. 80% of a single slower running product. Longer or repeated exposure to hydrogen led to overreduction [R_f(starting material) = 0.57; R_f(overreduced product) = 0.49 (EtOAc/PE, 1:2)]. The reaction mixture was passed through a glass fibre filter and concentrated. The residue was purified by silica gel column chromatography (0% → 5% acetone in toluene) to furnish **41** (112 mg, 0.15 mmol) in 74% yield as a colourless oil (20% starting material recovered). R_f = 0.52 (EtOAc/PE, 1:2). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.36–7.16 (m, 20 H, H_{Ar} Bn), 5.62 (dt, J = 7.4, 10.8 Hz, 1 H, =CH-2 pentenyl), 5.35 (dd, J = 9.2, 10.8 Hz, 1 H, =CH-1 pentenyl), 4.91 (d, J = 10.8 Hz, 1 H, C*H*H Bn), 4.84 (m, 2 H, C*H*H Bn, CH*H* Bn), 4.73 (d, J = 10.7 Hz, 1 H, C*H*H Bn), 4.69 (d, J = 10.7 Hz, 1 H, CH*H* Bn), 4.50 (d, J = 11.0 Hz, 1 H, CH*H* Bn), 4.46 (s, 2 H, CH_2 Bn), 3.72 (dd, J = 2.6, 9.0 Hz, 1 H, 6a-H), 3.61 (dd, J = 9.0, 9.0 Hz, 1 H, 3-H), 3.50 (dd, J = 9.2, 9.2 Hz 1 H, 1-H), 3.38 (dd, J = 7.7, 8.9 Hz, 1 H, 6b-H), 3.34–3.31 (m, 3 H, 4-H, CH_2-5 pentenyl), 3.25 (dd, J = 9.2, 9.2 Hz 1 H, 2-H), 2.93–2.86 (m, 3 H, 5-H, OCH_2-Ada), 2.28–2.20 (m, 1 H, C*H*H-3 pentenyl), 2.20–2.12 (m, 1 H, CH*H*-3 pentenyl), 1.95 (s, 3 H, 3× CH Ada), 1.77 (s, 1 H, NH), 1.67 (dd, J = 11.7, 36.7 Hz, 6 H, 3× CH_2 Ada), 1.62–1.54 (m, 2 H, CH_2-4 pentenyl), 1.52 (d, J = 2.5 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.0, 138.7, 138.5, 138.1 (4× C_q Bn), 134.3 (=CH-2 pentenyl), 129.5 (=CH-1 pentenyl), 128.68, 128.63, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.96, 127.91, 127.8, 127.7 (CH_{Ar} Bn), 87.9 (C-3), 84.6 (C-2), 82.0 (OCH_2-Ada), 80.6 (C-4), 75.9, 75.4, 75.2, 73.6 (4× CH_2 Bn), 70.9 (CH_2-5 pentenyl), 71.0 (C-6), 59.1 (C-5), 56.9 (C-1), 39.9 (CH_2 Ada), 37.5 (CH_2 Ada), 34.3 (C_q Ada), 29.7 (CH_2-4 pentenyl), 28.5 (CH Ada), 25.1 (CH_2-3 pentenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3031, 2900, 2848, 1497, 1453, 1360, 1209, 1152, 1096, 1072, 1027, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = 49.4 (c = 1.0, $CHCl_3$). HRMS: found 756.4622 $[M + H]^+$, calcd. for $[C_{50}H_{61}NO_5 + H]^+$ 756.4623.

(1*S*)-1-*C*-[(*Z*)-5-(Adamant-1-ylmethoxy)pent-1-enyl]-1-deoxynojirimycin (42): Compound **41** (45 mg, 60 μmol) was subjected to a Birch reduction (see general procedure G) to produce **42** (16 mg, 40 μmol) as a colourless oil in 67% yield after purification (silica gel: 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.34 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 5.69 (dt, J = 7.6, 10.8 Hz, 1 H, =CH-2 pentenyl), 5.32 (dd, J = 9.2, 10.8 Hz, 1 H, =CH-1 pentenyl), 3.91 (dd, J = 3.1, 10.9 Hz, 1 H, 6a-H), 3.48 (dd, J = 7.9, 10.9 Hz, 1 H, 6b-H), 3.41 (t, J = 6.3 Hz, 2 H, CH_2-5 pentenyl), 3.36 (dd, J = 9.2, 9.2 Hz 1 H, 1-H), 3.28 (dd, J = 8.9, 9.1 Hz, 1 H, 3-H), 3.14 (dd, J = 8.9, 9.6 Hz, 1 H, 4-H), 3.09 (d, J = 9.1, 9.2 Hz 1 H, 2-H), 3.01–2.96 (m, 2 H, OCH_2-Ada), 2.64 (ddd, J = 3.1, 7.9, 9.6 Hz, 1 H, 5-H), 2.28–2.18 (m, 2 H, CH_2-3 pentenyl), 1.95 (s, 3 H, 3× CH Ada), 1.73 (dd, J = 11.5, 41.9 Hz, 6 H, 3× CH_2 Ada), 1.67–1.59 (m, 2 H, CH_2-4 pentenyl), 1.58 (d, J = 2.4 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 135.7 (=CH-2 pentenyl), 130.4 (=CH-1 pentenyl), 83.1 (OCH_2-Ada), 80.3 (C-3), 76.5 (C-2), 73.8 (C-4), 72.0 (CH_2-5 pentenyl), 63.8 (C-6), 62.5 (C-5), 58.5 (C-1), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.8 (CH_2-4 pentenyl), 29.9 (CH Ada), 25.9 (CH_2-3 pentenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3319, 2900, 2848, 1661, 1448, 1344, 1096, 1005 cm^{-1}. $[\alpha]_D^{20}$ = 10.5 (c = 0.3, MeOH). HRMS: found 396.2742 $[M + H]^+$, calcd. for $[C_{22}H_{37}NO_5 + H]^+$ 396.2744.

(1*S*)-1-*C*-[5-(Adamant-1-ylmethoxy)pent-1-ynyl]-1-deoxynojirimycin (43): Compound **35**[28] (149 mg, 198 μmol) was subjected to a Birch reduction for 30 min (see general procedure G) to produce a ca. 4:1 mixture of **43** and **44** after silica gel column purification (0% → 10% MeOH in $CHCl_3$ with 0.5% NH_4OH), from which **43** (19 mg, 48 μmol) could be obtained in 24% yield as a colourless oil after HPLC purification [1 min: isocratic 30% B → 11.5 min: 45% B → 12.5 min: 100% B, 20 min: isocratic 100% B; t_R(**43**) = 6.0 min; t_R(**44**) = 8.2 min]. R_f = 0.37 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.92–3.87 (m, 2 H, 1-H, 6a-H), 3.84 (dd, J = 4.9, 11.9 Hz, 1 H, 6b-H), 3.56–3.51 (m, 2 H, 2-H, 4-H), 3.48 (t, J = 6.0 Hz, 2 H, CH_2-5 pentynyl), 3.35 (dd, J = 9.1 Hz, 1 H, 3-H), 3.07 (ddd, J = 3.3, 4.9, 10.6 Hz, 1 H, 5-H), 2.98 (s, 2 H, OCH_2-Ada), 2.39 (td, J = 1.6, 7.2 Hz, 2 H, CH_2-3 pentynyl), 1.94 (s, 3 H, 3× CH Ada), 1.84–1.64 (m, 8 H, 3× CH_2 Ada, CH_2-4 pentynyl), 1.56 (d, J = 2.4 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 90.2 (C_q pentynyl), 83.1 (OCH_2-Ada), 77.9 (C-3), 73.8 (C_q pentynyl), 73.3 (C-2), 70.9 (CH_2-5 pentynyl), 69.2 (C-4), 61.5 (C-5), 59.0 (C-6), 52.4 (C-1), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 29.6 (CH_2-4 pentynyl), 16.4 (CH_2-3 pentynyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3366, 2902, 2849, 1444, 1201, 1141, 1114, 1078, 1024 cm^{-1}. $[\alpha]_D^{20}$ = –3.3 (c = 0.2, MeOH). HRMS: found 394.2586 $[M + H]^+$, calcd. for $[C_{22}H_{35}NO_5 + H]^+$ 394.2588.

(1*S*)-1-*C*-[(*E*)-5-(Adamant-1-ylmethoxy)pent-1-enyl]-1-deoxynojirimycin (44): Compound **35**[28] (100 mg, 133 μmol) was subjected to a Birch reduction for 3 h with lithium instead of sodium (see general procedure G) to produce **44** (36 mg, 92 μmol) in 70% yield as a colourless oil after purification (0% → 10% MeOH in $CHCl_3$ with 0.5% NH_4OH). R_f = 0.35 (MeOH/$CHCl_3$, 1:4 + 0.5% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 6.03 (dt, J = 6.9, 15.4 Hz, 1 H, =CH-2 pentenyl), 5.47 (dd, J = 8.7, 15.4 Hz, 1 H, =CH-1 pentenyl), 3.92 (dd, J = 3.9, 11.9 Hz, 1 H, 6a-H), 3.86 (dd, J = 2.9, 11.9 Hz, 1 H, 6b-H), 3.60–3.52 (m, 2 H, 1-H, 4-H), 3.44–3.35 (m, 7 H, 2-H, 3-H, CH_2-5 pentenyl), 3.08 (dt, J = 3.3, 10.7 Hz, 1 H, 5-H), 2.98

(s, 2 H, OCH_2-Ada), 2.23 (dd, J = 6.7, 14.4 Hz, 2 H, CH_2-3 pentenyl), 1.95 (s, 3 H, 3 × CH Ada), 1.83-1.65 (m, 8 H, 3 × CH_2 Ada, CH_2-4 pentenyl), 1.57 (d, J = 2.4 Hz, 6 H, 3 × CH_2 Ada) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 142.3 (=CH-2 pentenyl), 123.9 (=CH-1 pentenyl), 83.1 (OCH_2-Ada), 78.3 (C-3), 72.5 (C-2), 71.7 (CH_2-5 pentenyl), 69.1 (C-4), 62.9 (C-1), 61.6 (C-5), 58.6 (C-6), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.4 (C-3), 29.9 (CH Ada), 29.8 (C-4) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3366, 2904, 2850, 1440, 1203, 1140 cm^{-1}. $[\alpha]_D^{20}$ = –3.4 (c = 0.1, MeOH). HRMS: found 396.2743 [M + H]$^+$, calcd. for $[C_{22}H_{37}NO_5 + H]^+$ 396.2744.

3-(Adamant-1-ylmethoxy)prop-2-ene (45): A stirred solution of adamantylmethanol (1.38 g, 8.3 mmol) in DMF (25 mL) was cooled to 0 °C, and sodium hydride (60% in mineral oil, 0.5 g, 12.5 mmol) was added. After stirring at 0 °C for 1 h, allyl bromide (1.46 mL, 16.8 mmol) was added. The resulting mixture was warmed to ambient temperature and stirred at ambient temperature for an additional 16 h. The reaction mixture was cooled to 0 °C and quenched by addition of water. The mixture was diluted with Et_2O (200 mL) and washed with water (3 × 200 mL). The organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography (0% → 5% EtOAc in PE) to produce **45** (1.359 g, 6.59 mmol) in 80% yield as a colourless liquid. R_f = 0.67 (100% toluene). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.94–5.80 (m, 1 H, =CH-2 propenyl), 5.25 (d, J = 17.3 Hz, 1 H, =C*H*H-1 propenyl), 5.12 (d, J = 10.4 Hz, 1 H, =CH*H*-1 propenyl), 3.92 (d, J = 5.0 Hz, 2 H, CH_2-3 propenyl), 2.98 (s, 2 H, OCH_2-Ada), 1.96 (s, 3 H), 1.68 (dd, J = 12.1, 26.0 Hz, 6 H), 1.55 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.5 (=CH-2 propenyl), 116.1 (=CH_2-1 propenyl), 81.4 (OCH_2-Ada), 72.3 (CH_2-3 propenyl), 39.8 (CH_2 Ada), 37.4 (CH_2 Ada), 34.1 (C_q Ada), 28.4 (CH Ada) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2902, 2849, 1733, 1453, 1378, 1258, 1158, 1090, 989, 919 cm^{-1}. MS (ESI): found 207.2 [M + H]$^+$, calcd. for $[C_{14}H_{22}O + H]^+$ 207.2.

4-(Adamant-1-ylmethoxy)but-2-ene (46): A solution of 3-buten-1-ol (0.35 mL, 4.0 mmol) and Et_3N (0.55 mL, 4.0 mmol) in DCM (40 mL) was cooled to –40 °C, and Tf_2O (0.73 mL, 4.4 mmol) was slowly added over 30 s. The mixture was warmed to 0 °C over a period of 1 h, after which TLC analysis indicated complete conversion to the volatile intermediate triflate [R_f(triflate) = 0.80 (EtOAc/PE, 1:2)]. The crude reaction mixture was poured into a stirred suspension of anhydrous K_2CO_3 (2.76 g, 10 mmol) and adamantylmethanol (3.32 g, 20 mmol) in DCM (80 mL). The resulting mixture was refluxed at 50 °C for 20 h. The suspension was cooled to ambient temperature and filtered. The solid residue was rinsed, and the combined filtrates were concentrated. The concentrate was purified by silica gel column chromatography (2% → 5% EtOAc in PE) to afforded **46** (875 mg, 3.97 mmol) in 99% yield as a volatile colourless liquid. R_f = 0.85 (EtOAc/PE, 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.89–5.76 (m, 1 H, =CH-2 butenyl), 5.06 (d, J = 17.2 Hz, 1 H, =C*H*H-1 butenyl), 5.00 (d, J = 10.2 Hz, 1 H, =CH*H*-1 butenyl), 3.42 (t, J = 6.8 Hz, 2 H, CH_2-4 butenyl), 2.97 (s, 2 H, OCH_2-Ada), 2.36–2.26 (m, 2 H, CH_2-3 butenyl), 1.95 (s, 3 H, 3 × CH Ada), 1.68 (dd, J = 12.1, 26.2 Hz, 7 H, 3 × CH_2 Ada), 1.54 (s, 6 H, 3 × CH_2 Ada) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6 (=CH-2 butenyl), 116.1 (=CH_2-1 butenyl), 82.0 (OCH_2-Ada), 71.0 (CH_2-4 butenyl), 39.9 (CH_2 Ada), 37.4 (CH_2 Ada), 34.3 (CH_2-3 butenyl), 34.2 (C_q Ada), 28.5 (CH Ada) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2899, 2848, 1641, 1451, 1359, 1157, 1109, 992, 911 cm^{-1}. MS (ESI): found 221.4 [M + H]$^+$, calcd. for $[C_{15}H_{24}O + H]^+$ 221.2.

5-(Adamant-1-ylmethoxy)pent-2-ene (47): A stirred solution of adamantylmethanol (1.38 g, 8.3 mmol) in DMF (25 mL) was cooled to 0 °C, and sodium hydride (60% in mineral oil, 0.5 g, 12.5 mmol) was added. After stirring at 0 °C for 1 h, 5-bromopent-1-ene (2.5 g, 16.8 mmol) was added. The resulting mixture was warmed to ambient temperature and stirred at ambient temperature for an additional 16 h. The reaction mixture was cooled to 0 °C and quenched by addition of water. The mixture was diluted with Et_2O (200 mL) and washed with water (3 × 200 mL). The organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography (0% → 5% EtOAc in PE) to produce **47** (1.036 g, 4.42 mmol) in 53% yield as a volatile colourless liquid. R_f = 0.73 (100% toluene). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.82 (ddt, J = 6.6, 10.1, 16.9 Hz, 1 H, =CH-2 pentenyl), 5.09–4.88 (m, 2 H, =CH_2-1 pentenyl), 3.38 (t, J = 6.4 Hz, 2 H, CH_2-5 pentenyl), 2.95 (s, 2 H, OCH_2-Ada), 2.20–2.05 (m, 2 H, CH_2-3 pentenyl), 1.95 (s, 3 H, 3 × CH Ada), 1.64 (m, 8 H, CH_2-4 pentenyl, 3 × CH_2 Ada), 1.53 (d, J = 2.8 Hz, 6 H, 3 × CH_2 Ada) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.7 (=CH-2 pentenyl), 114.7 (=CH_2-1 pentenyl), 82.1 (OCH_2-Ada), 71.0 (CH_2-5 pentenyl), 40.0 (CH_2 Ada), 37.5 (CH_2 Ada), 34.3 (C_q Ada), 30.5, 29.1 (CH_2-3, CH_2-4 pentenyl), 28.5 (CH Ada) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2899, 2848, 1641, 1451, 1361, 1157, 1111, 1050, 990, 910 cm^{-1}. MS (ESI): found 235.3 [M + H]$^+$, calcd. for $[C_{16}H_{26}O + H]^+$ 235.2.

α/β-Mixture of 2,3,4,6-tetra-*O*-benzyl-*N*-(4-methoxybenzyl)-D-glucopyranosylamine (49): A suspension of commercially availabe 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**48**, 21.6 g, 40 mmol), (*p*-methoxybenzyl)amine (15.7 mL, 200 mmol), *p*-toluenesulfonic acid (200 mg, 1 mmol) and Na_2SO_4 (17 g, 120 mmol) in toluene (400 mL) was refluxed for 18 h. The reaction mixture was cooled to room temp., diluted with EtOAc (300 mL) and successively washed with aq. 1 M HCl (2 × 300 mL), satd. aq. $NaHCO_3$ (2 × 200 mL) and satd. aq. NaCl (200 mL). The organic phase was dried (Na_2SO_4) and concentrated to provide **49** as a white solid that was used crude in the subsequent reaction. A small sample of crude **49** was purified by silica gel column chromatography (0% → 10% EtOAc in PE) for characterization. R_f = 0.75 (EtOAc/PE, 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.10 (m, 44 H, H_{Ar}-α/β Bn/PMB), 6.83 (d, J = 7.7 Hz, 4 H, H_{Ar}-α/β PMB), 5.06–4.43 (m, 17 H, CH_2-α/β Bn, 1α-H), 4.14–4.05 (m, 2 H, C*H*H-6, C*H*H PMB), 4.03 (d, J = 8.8 Hz, 1 H, 1β-H), 3.94–3.54 (m, 20 H, OMe-α/β PMB, CH_2-α/β PMB), 3.40 (d, J = 7.2 Hz, 1 H), 3.30 (dd, J = 8.1, 8.8 Hz, 1 H, 2β-H), 2.21 (br. s, 2 H, NHPMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 158.7 (*p*-C_q-α/β PMB), 139.1, 138.9, 138.64, 138.62, 138.4, 138.3, 138.2 (C_q-α/β Bn), 132.5, 132.4 (C_q-α/β PMB), 129.6, 129.5, 128.6, 128.58, 128.55, 128.51, 128.4, 128.1, 128.06, 128.02, 127.84, 127.81, 127.78, 127.73 (CH_{Ar}-α/β Bn/PMB), 113.9, 113.9 (CH_{Ar}-α/β PMB), 90.2 (C-1β), 84.1 (C-1α), 86.1, 82.7, 82.7, 80.4, 78.4, 78.3 (C-2, C-3, C-4 α/β), 75.8 (C-5β), 75.9, 75.7, 75.1, 75.1, 75.0, 73.7, 73.6, 73.0 (CH_2-α/β Bn), 69.0 (C-5α), 69.1, 68.9 (C-6α/β), 55.4, 55.3 (OMe-α/β PMB), 49.4, 49.3 (CH_2-α/β PMB) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3318, 3030, 2864, 1611, 1514, 1454, 1354, 1244, 1121, 1058, 1028, 1011, 971, 748, 732, 693 cm^{-1}. $[\alpha]_D^{20}$ = 25.7 (c = 1.8, $CHCl_3$). HRMS: found 660.3317 [M + H]$^+$, calcd. for $[C_{42}H_{45}NO_6 + H]^+$ 660.3320.

(1*R*/*S*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-[(4-methoxybenzyl)amino]-1-*C*-(prop-2-enyl)-D-glucitol (50): Allylmagnesium bromide (1 M in Et_2O, 350 mL, 350 mmol) was slowly added over a period of 30 min to a dry and cooled (0 °C) solution of **49** (23.1 g, 35 mmol) in Et_2O (50 mL). The reaction mixture was stirred for an additional 16 h and warmed to room temp. The reaction was quenched with satd. aq. NH_4Cl, poured into Et_2O (200 mL), and washed with satd. aq. NH_4Cl (2 × 200 mL). The organic phase was dried (Na_2SO_4), concentrated and purified by silica gel column chromatography (0% → 40% EtOAc in PE) to provide **50** [2.28 g, 32.5 mmol, inseparable (*R*)/(*S*) = 9:1 isomer mixture] in 93% yield as a colourless

oil. R_f = 0.40 (EtOAc/PE, 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.17 (m, 22 H, H_{Ar} Bn, H_{Ar} PMB), 6.81 (d, J = 8.5 Hz, 2 H, H_{Ar} PMB), 5.65–5.53 (m, 1 H, =CH propenyl), 5.01–4.93 (m, 2 H, =CH_2 propenyl), 4.85 (d, J = 11.4 Hz, 1 H, C*H*H Bn), 4.78 (d, J = 11.3 Hz, 1 H, C*H*H Bn), 4.69 (d, J = 11.3 Hz, 1 H, CH*H* Bn), 4.60–4.49 (m, 5 H, CH*H* Bn, C*H*H Bn, CH_2 Bn), 4.40 (d, J = 11.4 Hz, 1 H, CH*H* Bn), 4.27 (dd, J = 2.8, 7.5 Hz, 1 H, 3-H), 4.09–4.04 (m, 1 H, 5-H), 3.87–3.78 (m, 2 H, 2-H, C*H*H PMB), 3.76 (s, 3 H, OMe PMB), 3.66–3.51 (m, 2 H, 4-H, CH_2-6, CH*H* PMB), 2.62 (t, J = 5.1 Hz, 1 H, 1-H), 2.46–2.33 (m, 1 H, C*H*H propenyl), 2.33–2.19 (m, 1 H, CH*H* propenyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8 (p-C_q PMB), 139.1, 138.6, 138.35, 138.31 (C_q Bn/PMB), 136.30 (=CH propenyl), 129.8, 128.6, 128.5, 128.3, 128.0, 127.97, 127.92, 127.6 (CH_{Ar} Bn/PMB), 117.3 (=CH_2 propenyl), 113.9 (CH_{Ar} PMB), 80.3 (C-2), 79.6 (C-3), 77.9 (C-4), 74.7, 73.6, 73.0 (4× CH_2 Bn), 71.8 (C-6), 70.8 (C-5), 57.0 (C-1), 55.5 (OMe PMB), 50.5 (CH_2 PMB), 35.2 (CH_2 propenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3031, 2863, 1610, 1513, 1454, 1245, 1067, 1028, 912, 825, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = –0.4 (c = 2.6, $CHCl_3$). HRMS: found 702.3786 [M + H]$^+$, calcd. for [$C_{45}H_{51}NO_6$ + H]$^+$ 702.3789.

(1*R*)-2,3,4,6-Tetra-*O*-benzyl-*N*-[(4-methoxybenzyl)amino]-1-*C*-(prop-2-enyl)-L-*ido*-1-deoxynojirimycin (51): Methanesulfonyl chloride (0.56 mL, 7.2 mmol) was added to a cooled (0 °C) solution of **50** (4.21 g, 6.0 mmol) in pyridine (77 mL). The mixture was stirred for 4 h, warmed to room temp., and subsequently heated at 90 °C for 16 h [R_f(mesylate) = 0.73 (EtOAc/PE, 1:2)]. The reaction mixture was concentrated, redissolved in EtOAc (100 mL) and washed extensively with aq. satd. $CuSO_4$ (5 × 50 mL). The organic phase was dried ($MgSO_4$), concentrated and purified by silica gel column chromatography (0% → 10% EtOAc in PE) to provide **51** (3.21 g, 4.68 mmol) in 78% yield as a yellow oil. R_f = 0.70 (EtOAc/PE, 1:6.5). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.20 (m, 20 H, H_{Ar} Bn), 7.16 (d, J = 8.6 Hz, 2 H, H_{Ar} PMB), 6.81 (d, J = 8.7 Hz, 2 H, H_{Ar} PMB), 5.91–5.82 (m, 1 H, =CH propenyl), 5.00–4.90 (m, 2 H, =CH_2 propenyl), 4.81 (d, J = 10.9 Hz, 1 H, C*H*H Bn), 4.79 (d, J = 10.9 Hz, 1 H, CH*H* Bn), 4.60 (d, J = 11.3 Hz, 1 H, C*H*H Bn), 4.57–4.51 (m, 3 H, CH*H* Bn, CH_2 Bn), 4.49–4.45 (m, 2 H, CH_2 Bn), 4.03 (d, J = 14.5 Hz, 1 H, C*H*H PMB), 3.98 (d, J = 14.5 Hz, 1 H, CH*H* PMB), 3.83–3.67 (m, 7 H, 3-H, 5-H, CH_2-6, OMe PMB), 3.60 (dd, J = 5.8, 8.2 Hz, 1 H, 2-H), 3.49 (dd, J = 5.6, 11.6 Hz, 1 H, 4-H), 3.20–3.16 (m, 1 H, 1-H), 2.51–2.43 (m, 1 H, C*H*H propenyl), 2.37–2.29 (m, 1 H, CH*H* propenyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7 (p-C_q PMB), 139.3 (C_q Bn), 138.9 (=CH propenyl), 138.8 (C_q Bn), 132.8 (C_q PMB), 129.8, 129.3, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6 (CH_{Ar} Bn/PMB), 115.6 (=CH_2 propenyl), 113.8 (CH_{Ar} PMB), 81.0 (C-2), 80.2 (C-3), 78.8 (C-5), 75.3, 73.4, 72.8, 72.7 (CH_2 Bn), 70.6 (C-6), 59.6 (C-1), 58.9 (C-4), 57.4 (CH_2 PMB), 55.4 (OMe PMB) 33.8 (CH_2 propenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3030, 2865, 1609, 1511, 1454, 1364, 1243, 1072, 1029, 908, 825, 733, 695 cm^{-1}. $[\alpha]_D^{20}$ = 0.5 (c = 3.8, $CHCl_3$). HRMS: found 684.3680 [M + H]$^+$, calcd. for [$C_{45}H_{49}NO_5$ + H]$^+$ 684.3684.

(1*R*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-{[(9*H*-fluoren-9-ylmethoxy)carbonyl](4-methoxybenzyl)amino}-1-*C*-(prop-2-enyl)-D-glucitol (52): Aqueous $NaHCO_3$ (10 wt.-%, 6.3 mL, 15 mmol) was added to a solution of **50** (2.1 g, 3.0 mmol) in DCM (9 mL) and (9*H*-fluoren-9-ylmethoxy)carbonyl chloride (0.93 g, 3.6 mmol). The mixture was stirred vigorously for 16 h. The mixture was diluted with EtOAc (100 mL) and washed with water (2 × 100 mL). The organic layer was dried ($MgSO_4$), concentrated and purified by silica gel column chromatography (0% → 20%, EtOAc in PE) to afford **52** (2.602 g, 2.75 mmol) in 91% yield as a white foam. R_f = 0.50 (EtOAc/PE, 1:2). ^{1}H NMR (500 MHz, C_6D_6, 343 K): δ = 7.61–6.66 (m, 32 H, CH_{Ar} Bn/PMB/Fmoc), 5.56–5.29 (m, 1 H, =CH propenyl), 4.97–3.64 (m, 21 H, 6 × CH_2 Bn/PMB/Fmoc, CH Fmoc, =CH propenyl, =CH_2, propenyl, 1-H, H2, 3-H, 4-H, CH_2-6), 3.45–3.36 (m, 3 H, OMe PMB), 2.71–2.12 (m, 2 H, CH_2 propenyl) ppm. ^{13}C NMR (125 MHz, C_6D_6, 343 K): δ = 159.5, 145.6, 144.9, 142.1, 141.5, 139.7, 139.4, 139.0, 136.6, 135.9, 134.6, 134.1, 133.1, 130.5, 129.8, 129.6, 129.3, 129.1, 128.8, 128.7, 128.4, 128.26, 128.21, 128.0, 127.9, 127.8, 127.5, 127.3, 125.5, 125.4, 124.6, 120.4, 120.3, 117.3, 114.4, 114.2, 81.0, 79.7, 78.0, 76.0, 75.4, 74.6, 74.3, 74.2, 73.9, 72.3, 67.5, 65.6, 55.2, 51.1, 48.3, 35.4 ppm. $[\alpha]_D^{20}$ = 14.5 (c = 4.9, $CHCl_3$).IR (thin film): $\tilde{\nu}_{max.}$ = 3065, 3031, 2866, 1685, 1611, 1513, 1453, 1412, 1301, 1244, 1177, 1089, 1065, 1029, 916, 735, 696 cm^{-1}. HRMS: found 946.4292 [M + Na]$^+$, calcd. for [$C_{45}H_{51}NO_6$ + Na]$^+$ 946.4289.

(1*R*)-2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-{[(9*H*-fluoren-9-ylmethoxy)carbonyl](4-methoxybenzyl)amino}-1-*C*-(prop-2-enyl)-D-*arabino*-hex-5-ulose (53): Dess–Martin periodinane (0.73 g, 1.7 mmol) was added to a solution of **52** (1.0 g, 1.43 mmol) in DCM (17 mL). After the reaction mixture had been stirred for 6 h, satd. aq. $Na_2S_2O_3$ (5 mL) and satd. aq. $NaHCO_3$ (5 mL) were added and vigorously mixed for 10 min. The mixture was diluted with EtOAc (50 mL) and washed with water (2 × 15 mL). The organic phase was dried ($MgSO_4$), concentrated and purified by silica gel column chromatography (0% → 20% EtOAc in PE) to afforded **53** (1.32 g, 1.4 mmol) in 98% yield as a white foam. R_f = 0.55 (EtOAc/PE, 1:2). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.96–6.69 (m, 32 H, CH_{Ar} Bn/PMB/Fmoc), 5.87–3.53 (m, 21 H, 6 × CH_2 Bn/PMB/Fmoc, CH Fmoc, =CH propenyl, =CH_2, propenyl, 1-H, H2, 3-H, 4-H, CH_2-6), 3.43 (s, 3 H, OMe PMB), 2.88–2.03 (m, 2 H, CH_2 propenyl) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 207.1, 159.6, 144.9, 142.24, 142.21, 139.3, 138.8, 138.4, 135.8, 129.5, 129.2, 129.1, 128.98, 128.92, 128.7, 128.6, 127.8, 127.7, 127.3, 125.6, 120.6, 118.0, 114.2, 114.1, 75.4, 73.6, 55.1, 48.1 ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2934, 1728, 1693, 1611, 1513, 1453, 1412, 1301, 1246, 1177, 1106, 1029, 917, 738, 698 cm^{-1}. HRMS: found 944.4140 [M + Na]$^+$, calcd. for [$C_{60}H_{59}NO_8$ + Na]$^+$ 944.4133.

(1*R*)-2,3,4,6-Tetra-*O*-benzyl-*N*-[(4-methoxybenzyl)amino]-1-*C*-(prop-2-enyl)-1-deoxynojirimycin (54): Piperidine (75 μL, 0.76 mmol) was added to a cooled (0 °C) solution of **53** (0.5 g, 0.725 mmol) in DMF (5 mL). The resulting mixture was stirred at 0 °C for 30 min. The mixture was diluted with Et_2O (50 mL) and washed with water (2 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated. The residue was dissolved in MeOH (15 mL), and the mixture was cooled to –35 °C. The mixture was acidified to pH = 5 with AcOH followed by the successive addition of Na_2SO_4 (280 mg, 2 mmol) and $NaCNBH_3$ (160 mg, 2.53 mmol). The reaction mixture was stirred at –20 °C under argon for 16 h. The mixture was diluted with EtOAc (50 mL) and washed with satd. aq. $NaHCO_3$ (2 × 50 mL). The organic layer was dried ($MgSO_4$), concentrated and purified by silica gel column chromatography (0% → 10% EtOAc in PE) to provide **54** (403 mg, 0.59 mmol) in 81% yield as a colourless oil. R_f = 0.30 (EtOAc/PE, 1:6.5). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38–7.15 (m, 22 H, H_{Ar} Bn/PMB), 6.80 (d, J = 8.7 Hz, 2 H, H_{Ar} PMB), 5.76–5.67 (m, 1 H, =CH propenyl), 5.02–4.92 (m, 3 H, =CH_2 propenyl, C*H*H Bn), 4.90 (d, J = 10.7 Hz, 1 H, C*H*H Bn), 4.80 (d, J = 10.9 Hz, 1 H, CH*H* Bn), 4.58 (d, J = 10.7 Hz, 1 H, CH*H* Bn), 4.51–4.46 (m, 2 H, CH_2 Bn), 4.38–4.34 (m, 2 H, CH_2 Bn), 3.95 (d, J = 13.9 Hz, 1 H, C*H*H PMB), 3.84 (dd, J = 4.9, 10.4 Hz, 1 H, 6a-H), 3.81–3.69 (m, 8 H, 6b-H, 4-H, 3-H, 2-H, CH*H* PMB, OMe PMB), 3.07–3.04 (m, 2 H, 1-H, 5-H), 2.42–2.33 (m, 2 H, CH_2 propenyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.5 (p-C_q PMB), 139.2, 138.8,

138.6, 138.3 (4× C_q Bn), 137.9 (=CH propenyl), 132.7 (C_q PMB), 129.6 (=CH propenyl), 128.5, 128.5, 128.4, 128.1, 128.0, 128.0, 127.7, 127.6, 127.6, 127.6 (CH_{Ar} Bn/PMB), 115.4 (=CH_2 propenyl), 113.6 (CH_{Ar} PMB), 84.2, 79.3, 78.8 (C-2, C-3, C-4), 75.6, 75.3, 73.0, 72.2 (4× CH_2 Bn), 68.5 (C-6), 57.5, 56.6 (C-5, C-1), 55.3 (OMe PMB), 52.2 (CH_2 PMB), 29.1 (CH_2 propenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3031, 2862, 1610, 1511, 1454, 1362, 1301, 1244, 1171, 1091, 1066, 1028, 908, 827, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = 21.5 (*c* = 3.7, $CHCl_3$). HRMS: found 684.3679 $[M + H]^+$, calcd. for $[C_{45}H_{49}NO_5 + H]^+$ 684.3684.

(1*R*)-2,3,4,6-Tetra-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1-deoxy-1-*C*-(prop-2-enyl)-L-*ido*-nojirimycin (55): Compound **51** (3.02 g, 4.41 mmol) was subjected to general procedure E to provide **55** (2.32 g, 3.31 mmol) in 75% yield as a colourless oil after purification (0% → 5% EtOAc in toluene). R_f(intermediate amine) = 0.60 (EtOAc/PE, 2:1); R_f(**55**) = 0.53 (EtOAc/PE, 1:4). ^{1}H NMR (500 MHz, C_6D_6, 343 K, major rotamer): δ = 7.38–6.96 (m, 25 H), 6.17–5.93 (m, 1 H, =CH propenyl), 5.25–4.80 (m, 7 H, 5-H, CH_2 Z, CH_2 Bn, =CH_2 propenyl), 4.66–4.28 (m, 7 H, 1-H, 3× CH_2 Bn), 3.95–3.89 (m, 2 H, 3-H, 6a-H), 3.74 (dd, *J* = 6.1, 10.1, 1 Hz, 6b-H), 3.54 (dd, *J* = 7.3, 9.3 Hz, 1 H, 4-H), 3.47 (dd, *J* = 6.7, 9.2 Hz, 1 H, 2-H), 2.82-2.71 (m, 1 H, C*H*H propenyl), 2.54–2.40 (m, 1 H, CH*H* propenyl) ppm. ^{13}C NMR (125 MHz, C_6D_6, 343 K, major rotamer): δ = 156.6 (C=O Z), 140.1, 139.2, 139.1, 137.6 (C_q Bn/Z), 137.4 (=CH propenyl), 128.8, 128.7, 128.6, 128.4, 128.3, 128.28, 128.22, 128.1, 128.0, 127.9, 127.8, 127.7 (CH_{Ar} Bn/Z), 116.5 (=CH_2 propenyl), 80.7 (C-2), 80.0 (C-4), 79.2 (C-3), 75.7, 73.7, 73.5, 73.4 (CH_2 Bn), 70.3 (C-6), 68.1 (CH_2 Z), 54.4 (C-1), 53.8 (C-5), 34.7 (CH_2 propenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3065, 3031, 2868, 1696, 1496, 1453, 1416, 1364, 1308, 1210, 1092, 1026, 995, 911, 733, 695 cm^{-1}. $[\alpha]_D^{20}$ = –9.9 (*c* = 5.5, $CHCl_3$). HRMS: found 698.3476 $[M + H]^+$, calcd. for $[C_{45}H_{48}NO_6 + H]^+$ 698.3476.

(1*R*)-2,3,4,6-Tetra-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1-deoxy-1-*C*-(prop-2-enyl)nojirimycin (56): Compound **54** (2.07 g, 3.03 mmol) was subjected to general procedure E to provide **56** (1.38 g, 1.98 mmol) in 65% yield as a colourless oil after purification (0% → 5% EtOAc in toluene). R_f(intermediate amine) = 0.65 (EtOAc/PE, 2:1); R_f(**56**) = 0.56 (EtOAc/PE, 1:4). ^{1}H NMR (600 MHz, $CDCl_3$, major rotamer): δ = 7.44–7.16 (m, 25 H, CH_{Ar} Bn Z), 5.85 (s, 1 H, =CH propenyl), 5.14–5.09 (m, 2 H, CH_2 Z), 4.98–4.88 (m, 2 H, =CH_2 propenyl), 4.68–4.33 (m, 9 H, 1-H, 4× CH_2 Bn), 4.28–4.23 (m, 1 H, 5-H), 3.98 (dd, *J* = 2.0, 3.6 Hz, 1 H, 4-H), 3.88 (d, *J* = 8.3 Hz, 1 H, 3-H), 3.75 (dd, *J* = 5.5, 8.1 Hz, 1 H, 2-H), 3.66 (s, 1 H, 6a-H), 3.56 (s, 1 H, 6b-H), 2.65–2.59 (m, 1 H, C*H*H propenyl), 2.59–2.52 (m, 1 H, CH*H* propenyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.0 (C=O Z), 138.4, 138.3, 138.3, 137.9 (C_q Bn), 136.7 (=CH propenyl), 136.5 (C_q Z), 128.6, 128.57, 128.52, 128.45, 128.41, 128.3, 128.2, 128.17, 128.12, 128.05, 128.02, 127.98, 127.95, 127.86, 127.82, 127.79, 127.74, 127.5, 127.3 (CH_{Ar} Bn/Z), 116.1 (=CH_2 propenyl), 81.5 (C-3), 80.6 (C-2), 77.0 (C-4), 73.0, 72.5, 72.3, 71.7 (4× CH_2 Bn), 69.9 (C-6), 67.3 (CH_2 Z), 54.6 (C-5), 52.8 (C-1), 34.1 (CH_2 propenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3032, 2871, 1698, 1495, 1453, 1417, 1270, 1206, 1093, 1026, 995, 913, 734, 694 cm^{-1}. $[\alpha]_D^{20}$ = 9.2 (*c* = 4.6, $CHCl_3$). HRMS: found 698.3477 $[M + H]^+$, calcd. for $[C_{45}H_{48}NO_6 + H]^+$ 698.3476.

α/β-Mixture of 2,3,4-Tri-*O*-benzyl-D-xylopyranose (58): A dry and cooled (0 °C) solution of D-xylose (**57**; 10 g, 66.6 mmol) in DMF (333 mL) was charged with sodium hydride (60% in mineral oil, 11.72 g, 293 mmol) and stirred at 0 °C for 1 h. Next, benzyl bromide (34 mL, 286 mmol) was added to the suspension over a period of 5 min. The reaction mixture was stirred for 20 h and warmed to room temp. The reaction mixture was quenched with water and concentrated. The residue was dissolved in Et_2O (400 mL) and washed successively with water (300 mL) and satd. aq. NaCl (200 mL). The organic phase was dried (Na_2SO_4) and concentrated to provide a yellow oil that was used crude in the next reaction [R_f(tetrabenzylated intermediate) = 0.69 (EtOAc/PE, 1:3)]. The crude intermediate was suspended in a mixture of AcOH (210 mL) and aq. 1 M HCl (93 mL) and refluxed at 105 °C for 4 h, after which TLC analysis indicated complete consumption of the starting material. The reaction mixture was concentrated and coevaporated with toluene (2× 200 mL). The residue was transferred into aq. satd. $NaHCO_3$ (400 mL) and extracted with EtOAc (3× 300 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The product was precipitated from PE/EtOAc to provide **58** (11.34 g, 27 mmol) as a white fluffy solid after drying at 50 °C for 20 h. The mother liquor was concentrated and purified by silica gel column chromatography (10% → 33% EtOAc in PE) to provide additional **49** (4.10 g, 9.76 mmol) and an overall yield of 55%. R_f = 0.20 (EtOAc/PE, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, major α-anomer): δ = 7.40–7.25 (m, 15 H, H_{Ar} Bn), 5.08 (d, *J* = 2.1 Hz, 1 H, 1α-H), 4.90–4.82 (m, 2 H, CH_2 Bn), 4.76–4.60 (m, 4 H, 2× CH_2 Bn), 3.87 (dd, *J* = 9.1 Hz, 1 H, 3-H), 3.79 (dd, *J* = 10.6 Hz, 1 H, 5a-H), 3.65 (dd, *J* = 4.8, 11.8 Hz, 1 H, 5b-H), 3.59–3.50 (m, 1 H, 4-H), 3.47 (d, *J* = 8.9 Hz, 1 H, 2-H), 3.29 (s, 1 H, OH-1) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, α/β-mixture): δ = 138.8, 138.4, 138.0 (C_q Bn), 128.7, 128.6, 128.5, 128.2, 127.9, 127.8 (CH_{Ar} Bn), 97.9 (C-1β), 91.6 (C-1α), 83.4 (C-3β), 82.6 (C-2β), 80.7 (C-3α), 79.6 (C-2α), 77.8 (C-4β), 77.7 (C-4α), 75.7 (CH_2 Bn α), 75.6 (CH_2 Bn β), 74.9 (CH_2 Bn β), 73.5 (CH_2 Bn α), 73.4 (CH_2 Bn β), 73.3 (CH_2 Bn α), 63.9 (C-5β), 60.4 (C-5α) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3040, 2870, 1599, 1454, 1357, 1071, 1060, 747, 693 cm^{-1}. $[\alpha]_D^{20}$ = +16.3 (*c* = 0.6, $CHCl_3$). MS (ESI): found 421.3 $[M + H]^+$, calcd. for $[C_{26}H_{28}O_5 + H]^+$ 421.2.

α/β-Mixture of 2,3,4-Tri-*O*-benzyl-*N*-(4-methoxybenzyl)-D-xylopyranosylamine (59): A suspension of **58** (2.1 g, 5 mmol), (*p*-methoxybenzyl)amine (6.5 mL, 50 mmol), (±)-camphor-10-sulfonic acid (1.162 g, 5 mmol) and Na_2SO_4 (2.8 g, 20 mmol) in toluene (50 mL) was refluxed for 2.5 h, after which TLC analysis indicated complete consumption of **58** (R_f = 0.20 in EtOAc/PE, 1:3). The reaction mixture was cooled to room temp., diluted with EtOAc (200 mL) and successively washed with aq. 1 M HCl (2× 200 mL), satd. aq. $NaHCO_3$ (2× 100 mL) and satd. aq. NaCl (100 mL). The organic phase was dried (Na_2SO_4) and concentrated to provide **59** as a white solid that was used crude in the subsequent reaction. A small sample of crude **59** was purified by silica gel column chromatography (10% → 25% EtOAc in PE) for characterization. R_f = 0.55 (EtOAc/PE, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.20 (m, 34 H, H_{Ar}-α/β Bn/PMB), 6.90–6.80 (m, 4 H, H_{Ar}-α/β PMB), 4.99–4.58 (m, 11 H, CH_2-α/β Bn), 4.50–4.44 (m, 2 H, 1α-H, C*H*-α Bn), 4.03–3.75 (m, 14 H, 1β-H, OMe-α/β PMB, CH_2-α/β PMB), 3.63–3.56 (m, 4 H), 3.56–3.44 (m, 4 H), 3.24–3.13 (m, 2 H), 2.05–1.79 (m, 1 H, NHPMB), 1.75–1.48 (m, 1 H, NHPMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 158.8 (*p*-C_q-α/β PMB), 138.9, 138.7, 138.7, 138.5, 138.3 (C_q-α/β Bn), 132.5, 132.4 (C_q-α/β PMB), 129.6, 129.5, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8 (CH_{Ar}-α/β Bn/PMB), 114.0, 113.9 (CH_{Ar}-α/β PMB), 90.7 (C-1β), 84.2 (C-1α), 85.2, 82.3, 80.2, 79.3, 78.6, 77.7 (H-2, H-3, H-4 α/β), 75.9, 75.3, 75.2, 73.5, 73.2, 73.1 (CH_2-α/β Bn), 65.2 (C-5β), 60.3 (C-5α), 55.5, 55.5 (OMe-α/β PMB), 49.5 (CH_2-β PMB), 49.1 (CH_2-α PMB) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3302, 3030, 2861, 1611, 1514, 1455, 1358, 1242, 1179, 1071, 1030, 933, 894, 814, 748, 693 cm^{-1}. $[\alpha]_D^{20}$ = 0.8 (*c* = 0.5, $CHCl_3$). MS (ESI): found 540.4 $[M + H]^+$, calcd. for $[C_{34}H_{37}NO_5 + H]^+$ 540.3.

(1*R*/*S*)-2,3,4-Tri-*O*-benzyl-1-deoxy-1-[(4-methoxybenzyl)amino]-1-*C*-(prop-2-enyl)-D-xylitol (60): Allylmagnesium bromide (1 M in Et_2O, 23 mL, 23 mmol) was slowly added over a period of 2 min to a dry and cooled (0 °C) solution of **59** (2.14 g, 2.3 mmol) in THF (23 mL). The reaction mixture was stirred at 0 °C for an additional 5 min and then warmed to room temp. After stirring at room temp. for 1 h, the reaction was quenched with satd. aq. NH_4Cl. The mixture was poured into additional satd. aq. NH_4Cl (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic phases were dried (Na_2SO_4), concentrated and purified by silica gel column chromatography (10% → 50% EtOAc in PE) to provide **60** [1.31 g, 2.25 mmol, inseparable (*R*)/(*S*) = 5:1 isomer mixture] in 97% yield as a colourless oil. R_f = 0.11 (EtOAc/PE, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.18 (m, 15 H, H_{Ar} Bn), 7.16 (d, *J* = 8.6 Hz, 2 H, H_{Ar} PMB), 6.79 (d, *J* = 8.7 Hz, 2 H, H_{Ar} PMB), 5.71–5.51 (m, 1 H, =CH propenyl), 5.01–4.91 (m, 2 H, =CH_2 propenyl), 4.80 (d, *J* = 11.4 Hz, 1 H, C*H*H Bn), 4.75 (d, *J* = 11.4 Hz, 1 H, C*H*H Bn), 4.67 (d, *J* = 11.4 Hz, 1 H, CH*H* Bn), 4.58–4.50 (m, 2 H, C*H*H Bn, CH*H* Bn), 4.37 (d, *J* = 11.7 Hz, 1 H, CH*H* Bn), 4.07 (dd, *J* = 4.1, 7.0 Hz, 1 H, 3-H), 3.81–3.60 (m, 7 H, 2-H, CH_2-5, C*H*H PMB, OMe PMB), 3.51 (d, *J* = 12.7 Hz, 1 H, CH*H* PMB), 3.44–3.35 (m, 1 H, 4-H), 2.64–2.57 (m, 1 H, 1-H), 2.48–2.31 (m, 2 H, CH_2 propenyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5 (*p*-C_q PMB), 138.7, 138.3, 138.2 (C_q Bn), 136.0 (=CH propenyl), 132.5 (C_q PMB), 129.6, 129.2, 128.2, 127.9, 127.8, 127.6, 127.5, 127.3 (CH_{Ar} Bn/PMB), 116.9 (=CH_2 propenyl), 113.5 (CH_{Ar} PMB), 79.9, 79.8, 78.5 (C-2, C-3, C-4), 74.5, 74.1, 71.9 (CH_2 Bn), 61.5 (C-5), 56.0 (C-1), 55.0 (OMe PMB), 50.2 (CH_2 PMB), 35.1 (CH_2 propenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2868, 1610, 1513, 1454, 1245, 1028, 913, 824, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = –17.7 (*c* = 3.3, $CHCl_3$). HRMS: found 582.3209 [M + H]$^+$, calcd. for [$C_{37}H_{44}NO_5$ + H]$^+$ 582.3214.

(1*R*)-2,3,4-Tri-*O*-benzyl-1,5-dideoxy-1,5-imino-*N*-[(4-methoxybenzyl)amino]-1-*C*-(prop-2-enyl)-D-xylitol (61): Diethyl azodicarboxylate (1.8 mL, 3.92 mmol, 2.2 M in toluene) was added over a period of 1 min to a dry solution of **60** (1.14 g, 1.96 mmol) and PPh_3 (1.03 g, 3.92 mmol) in DCM (10 mL). The reaction mixture was stirred for 20 h and subsequently quenched by addition of water. The mixture was concentrated and purified by silica gel column chromatography (0% → 20% EtOAc in toluene) to produce **61** (976 mg, 1.73 mmol) in 88% yield as a colourless oil.[45] R_f = 0.60 (EtOAc/PE, 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.08 (m, 17 H, H_{Ar} Bn/PMB), 6.78 (d, *J* = 8.7 Hz, 2 H, H_{Ar} PMB), 5.92–5.79 (m, 1 H, =CH propenyl), 5.14–4.37 (m, 8 H, =CH_2 propenyl, 3 × CH_2 Bn), 3.73–3.46 (m, 8 H, 2-H, 3-H, 4-H, OMe PMB, CH_2 PMB), 3.13 (dt, *J* = 4.9, 7.6 Hz, 1 H, 1-H), 2.78 (dd, *J* = 5.2, 12.3 Hz, 1 H, 5a-H), 2.53 (dd, *J* = 10.5, 11.9 Hz, 1 H, 5b-H), 2.49–2.32 (m, 2 H, CH_2 propenyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6 (*p*-C_q PMB), 139.2, 138.6, 138.5 (3 × C_q Bn), 138.2 (=CH propenyl), 131.0 (C_q PMB), 129.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.3, 127.2 (CH_{Ar} Bn/PMB), 115.3 (=CH_2 propenyl), 113.5 (CH_{Ar} PMB), 82.6, 80.3, 78.2 (C2, C-3, C-4), 75.2, 72.5, 72.2 (3 × CH_2 Bn), 59.5 (C-2), 58.0 (CH_2 PMB), 54.8 (OMe PMB), 47.7 (C-5), 27.6 (CH_2 propenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3031, 2904, 1610, 1512, 1455, 1364, 1244, 1069, 1029, 908, 822, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = 27.1 (*c* = 2.8, $CHCl_3$). HRMS: found 564.3103 [M + H]$^+$, calcd. for [$C_{37}H_{41}NO_4$ + H]$^+$ 544.3108.

(1*R*)-2,3,4-Tri-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1,5-dideoxy-1,5-imino-1-*C*-(prop-2-enyl)-D-xylitol (62): Compound **61** (1.42 g, 2.52 mmol) was subjected to general procedure E to provide **62** (1.27 g, 2.20 mmol) in 87% yield as a colourless oil after purification (0% → 5% EtOAc in toluene). R_f(intermediate amine) = 0.11 (EtOAc/PE, 1:1 + 2% Et_3N); R_f(**62**) = 0.50 (EtOAc/PE, 1:4). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers, a/b ≈ 1:1): δ = 7.41–7.20 (m, 40 H, $H_{Ar}^{a/b}$ Bn Z), 5.78–5.65 (m, 1 H, =CH^a propenyl), 5.62–5.50 (m, 1 H, =CH^b propenyl), 5.16–4.90 (m, 8 H, $CH_2^{a/b}$ Z, =$CH_2^{a/b}$ propenyl), 4.89–4.81 (m, 4 H, $CH_2^{a/b}$ Bn), 4.77–4.72 (m, 1 H, 1^a-H), 4.72–4.59 (m, 8 H, 2 × $CH_2^{a/b}$ Bn), 4.45–4.39 (m, 2 H, 1^b-H, C*H*H-5^a), 4.17 (dd, *J* = 5.7, 13.7 Hz, 1 H, CH*H*-5^a), 3.68 (dd, *J* = 8.6, 8.6 Hz, 2 H, 3$^{a/b}$-H), 3.60–3.37 (m, 4 H, 2$^{a/b}$-H, 4$^{a/b}$-H), 2.80–2.70 (m, 2 H, CH_2-5^b), 2.64–2.50 (dd, 2 H, C*H*H$^{a/b}$ propenyl), 2.35–2.25 (dt, 2 H, CH*H*$^{a/b}$ propenyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers, a/b ≈ 1:1): δ = 155.7, 155.6 (C=O$^{a/b}$ Z), 138.9, 138.2, 138.2 (3 × $C_q^{a/b}$ Bn), 136.7, 136.6 ($C_q^{a/b}$ Z), 134.5, 134.4 (=$CH^{a/b}$ propenyl), 128.65, 128.61, 128.5, 128.4, 128.27, 128.22, 128.1, 128.08, 128.03, 127.96, 127.92, 127.8, 127.7 ($CH_{Ar}^{a/b}$ Bn Z), 117.6, 117.4 (=$CH_2^{a/b}$ propenyl), 82.2, 82.0 (C-3$^{a/b}$), 79.8 (C-2$^{a/b}$), 78.4, 78.3 (C-4$^{a/b}$), 75.8 ($CH_2^{a/b}$ Bn), 73.3 (CH_2^a Bn), 73.2 ($CH_2^{a/b}$ Bn), 72.8 (CH_2^b Bn), 67.6, 67.5 ($CH_2^{a/b}$ Z), 53.0, 52.3 (C-1$^{a/b}$), 41.1, 40.8 (C-5$^{a/b}$), 29.8, 29.7 ($CH_2^{a/b}$ propenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3032, 2872, 1698, 1495, 1453, 1423, 1349, 1314, 1209, 1095, 1026, 991, 913, 734, 695 cm^{-1}. $[\alpha]_D^{20}$ = 13.8 (*c* = 3.4, $CHCl_3$). HRMS: found 578.2899 [M + H]$^+$, calcd. for [$C_{37}H_{39}NO_5$ + H]$^+$ 578.2801.

(1*R*)-1-*C*-[(*E*/*Z*)-4-(Adamant-1-ylmethoxy)but-2-enyl]-2,3,4,6-tetra-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1-deoxy-L-*ido*-nojirimycin (63): Compound **55** (275 mg, 395 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **45** to produce **63** (306 mg, 349 μmol) in 88% yield as a mixture of (*E*)/(*Z*) isomers in an unassignable ca. 2:1 ratio after purification (0% → 10% EtOAc in PE). R_f = 0.47 (EtOAc/PE, 1:5). ^{1}H NMR [400 MHz, $CDCl_3$, (*E*)/(*Z*) isomers]: δ = 7.45–7.19 (m, 25 H, H_{Ar} Bn Z H), 5.83–5.40 (m, 2 H, =CH-2 butenyl, =CH-3 butenyl), 5.23–4.93 (m, 3 H, 5-H, CH_2 Z), 4.93–4.39 (m, 9 H, 1-H, 4 × CH_2 Bn), 3.99–3.45 (m, 7 H, 2-H, 3-H, 4-H, CH_2-6, CH_2-4 butenyl), 2.98–2.84 (m, 2 H, OCH_2-Ada), 2.75–2.52 (m, 2 H, CH_2-4 butenyl), 2.42–2.24 (m, 2 H, CH_2-1 butenyl), 2.06–1.84 (m, 3 H, 3 × CH Ada), 1.83–1.43 (m, 12 H, 6 × CH_2 Ada) ppm. ^{13}C NMR [100 MHz, $CDCl_3$, (*E*)/(*Z*) isomers]: δ = 156.4 (C=O Z), 139.0, 138.4 (C_q Bn), 131.3, 131.1, 129.9, 129.3 [=CH (*E*)/(*Z*) butenyl], 128.6, 128.5, 128.5, 128.2, 128.1, 127.9, 127.7, 127.5 [=CH (*E*)/(*Z*) butenyl, CH_{Ar} Bn/Z], 81.3 (OCH_2-Ada), 80.2 (C-2), 79.6 (C-4), 78.7 (C-3), 75.9, 74.1, 73.6, 73.4, 73.1 (CH_2 Bn), 72.2 (CH_2-4 butenyl), 69.6 (C-6), 67.8 (CH_2 Z), 54.1, 53.5, 53.2, 52.7 (C-1, C-5), 40.0 (CH_2 Ada), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 33.0, 33.0 (CH_2-1 butenyl), 28.5 (CH Ada) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3032, 2900, 2848, 1698, 1453, 1403, 1360, 1302, 1209, 1069, 1026, 734, 695 cm^{-1}. $[\alpha]_D^{20}$ = –6.0 (*c* = 0.6, $CHCl_3$). HRMS: found 876.4840 [M + H]$^+$, calcd. for [$C_{57}H_{65}NO_7$ + H]$^+$ 876.4834.

(1*R*)-1-*C*-[(*E*/*Z*)-5-(Adamant-1-ylmethoxy)pent-2-enyl]-2,3,4,6-tetra-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1-deoxy-L-*ido*-nojirimycin (64): Compound **55** (275 mg, 395 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **46** to produce **64** (260 mg, 292 μmol) in 74% yield as a mixture of (*E*)/(*Z*) isomers in an unassignable ca. 2:1 ratio after purification (0% → 10% EtOAc in PE). R_f = 0.50 (EtOAc/PE, 1:5). ^{1}H NMR [400 MHz, $CDCl_3$, (*E*)/(*Z*) isomers]: δ = 7.48–7.14 (m, 25 H, H_{Ar} Bn Z H H), 5.87–5.23 (m, 2 H, =CH-2 pentenyl, =CH-3 pentenyl), 5.23–4.92 (m, 3 H, 5-H, CH_2 Z), 4.92–4.36 (m, 9 H, 1-H, 4 × CH_2 B), 3.97–3.44 (m, 5 H, 2-H, 3-H, 4-H, CH_2-6), 3.40–3.17 (m, 2 H, CH_2-5 pentenyl), 2.99–2.86 (m, 2 H, OCH_2-Ada), 2.77–2.47 (m, 1 H, C*H*H-1 pentenyl), 2.40–2.09 (m, 3 H, CH*H*-1 pentenyl, CH_2-4 pentenyl), 2.09–1.87 (m, 3 H, 3 × CH Ada), 1.81–1.43 (m, 12 H, 6 × CH_2 Ada) ppm. ^{13}C NMR [100 MHz, $CDCl_3$, (*E*)/(*Z*) isomers]: δ = 156.4 (C=O Z), 138.9, 138.5, 138.2, 138.1 (C_q Bn), 136.6 (C_q Z), 131.2, 130.9 [=CH (*E*)/(*Z*) pentenyl], 128.5, 128.4, 128.3, 128.1,

128.07, 128.03, 127.99, 127.92, 127.7, 127.6, 127.3 (CH_{Ar} Bn Z), 126.9, 126.7, 125.6 [=CH (*E*)/(*Z*) pentenyl], 81.9 (OCH_2-Ada), 80.1, 79.5, 79.4, 79.2, 78.9, 78.8, 78.7, 78.6 (C-2, C-3, C-4), 75.8, 75.7, 73.9, 73.4, 73.1, 72.9, 72.5, 72.2, 72.0, 71.9, 71.4 (CH_2 Bn, CH_2-5 pentenyl), 69.1 (C-6), 67.7 (CH_2 Z), 54.6, 53.9, 53.6, 53.2, 52.5 (C-1, C-5), 39.8, 39.6, 39.1 (CH_2 Ada), 37.3, 37.2, 37.2 (CH_2 Ada), 34.5, 34.1, 33.7 (C_q Ada), 32.7 (CH_2-1 pentenyl), 28.4, 28.2, 28.1 (CH Ada, CH_2-4 pentenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2902, 2849, 1698, 1453, 1416, 1271, 1093, 1026, 734, 695 cm^{-1}. $[\alpha]_D^{20}$ = –7.8 (*c* = 1.0, $CHCl_3$). HRMS: found 890.4996 $[M + H]^+$, calcd. for $[C_{58}H_{67}NO_7 + H]^+$ 890.4990.

(1*R*)-1-*C*-[(*E*/*Z*)-6-(Adamant-1-ylmethoxy)hex-2-enyl]-2,3,4,6-tetra-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1-deoxy-L-*ido*-nojirimycin (65): Compound **55** (275 mg, 395 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **47** to produce **65** (312 mg, 345 μmol) in 87% yield as a mixture of (*E*)/(*Z*) isomers in an unassignable ca. 2:1 ratio after purification (0% → 10% EtOAc in PE). R_f = 0.52 (EtOAc/PE, 1:5). ^1H NMR [400 MHz, $CDCl_3$, (*E*)/(*Z*) isomers]: δ = 7.45–7.14 (m, 25 H, H_{Ar} Bn Z H), 5.58–5.24 (m, 2 H, =CH-2 hexenyl, =CH-3 hexenyl), 5.23–4.98 (m, 3 H, 5-H, CH_2 Z), 4.94–4.37 (m, 9 H, 1-H, 4× CH_2 Bn), 3.95–3.45 (m, 5 H, 2-H, 3-H, 4-H, CH_2-6), 3.38–3.26 (m, 2 H, CH_2-6 hexenyl), 2.93 (s, 2 H, OCH_2-Ada), 2.79–2.51 (m, 1 H, C*H*H-1 hexenyl), 2.32–2.18 (m, 1 H, CH*H*-1 hexenyl), 2.09–1.80 (m, 5 H, CH_2-4 hexenyl, 3× CH Ada), 1.77–1.40 (m, 16 H, CH_2-5 hexenyl, 6× CH_2 Ada) ppm. ^{13}C NMR [100 MHz, $CDCl_3$, (*E*)/(*Z*) isomers]: δ = 156.5 (C=O Z), 139.0, 138.5, 138.4, 138.3, 137.9 (C_q Bn), 136.8, 136.6 (C_q Z), 132.4, 132.3, 130.9 [=CH (*E*)/(*Z*) hexenyl], 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.4 [=CH (*E*)/(*Z*) hexenyl, CH_{Ar} Bn Z], 127.1, 127.0 [=CH (*E*)/(*Z*) hexenyl], 82.0 (OCH_2-Ada), 80.3, 80.2 (C-2), 79.5 (C-4), 78.7, 78.7 (C-3), 75.9, 75.8, 73.6, 73.4, 73.3, 73.1 (CH_2 Bn), 71.3, 71.2, 71.1 (CH_2-6 hexenyl), 69.9, 69.7 (C-6), 67.8, 67.7 (CH_2 Z), 55.5, 54.3, 53.8, 53.4, 53.2, 52.7 (C-1, C-5), 39.9 (CH_2 Ada), 37.4 (CH_2 Ada), 34.3 (C_q Ada), 33.2, 32.8 (CH_2-1 hexenyl), 29.6, 29.3 (CH_2 hexenyl), 28.5 (CH Ada), 27.6, 27.2 (CH_2 hexenyl), 24.3, 24.2 (CH_2 hexenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3031, 2901, 2848, 1698, 1453, 1416, 1364, 1273, 1094, 1026, 734, 695 cm^{-1}. $[\alpha]_D^{20}$ = –10.5 (*c* = 2.0, $CHCl_3$). HRMS: found 904.5153 $[M + H]^+$, calcd. for $[C_{59}H_{69}NO_7 + H]^+$ 904.5147.

(1*R*)-1-*C*-[(*E*/*Z*)-4-(Adamant-1-ylmethoxy)but-2-enyl]-2,3,4,6-tetra-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1-deoxynojirimycin (66): Compound **56** (275 mg, 395 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **45** to produce **66** (303 mg, 346 μmol) in 87% yield as a 3.3:1 mixture of (*E*)/(*Z*) isomers after purification (0% → 10% EtOAc in PE). R_f = 0.51 (EtOAc/PE, 1:5). ^1H NMR [400 MHz, $CDCl_3$, (*E*) isomer]: δ = 7.45–7.19 (m, 25 H, H_{Ar} Bn Z), 5.74–5.40 (m, 2 H, =CH-2 butenyl, =CH-3 butenyl), 5.21–5.06 (m, 2 H, CH_2 Z), 4.72–4.38 (m, 8 H, 4× CH_2 Bn), 4.33 (s, 1 H, 1-H), 4.22 (s, 1 H, 5-H), 4.00–3.70 (m, 5 H, 2-H, 3-H, 4-H, CH_2-4 butenyl), 3.68–3.51 (m, 2 H, CH_2-6), 2.89 (s, 2 H, OCH_2-Ada), 2.66–2.47 (m, 2 H, CH_2-1 butenyl), 1.93 (s, 3 H, 3× CH Ada), 1.73–1.45 (m, 12 H, 6× CH_2 Ada) ppm. ^{13}C NMR [100 MHz, $CDCl_3$, (*E*) isomer]: δ = 156.0 (C=O Z), 138.5, 138.4, 138.4, 138.0 (4× C_q Bn), 136.7 (C_q Z), 131.4 [=CH-2 (*E*) isomer butenyl], 130.3 [=CH-2 (*Z*) isomer butenyl], 128.8, 128.77, 128.74, 128.69, 128.64, 128.58, 128.52, 128.51, 128.36, 128.33, 128.28, 128.24, 128.05, 128.02, 127.9, 127.8, 127.6, 127.4 [=CH-3 (*E*)/(*Z*) butenyl, CH_{Ar} Bn Z], 81.6 (C-3), 81.2 (OCH_2-Ada), 80.8 (C-2), 77.2 (C-4), 73.1, 72.7, 72.4, 72.3, 71.8 (CH_2 Bn, CH_2-4 butenyl), 70.0 (C-6), 67.4 (CH_2 Z), 54.7 (C-5), 53.1 (C-1), 39.9 (CH_2 Ada), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 32.8 (CH_2-1 butenyl), 28.5 (CH Ada) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3032, 2900, 2848, 1698, 1453, 1403, 1302, 1209, 1069, 1026, 734, 695 cm^{-1}. $[\alpha]_D^{20}$ = 6.5 (*c* = 2.8, $CHCl_3$). HRMS: found 876.4840 $[M + H]^+$, calcd. for $[C_{57}H_{65}NO_7 + H]^+$ 876.4834.

(1*R*)-1-*C*-[(*E*/*Z*)-5-(Adamant-1-ylmethoxy)pent-2-enyl]-2,3,4,6-tetra-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1-deoxynojirimycin (67): Compound **56** (275 mg, 395 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **46** to produce **67** (289 mg, 325 μmol) in 82% yield as a 2.5:1 mixture of (*E*)/(*Z*) isomers after purification (0% → 10% EtOAc in PE). R_f = 0.53 (EtOAc/PE, 1:5). ^1H NMR [400 MHz, $CDCl_3$, (*E*) isomer]: δ = 7.47–7.15 (m, 25 H, H_{Ar} Bn Z), 5.55–5.29 (m, 2 H, =CH-2 pentenyl, =CH-3 pentenyl), 5.19–5.07 (m, 2 H, CH_2 Z), 4.74–4.39 (m, 8 H, 4× CH_2 Bn), 4.39–4.27 (m, 1 H, 1-H), 4.27–4.16 (m, 1 H, 5-H), 3.99–3.91 (m, 1 H, 4-H), 3.88–3.76 (m, 1 H, 3-H), 3.73 (dd, *J* = 5.5, 9.0 Hz, 1 H, 2-H), 3.71–3.50 (m, 2 H, CH_2-6), 3.26 (t, *J* = 7.1 Hz, 2 H, CH_2-5 pentenyl), 2.90 (s, 2 H, OCH_2-Ada), 2.62–2.48 (m, 2 H, CH_2-1 pentenyl), 2.29–2.09 (m, 2 H, CH_2-4 pentenyl), 1.93 (s, 3 H, 3× CH Ada), 1.77–1.45 (m, 12 H, 6× CH_2 Ada) ppm. ^{13}C NMR [100 MHz, $CDCl_3$, (*E*) isomer]: δ = 156.2 (C=O Z), 138.5 (C_q Bn), 129.8, 129.5, 129.0, 128.78, 128.74, 128.6, 128.59, 128.54, 128.47, 128.44, 128.3, 128.2, 128.0, 127.9, 127.85, 127.82, 127.7, 127.5, 127.1 [=CH-2, =CH-3 (*E*)/(*Z*) pentenyl, CH_{Ar} Bn Z], 82.1 (OCH_2-Ada), 81.8 (C-3), 80.8 (C-2), 77.3 (C-4), 73.1, 72.7, 72.4, 71.9, 71.7 (CH_2 Bn, CH_2-5 pentenyl), 70.1 (C-6), 67.4 (CH_2 Z), 54.7 (C-5), 53.0 (C-1), 39.9 (CH_2 Ada), 37.5 (CH_2 Ada), 34.3 (C_q Ada), 33.2 (CH_2-1 pentenyl), 28.5 (CH Ada), 28.0 (CH_2-4 pentenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2902, 2849, 1698, 1453, 1404, 1268, 1090, 1069, 1026, 734, 695 cm^{-1}. $[\alpha]_D^{20}$ = 3.4 (*c* = 1.1, $CHCl_3$). HRMS: found 890.4996 $[M + H]^+$, calcd. for $[C_{58}H_{67}NO_7 + H]^+$ 890.4990.

(1*R*)-1-*C*-[(*E*/*Z*)-6-(Adamant-1-ylmethoxy)hex-2-enyl]-2,3,4,6-tetra-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1-deoxynojirimycin (68): Compound **56** (275 mg, 395 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **47** to produce **68** (305 mg, 338 μmol) in 85% yield as a 2:1 mixture of (*E*)/(*Z*) isomers after purification (0% → 10% EtOAc in PE). R_f = 0.55 (EtOAc/PE, 1:5). ^1H NMR [400 MHz, $CDCl_3$, (*E*) isomer]: δ = 7.41–7.12 (m, 25 H, H_{Ar} Bn Z H), 5.52–5.27 (m, 2 H, =CH-2 hexenyl, =CH-3 hexenyl), 5.16–5.06 (m, 2 H, CH_2 Z), 4.68–4.38 (m, 8 H, 4× CH_2 Bn), 4.38–4.28 (m, 1 H, 1-H), 4.24–4.14 (m, 1 H, 5-H), 3.98–3.91 (m, 1 H, 4-H), 3.90–3.83 (m, 1 H, 3-H), 3.77–3.69 (m, 1 H, 2-H), 3.69–3.50 (m, 2 H, CH_2-6), 3.36–3.21 (m, 2 H, CH_2-6 hexenyl), 2.97–2.87 (m, 2 H, OCH_2-Ada), 2.61–2.39 (m, 2 H, CH_2-1 hexenyl), 2.07–1.88 (m, 5 H, CH_2-4 hexenyl, 3× CH Ada), 1.77–1.45 (m, 14 H, CH_2-5 hexenyl, 6× CH_2 Ada) ppm. ^{13}C NMR [100 MHz, $CDCl_3$, (*E*) isomer]: δ = 156.1 (C=O Z), 138.5, 138.5, 138.4, 138.1 (C_q Bn), 136.7 (C_q Z), 131.9 [=CH-3 (*E*) hexenyl], 130.5 [=CH-3 (*Z*) hexenyl], 128.78, 128.72, 128.54, 128.52, 128.4, 128.36, 128.32, 128.29, 128.24, 128.06, 128.02, 127.97, 127.95, 127.7, 127.68, 127.64, 127.4 [=CH-2 (*E*)/(*Z*) hexenyl, CH_{Ar} Bn Z], 82.0 (OCH_2-Ada), 81.8 (C-3), 80.8 (C-2), 77.4 (C-4), 73.1, 72.8, 72.4, 72.0, 71.3 (CH_2 Bn, CH_2-6 hexenyl), 70.0 (C-6), 67.4 (CH_2 Z), 54.7 (C-5), 53.4 (C-1), 39.9 (CH_2 Ada), 37.5 (CH_2 Ada), 34.3 (C_q Ada), 32.8 (CH_2-1 hexenyl), 29.3 (CH_2-5 hexenyl), 28.5 (CH Ada), 23.9 (CH_2-4 hexenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3031, 2901, 2848, 1698, 1453, 1403, 1361, 1267, 1210, 1089, 1070, 1026, 734, 695 cm^{-1}. $[\alpha]_D^{20}$ = 4.8 (*c* = 2.8, $CHCl_3$). HRMS: found 904.5152 $[M + H]^+$, calcd. for $[C_{59}H_{69}NO_7 + H]^+$ 904.5147.

(1*R*)-1-*C*-[(*E*/*Z*)-4-(Adamant-1-ylmethoxy)but-2-enyl]-2,3,4-tri-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1,5-dideoxy-1,5-imino-D-xylitol (69): Compound **62** (200 mg, 346 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **45** to produce

69 (170 mg, 225 μmol) in 65% yield as a 5:1 mixture of (*E*)/(*Z*) isomers after purification (0% → 10% EtOAc in PE). R_f = 0.51 (EtOAc/PE, 1:4). ^{1}H NMR [500 MHz, $CDCl_3$, (*E*) isomer rotamers, a/b ≈ 1:1]: δ = 7.39–7.21 (m, 40 H, $H_{Ar}^{a/b}$ Bn Z), 5.61–5.51 (m, 3 H, =CH-3$^{a/b}$ butenyl, =CH-2^a butenyl), 5.49–5.39 (m, 1 H, =CH-2^b butenyl), 5.16–5.02 (m, 4 H, $CH_2^{a/b}$ Z), 4.91–4.81 (m, 4 H, $CH_2^{a/b}$ Bn), δ = 4.75–4.57 (m, 9 H, 2× $CH_2^{a/b}$ Bn, 1^a-H), 4.48–4.38 (m, 2 H, 1^b-H, C*H*H-5^a), 4.16 (dd, *J* = 5.7, 13.6 Hz, 1 H, CH*H*-5^a), 4.00–3.71 (m, 4 H, CH_2-4$^{a/b}$ butenyl), 3.68 (dd, *J* = 9.2, 9.4 Hz, 2 H, 3$^{a/b}$-H), 3.56 (dd, *J* = 5.9, 9.4 Hz, 1 H, 2^a-H), 3.53–3.35 (m, 3 H, 2^b-H, 4$^{a/b}$-H), 2.98–2.85 (m, 4 H, OCH_2-Ada$^{a/b}$), 2.79–2.69 (m, 2 H, CH_2-5^b), 2.63–2.51 (m, 2 H, C*H*H-1$^{a/b}$ butenyl), 2.36–2.26 (m, 2 H, CH*H*-1$^{a/b}$ butenyl), 1.94 (s, 6 H, 6× CH Ada$^{a/b}$) 1.67 (dd, *J* = 11.7, 30.7 Hz, 12 H, 6× CH_2 Ada$^{a/b}$), 1.51 (s, 12 H, 6× CH_2 Ada$^{a/b}$) ppm. ^{13}C NMR [125 MHz, $CDCl_3$, (*E*) isomer rotamers, a/b ≈ 1:1]: δ = 155.5, 155.5 (C=O$^{a/b}$ Z), 138.9, 138.3, 138.2, 138.1, 138.0 (3× $C_q^{a/b}$ Bn), 136.7, 136.6 ($C_q^{a/b}$ Z), 130.3, 130.1 (=CH-3$^{a/b}$ butenyl), 128.9 (=CH-2^a butenyl), 128.65, 128.62, 128.57, 128.55, 128.52, 128.4, 128.27, 128.23, 128.06, 128.02, 127.98, 127.96 (=CH-2^b butenyl, $CH_{Ar}^{a/b}$ Bn/Z), 82.1, 82.0 (C-3$^{a/b}$), 81.1, 81.0 (OCH_2-Ada$^{a/b}$), 79.7 (C-2$^{a/b}$), 78.3, 78.2 (C-4$^{a/b}$), 75.8, 75.8, 73.3, 73.2, 72.8 ($CH_2^{a/b}$ Bn), 71.8, 71.7 (CH_2-4$^{a/b}$ butenyl), 67.5, 67.5 ($CH_2^{a/b}$ Z), 53.1, 52.3 (C-1$^{a/b}$), 41.1, 40.8 (C-5$^{a/b}$), 39.8 ($CH_2^{a/b}$ Ada), 37.3 ($CH_2^{a/b}$ Ada), 34.1, 34.1 ($C_q^{a/b}$ Ada), 28.4 (CH $^{a/b}$ Ada), 28.3, 28.2 (CH-1$^{a/b}$ butenyl). IR (thin film): $\tilde{\nu}_{max.}$ = 2901, 2848, 1700, 1452, 1423, 1352, 1314, 1238, 1199, 1158, 1097, 970, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = –7.8 (*c* = 1.6, $CHCl_3$). HRMS: found 778.4076 [M + Na]$^+$, calcd. for [$C_{49}H_{57}NO_6$ + Na]$^+$ 778.4078.

(1*R*)-1-*C*-[(*E*/*Z*)-5-(Adamant-1-ylmethoxy)pent-2-enyl]-2,3,4-tri-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1,5-dideoxy-1,5-imino-D-xylitol (70): Compound **62** (200 mg, 346 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **46** to produce **70** (190 mg, 247 μmol) in 71% yield as a 2:1 mixture of (*E*)/(*Z*) isomers after purification (0% → 10% EtOAc in PE). R_f = 0.53 (EtOAc/PE, 1:4). ^{1}H NMR [500 MHz, $CDCl_3$, (*E*)/(*Z*) isomers, Z rotamers, a/b ≈ 1:1]: δ = 7.38–7.21 (m, 40 H, $H_{Ar}^{a/b}$ Bn Z), 5.53–5.42 (m, 2 H, =CH-3$^{a/b}$ pentenyl), 5.42–5.34 (m, 1 H, =CH-2^a pentenyl), 5.28–5.20 (m, 1 H, =CH-2^b pentenyl), 5.17–4.99 (m, 4 H, $CH_2^{a/b}$ Z), 4.91–4.80 (m, 4 H, $CH_2^{a/b}$ Bn), 4.76–4.60 (m, 9 H, 2× $CH_2^{a/b}$ Bn, 1^a-H), 4.45–4.36 (m, 2 H, 1^b-H, C*H*H-5^a), 4.22–4.13 (m, 1 H, CH*H*-5^a), 3.73–3.64 (m, 2 H, 3$^{a/b}$-H), 3.56 (dd, *J* = 5.9, 9.4 Hz, 1 H, 2^a-H), 3.53–3.25 (m, 7 H, 2^b-H, 4$^{a/b}$-H, CH_2-5$^{a/b}$ pentenyl), 2.98–2.88 (m, 4 H, OCH_2-Ada$^{a/b}$), 2.77–2.70 (m, 2 H, CH_2-5^b), 2.59–2.10 (m, 8 H, CH_2-1$^{a/b}$, CH_2-4$^{a/b}$ pentenyl), 1.95 (s, 6 H, 6× CH Ada$^{a/b}$), 1.67 (dd, *J* = 11.7, 29.8 Hz, 12 H, 6× CH_2 Ada$^{a/b}$), 1.56–1.50 (m, 12 H, 6× CH_2 Ada$^{a/b}$) ppm. ^{13}C NMR [125 MHz, $CDCl_3$, (*E*)/(*Z*) isomers, Z rotamers, a/b ≈ 1:1]: δ = 155.63, 155.61, 155.57, 155.53 [C=O$^{a/b}$ (*E*)/(*Z*) Z], 138.9, 138.3, 138.27, 138.25, 138.23, 138.21 [3× $C_q^{a/b}$ (*E*)/(*Z*) Bn], 136.76, 136.72, 136.68, 136.61 [$C_q^{a/b}$ (*E*)/(*Z*) Z] 130.1, 129.8 [=CH-3$^{a/b}$ (*E*) pentenyl], 128.8, 128.7, 128.66, 128.62, 128.61, 128.5, 128.4, 128.26, 128.22, 128.06, 128.05, 128.02, 127.98, 127.95, 127.93, 127.8, 127.7 [=CH-3$^{a/b}$ (*Z*) pentenyl, $CH_{Ar}^{a/b}$ (*E*)/(*Z*) Bn Z], 127.4, 127.3 [=CH-2$^{a/b}$ (*E*) pentenyl], 126.8, 126.7 [=CH-2$^{a/b}$ (*Z*) pentenyl], 82.3, 82.2, 82.14, 82.11 [C-3$^{a/b}$ (*E*)/(*Z*)], 82.1, 82.07, 82.0, 82.02 [OCH_2-Ada$^{a/b}$ (*E*)/(*Z*)], 79.95, 79.92, 79.85, 79.82 [C-2$^{a/b}$ (*E*)/(*Z*)], 78.4, 78.38, 78.33 [C-4$^{a/b}$ (*E*)/(*Z*)], 75.96, 75.94, 75.87, 75.82, 73.37, 73.34, 73.22, 73.20, 73.1, 72.9, 72.7 [$CH_2^{a/b}$ (*E*)/(*Z*) Bn], 71.6, 71.4, 71.2, 71.1 [CH_2-5$^{a/b}$ (*E*)/(*Z*) pentenyl], 67.6, 67.59, 67.54, 67.4 [$CH_2^{a/b}$ (*E*)/(*Z*) Z], 53.5, 53.2, 53.0, 52.9 [C-1$^{a/b}$ (*E*)/(*Z*)], 41.15, 41.12, 40.9, 40.8 [C-5$^{a/b}$ (*E*)/(*Z*)], 39.9 [$CH_2^{a/b}$ (*E*)/(*Z*) Ada], 37.4 [$CH_2^{a/b}$ (*E*)/(*Z*) Ada], 34.2 [$C_q^{a/b}$ (*E*)/(*Z*) Ada], 33.1, 33.0 [CH_2-4$^{a/b}$ (*E*)/(*Z*) pentenyl], 28.6, 28.5, 28.2 [CH_2-1$^{a/b}$ (*E*)/(*Z*) pentenyl], 28.4 (CH$^{a/b}$ Ada), 23.2 [CH_2-1$^{a/b}$ (*E*)/(*Z*) pentenyl]. IR (thin film) ppm. $\tilde{\nu}_{max.}$ = 2901, 2848, 1700, 1453, 1423, 1360, 1314, 1237, 1198, 1158, 1098, 970, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = –11.6 (*c* = 1.7, $CHCl_3$).HRMS: found 770.4416 [M + H]$^+$, calcd. for [$C_{50}H_{59}NO_6$ + H]$^+$ 770.4415.

(1*R*)-1-*C*-[(*E*/*Z*)-6-(Adamant-1-ylmethoxy)hex-2-enyl]-2,3,4-tri-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1,5-dideoxy-1,5-imino-D-xylitol (71): Compound **62** (200 mg, 346 μmol) underwent a cross-metathesis reaction (see general procedure F) with alkene **47** to produce **71** (222 mg, 280 μmol) in 82% yield as a 3:1 mixture of (*E*)/(*Z*) isomers after purification (0% → 10% EtOAc in PE). R_f = 0.55 (EtOAc/PE, 1:4). ^{1}H NMR [500 MHz, $CDCl_3$, (*E*)/(*Z*) isomers, Z rotamers, a/b ≈ 1:1]: δ = 7.39–7.19 (m, 40 H, $H_{Ar}^{a/b}$ Bn/Z), 5.52–5.39 (m, 2 H, =CH-3$^{a/b}$ hexenyl), 5.37–5.29 (m, 1 H, =CH-2^a hexenyl), 5.25–5.18 (m, 1 H, =CH-2^b hexenyl), 5.15–5.01 (m, 4 H, $CH_2^{a/b}$ Z), 4.90–4.80 (m, 4 H, $CH_2^{a/b}$ Bn), 4.73–4.59 (m, 9 H, 2× $CH_2^{a/b}$ Bn, 1^a-H), 4.45–4.36 (m, 2 H, 1^b-H, C*H*H-5^a), 4.20–4.13 (m, 1 H, CH*H*-5^a), 3.71–3.65 (m, 2 H, 3$^{a/b}$-H), 3.59–3.53 (m, 1 H, 2^a-H), 3.53–3.43 (m, 2 H, 2^b-H, 4^a-H), 3.43–3.37 (m, 1 H, 4^b-H), 3.36–3.29 (m, 4 H, CH_2-6$^{a/b}$ hexenyl), 2.97–2.92 (m, 4 H, OCH_2-Ada$^{a/b}$), 2.79–2.70 (m, 2 H, CH_2-5^b), 2.57–1.93 (m, 14 H, CH_2-1$^{a/b}$, CH_2-4$^{a/b}$ hexenyl, 6× CH Ada$^{a/b}$), 1.74–1.48 (m, 28 H, CH_2-5$^{a/b}$ hexenyl, 12× CH_2 Ada$^{a/b}$) ppm. ^{13}C NMR [125 MHz, $CDCl_3$, (*E*)/(*Z*) isomers, Z rotamers, a/b ≈ 1:1]: δ = 155.7, 155.6, 155.57, 155.55 [C=O$^{a/b}$ (*E*)/(*Z*) Z], 139.0, 138.9, 138.3, 138.28, 138.23, 138.21, 138.20 [3× $C_q^{a/b}$ (*E*)/(*Z*) Bn], 136.75, 136.72, 136.66, 136.63 [$C_q^{a/b}$ (*E*)/(*Z*) Z], 133.3, 133.0 [=CH-3$^{a/b}$ (*E*) hexenyl], 132.1, 131.9 [=CH-3$^{a/b}$ (*Z*) hexenyl], 128.68, 128.63, 128.59, 128.55, 128.4, 128.2, 128.06, 128.02, 128.01, 127.97, 127.95, 127.93, 127.92, 127.87, 127.85, 127.6 [$H_{Ar}^{a/b}$ (*E*)/(*Z*) Bn Z], 125.9, 125.7 [=CH-2$^{a/b}$ (*E*) hexenyl], 125.6, 125.4 [=CH-2$^{a/b}$ (*Z*) hexenyl], 82.4, 82.26, 82.25 [C-3$^{a/b}$ (*E*)/(*Z*)], 82.1, 82.05, 82.03 [OCH_2-Ada$^{a/b}$ (*E*)/(*Z*)], 79.9, 79.8 [C-2$^{a/b}$ (*E*)/(*Z*)], 78.4, 78.3, 78.2 [C-4$^{a/b}$ (*E*)/(*Z*)], 75.9, 75.84, 75.83, 75.82, 73.34, 73.33, 73.2, 73.1, 72.9, 72.7 [$CH_2^{a/b}$ (*E*)/(*Z*) Bn], 71.03, 71.01, 70.8 [CH_2-6$^{a/b}$ (*E*)/(*Z*) hexenyl], 67.54, 67.51, 67.50, 67.4 [$CH_2^{a/b}$ (*E*)/(*Z*) Z], 53.6, 53.3, 53.0, 52.4 [C-1$^{a/b}$ (*E*)/(*Z*)], 41.1, 41.1, 40.9, 40.8 [C-5$^{a/b}$ (*E*)/(*Z*)], 39.9 [$CH_2^{a/b}$ (*E*)/(*Z*) Ada], 37.4, 37.4 [$CH_2^{a/b}$ (*E*)/(*Z*) Ada], 34.2 [$C_q^{a/b}$ (*E*)/(*Z*) Ada], 29.6, 29.54, 29.51, 29.3, 29.2, 28.9, 28.52, 28.51 [$CH_2^{a/b}$ (*E*)/(*Z*) hexenyl], 28.42, 28.41 (CH$^{a/b}$ Ada), 24.21, 24.20, 23.0, 22.9 [$CH_2^{a/b}$ (*E*)/(*Z*) hexenyl] ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2901, 2848, 1700, 1452, 1423, 1360, 1314, 1239, 1206, 1157, 1098, 969, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = –10.4 (*c* = 2.0, $CHCl_3$). HRMS: found 784.4572 [M + H]$^+$, calcd. for [$C_{51}H_{61}NO_6$ + H]$^+$ 784.4572.

(1*R*)-2,3,4-Tri-*O*-benzyl-*N*-[(benzyloxy)carbonyl]-1,5-dideoxy-1,5-imino-1-*C*-[(*E*/*Z*)-non-2-enyl]-D-xylitol (72): Compound **62** (200 mg, 346 μmol) underwent a cross-metathesis reaction (see general procedure F) with oct-1-ene to produce **72** (197 mg, 297 μmol) in 86% yield as a 5:1 mixture of (*E*)/(*Z*) isomers after purification (0% → 10% EtOAc in PE). R_f = 0.61 (EtOAc/PE, 1:4). ^{1}H NMR [500 MHz, $CDCl_3$, (*E*) isomer rotamers, a/b ≈ 1:1]: δ = 7.41–7.03 (m, 40 H, $H_{Ar}^{a/b}$ Bn Z), 5.39–5.30 (m, 2 H, =CH-3$^{a/b}$ nonenyl), 5.24–5.17 (m, 1 H, =CH-2^a nonenyl), 5.13–5.06 (m, 1 H, =CH-2^b nonenyl), 5.06–4.93 (m, 4 H, $CH_2^{a/b}$ Z), 4.82–4.72 (m, 4 H, $CH_2^{a/b}$ Bn), 4.65–4.50 (m, 9 H, 2× $CH_2^{a/b}$ Bn, 1^a-H), 4.35–4.27 (m, 2 H, 1^b-H, C*H*H-5^a), 4.07 (dd, *J* = 5.7, 13.7 Hz, 1 H, CH*H*-5^a), 3.63–3.55 (m, 2 H, 3$^{a/b}$-H), 3.47 (dd, *J* = 5.9, 9.5 Hz, 1 H, 2^a-H), 3.44–3.36 (m, 2 H, 2^b-H, 4^a-H), 3.32 (ddd, *J* = 5.9, 8.8, 11.2 Hz, 1 H, 4^b-H), 2.68–2.62 (m, 2 H, CH_2-5^b), 2.50–2.34 (m, 2 H, C*H*H-1$^{a/b}$ nonenyl), 2.19–2.09 (m, 2 H, CH*H*-1$^{a/b}$ nonenyl), 1.87–1.74 (m, 4 H, CH_2-4$^{a/b}$ nonenyl), 1.29–1.11 (m, 16 H, 4× $CH_2^{a/b}$ nonenyl), 0.83–0.75 (m, 6 H, CH_3-9$^{a/b}$ nonenyl) ppm. ^{13}C NMR [125 MHz,

$CDCl_3$, (*E*) isomer rotamers, a/b ≈ 1:1]: δ = 155.8, 155.6 (C=O$^{a/b}$ Z), 139.0, 138.4, 138.33, 138.31, 138.2 (3× $C_q^{a/b}$ Bn), 136.8, 136.7 ($C_q^{a/b}$ Z), 134.0, 133.7 (=CH-3$^{a/b}$ nonenyl), 128.7, 128.67, 128.62, 128.61, 128.5, 128.2, 128.16, 128.12, 128.07, 128.03, 128.02, 127.96, 127.92, 127.7 ($CH_{Ar}^{a/b}$ Bn/Z), 125.5, 125.3 (=CH-2$^{a/b}$ nonenyl), 82.3, 82.1 (C-3$^{a/b}$), 80.0 (C-2$^{a/b}$), 78.5, 78.4 (C-4$^{a/b}$), 75.9, 75.9, 73.4, 73.3, 73.2, 72.8 ($CH_2^{a/b}$ Bn), 67.54, 67.53 ($CH_2^{a/b}$ Z), 53.3, 52.5 (C-1$^{a/b}$), 41.1, 40.8 (C-5$^{a/b}$), 32.8, 32.7 (CH_2-4$^{a/b}$ nonenyl), 31.9 ($CH_2^{a/b}$ nonenyl), 29.6, 29.5 ($CH_2^{a/b}$ nonenyl), 29.1, 29.0 ($CH_2^{a/b}$ nonenyl), 28.6, 28.5 (CH_2-1$^{a/b}$ nonenyl), 22.8 ($CH_2^{a/b}$ nonenyl), 14.3 (CH_3-9 nonenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 2926, 2855, 1700, 1454, 1423, 1359, 1313, 1203, 1096, 968, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = –11.9 (*c* = 1.7, $CHCl_3$). HRMS: found 662.3839 [M + H]$^+$, calcd. for $[C_{43}H_{51}NO_5 + H]^+$ 662.3840.

(1*R*)-1-*C*-[4-(Adamant-1-ylmethoxy)butyl]-1-deoxy-L-*ido*-nojirimycin (73): Compound **63** (141 mg, 161 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **73** (33 mg, 86 μmol) as a colourless oil in 53% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 25% B → 11.5 min: 45% B → 12.5 min: 100% B, 15 min: isocratic 100% B; t_R = 9.0 min). R_f = 0.49 (MeOH/$CHCl_3$, 1:3 + 2% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 4.02 (dd, *J* = 3.5, 3.5 Hz, 1 H, 3-H), 3.93–3.90 (m, 1 H, 4-H), 3.90–3.88 (m, 1 H, 2-H), 3.87–3.81 (m, 2 H, CH_2-6), 3.54–3.50 (m, 1 H, 5-H), 3.44–3.39 (m, 3 H, 1-H, CH_2-4 butyl), 2.98 (s, 2 H, OCH_2-Ada), 2.00–1.92 (m, 4 H, C*H*H-1 butyl, 3× CH Ada), 1.79–1.66 (m, 7 H, CH*H*-1 butyl, 3× CH_2 Ada), 1.66–1.58 (m, 2 H, CH_2-3 butyl), 1.58–1.50 (m, 7 H, 3× CH_2 Ada, C*H*H-2 butyl), 1.46–1.38 (m, 1 H, CH*H*-2 butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.3 (OCH_2-Ada), 72.3 (CH_2-4 butyl), 69.2 (C-4), 69.0 (C-2), 68.2 (C-3), 60.6 (C-6), 58.8 (C-5), 56.9 (C-5), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.6 (CH_2-3 butyl), 29.9 (CH Ada), 28.9 (CH_2-1 butyl), 22.9 (CH_2-2 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3328, 2902, 2848, 1451, 1068, 996 cm^{-1}. $[\alpha]_D^{20}$ = –14.0 (*c* = 0.2, MeOH). HRMS: found 384.2747 [M + H]$^+$, calcd. for $[C_{21}H_{37}NO_5 + H]^+$ 384.2744.

(1*R*)-1-*C*-[5-(Adamant-1-ylmethoxy)pentyl]-1-deoxy-L-*ido*-nojirimycin (74): Compound **64** (139 mg, 156 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **74** (46 mg, 116 μmol) as a colourless oil in 73% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 10% B → 12 min: 100% B → 12 min: 100% B, 15 min: isocratic 100% B; t_R = 7.4 min). R_f = 0.50 (MeOH/$CHCl_3$, 1:3 + 2% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 4.02 (t, *J* = 3.5 Hz, 1 H, 3-H), 3.93–3.91 (m, 1 H, 4-H), 3.91–3.88 (m, 1 H, 2-H), 3.86–3.80 (m, 2 H, CH_2-6), 3.54–3.50 (m, 1 H, 5-H), 3.43–3.38 (m, 3 H, 1-H, CH_2-5 pentyl), 2.97 (s, 2 H, OCH_2-Ada), 2.00–1.91 (m, 4 H, C*H*H-1 pentyl, 3× CH Ada), 1.79–1.65 (m, 7 H, CH*H*-1 pentyl, 3× CH_2 Ada), 1.64–1.57 (m, 2 H, CH_2-4 pentyl), 1.56 (d, *J* = 2.2 Hz, 6 H, 3× CH_2 Ada), 1.53–1.41 (m, 3 H, C*H*H-2 pentyl, CH_2-3 pentyl), 1.41–1.33 (m, 1 H, CH*H*-2 pentyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 72.5 (CH_2-5 pentyl), 69.2 (C-4), 69.0 (C-2), 68.2 (C-3), 60.6 (C-6), 58.8 (C-5), 56.9 (C-1), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.6 (CH_2-4 pentyl), 29.9 (CH Ada), 29.0 (CH_2-1 pentyl), 27.3 (CH_2-3 pentyl), 25.9 (CH_2-2 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3331, 2902, 2849, 1590, 1451, 1259, 1068, 998 cm^{-1}. $[\alpha]_D^{20}$ = –14.3 (*c* = 0.3, MeOH). HRMS: found 398.2897 [M + H]$^+$, calcd. for $[C_{22}H_{39}NO_5 + H]^+$ 398.2901.

(1*R*)-1-*C*-[6-(Adamant-1-ylmethoxy)hexyl]-1-deoxy-L-*ido*-nojirimycin (75): Compound **65** (154 mg, 170 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **75** (51 mg, 124 μmol) as a colourless oil in 73% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 10% B → 12 min: 100% B → 12 min: 100% B, 15 min: isocratic 100% B; t_R = 7.8 min). R_f = 0.53 (MeOH/$CHCl_3$, 1:3 + 2% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 4.02 (dd, *J* = 3.5 Hz, 1 H, 3-H), 3.92–3.90 (m, 1 H, 4-H), 3.90–3.87 (m, 1 H, 2-H), 3.86–3.80 (m, 2 H, CH_2-6), 3.53–3.49 (m, 1 H, 5-H), 3.43–3.37 (m, 3 H, 1-H, CH_2-6 hexyl), 2.97 (s, 2 H, OCH_2-Ada), 1.99–1.91 (m, 4 H, C*H*H-1 hexyl, 3× CH Ada), 1.79–1.65 (m, 7 H, CH*H*-1 hexyl, 3× CH_2 Ada), 1.60–1.54 (m, 8 H, CH_2-5 hexyl, 3× CH_2 Ada), 1.51–1.31 (m, 6 H, 3× CH_2 hexyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 72.7 (CH_2-6 hexyl), 69.2 (C-4), 69.0 (C-2), 68.2 (C-3), 60.6 (C-6), 58.8 (C-5), 57.0 (C-1), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.7 (CH_2-5 hexyl), 30.5 (CH_2 hexyl), 29.9 (CH Ada), 29.0 (CH_2-1 hexyl), 27.3 (CH_2 hexyl), 26.1 (CH_2 hexyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3327, 2901, 2848, 1590, 1451, 1203, 1111, 1068, 999 cm^{-1}. $[\alpha]_D^{20}$ = –11.0 (*c* = 0.3, MeOH). HRMS: found 412.3055 [M + H]$^+$, calcd. for $[C_{23}H_{41}NO_5 + H]^+$ 412.3057.

(1*R*)-1-*C*-[4-(Adamant-1-ylmethoxy)butyl]-1-deoxynojirimycin (76): Compound **66** (155 mg, 177 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **76** (38 mg, 99 μmol) as a colourless oil in 56% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 25% B → 11.5 min: 45% B → 12.5 min: 100% B, 15 min: isocratic 100% B; t_R = 8.3 min). R_f = 0.32 (MeOH/$CHCl_3$, 1:3 + 2% NH_4OH). ^{1}H NMR (500 MHz, MeOD): δ = 3.90–3.80 (m, 2 H, CH_2-6), 3.73 (dd, *J* = 4.1, 7.1 Hz, 1 H, 2-H), 3.64 (dd, *J* = 7.0, 7.1 Hz, 1 H, 3-H), 3.49 (dd, *J* = 7.0, 7.0 Hz, 1 H, 4-H), 3.41 (t, *J* = 6.2 Hz, 2 H, CH_2-4 butyl), 3.38–3.32 (m, 1 H, 1-H), 3.22–3.14 (m, 1 H, 5-H), 2.97 (s, 2 H, OCH_2-Ada), 1.94 (s, 3 H, 3× CH Ada), 1.91–1.85 (m, 1 H, C*H*H-1 butyl), 1.71 (dd, *J* = 12.1, 39.6 Hz, 7 H, 3× CH_2 Ada), 1.65–1.58 (m, 3 H, CH*H*-1 butyl, CH_2-3 butyl), 1.58–1.54 (m, 7 H, 3× CH_2 Ada), 1.54–1.44 (m, 2 H, CH_2-2 butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.3 (OCH_2-Ada), 74.1 (C-3), 72.4 (CH_2-4 butyl), 72.0 (C-2), 71.5 (C-4), 60.7 (C-6), 58.3 (C-5), 56.2 (C-1), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.7 (CH_2-3 butyl), 29.9 (CH Ada), 26.8 (CH_2-1 butyl), 24.1 (CH_2-2 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3326, 2902, 2848, 1594, 1452, 1362, 1157, 1094 cm^{-1}. $[\alpha]_D^{20}$ = 10.9 (*c* = 0.2, MeOH). HRMS: found 384.2746 [M + H]$^+$, calcd. for $[C_{21}H_{37}NO_5 + H]^+$ 384.2744.

(1*R*)-1-*C*-[5-(Adamant-1-ylmethoxy)pentyl]-1-deoxynojirimycin (77): Compound **67** (148 mg, 155 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **77** (54 mg, 136 μmol) as a colourless oil in 82% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 10% B → 12 min: 100% B → 12 min: 100% B, 15 min: isocratic 100% B; t_R = 7.2 min). R_f = 0.33 (MeOH/$CHCl_3$, 1:3 + 2% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 4.00 (dd, *J* = 7.1, 12.0 Hz, 1 H, 6a-H), 3.83 (dd, *J* = 3.8, 12.0 Hz, 1 H, 6b-H), 3.78 (dd, *J* = 3.6, 6.5 Hz, 1 H, 2-H), 3.72 (t, *J* = 6.5, 6.6 Hz, 1 H, 3-H), 3.63 (t, *J* = 6.6, 6.6 Hz, 1 H, 4-H), 3.47 (td, *J* = 3.6, 6.9 Hz, 1 H, 1-H), 3.40 (t, *J* = 6.3 Hz, 2 H, CH_2-5 pentyl), 3.36–3.32 (m, 1 H, 5-H), 2.97 (s, 2 H, OCH_2-Ada), 1.98–1.91 (m, 4 H, C*H*H-1 pentyl, 3× CH Ada), 1.72 (dd, *J* = 11.9, 48.4 Hz, 6 H, 3× CH_2 Ada), 1.66–1.57 (m, 3 H, CH*H*-1 pentyl, CH_2-4 pentyl), 1.56 (d, *J* = 2.5 Hz, 6 H, 3× CH_2 Ada), 1.52–1.41 (m, 4 H, CH_2-2, CH_2-3 pentyl) ppm. ^{13}C NMR (150 MHz,

MeOD): δ = 81.7 (OCH_2-Ada), 71.2 (C-3), 71.0 (CH_2-5 pentyl), 68.8 (C-2), 68.0 (C-4), 58.0 (C-5), 57.0 (C-6), 53.5 (C-1), 48.0 (C-6), 39.4 (CH_2 Ada), 36.9 (CH_2 Ada), 33.8 (C_q Ada), 29.0 (CH_2-4 pentyl), 28.4 (CH Ada), 26.0, 25.8, 25.5 (3× CH_2 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3328, 2901, 2849, 1454, 1363, 1087 cm^{-1}. $[\alpha]_D^{20}$ = 7.6 (*c* = 0.6, MeOH). HRMS: found 398.2898 $[M + H]^+$, calcd. for $[C_{22}H_{39}NO_5 + H]^+$ 398.2901.

(1*R*)-1-*C*-[6-(Adamant-1-ylmethoxy)hexyl]-1-deoxynojirimycin (78): Compound **68** (158 mg, 175 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **78** (58 mg, 141 μmol) as a colourless oil in 81% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 10% B → 12 min: 100% B → 12 min: 100% B, 15 min: isocratic 100% B; t_R = 7.8 min). R_f = 0.35 (MeOH/$CHCl_3$, 1:3 + 2% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 4.00 (dd, *J* = 7.1, 12.0 Hz, 1 H, 6a-H), 3.83 (dd, *J* = 3.8, 12.0 Hz, 1 H, 6b-H), 3.78 (dd, *J* = 3.6, 6.6 Hz, 1 H, 2-H), 3.71 (dd, *J* = 6.6, 6.7 Hz, 1 H, 3-H), 3.62 (dd, *J* = 6.7, 6.7 Hz, 1 H, 4-H), 3.46 (td, *J* = 3.6, 6.9 Hz, 1 H, 1-H), 3.38 (t, *J* = 6.4 Hz, 2 H, CH_2-6 hexyl), 3.34–3.32 (m, 1 H, 5-H), 2.97 (s, 2 H, OCH_2-Ada), 1.98–1.90 (m, 4 H, CH*H*-1 hexyl, 3× CH Ada), 1.72 (dd, *J* = 11.8, 48.2 Hz, 6 H, 3× CH_2 Ada), 1.65–1.60 (m, 1 H, CH*H*-1 hexyl), 1.59–1.54 (m, 8 H, CH_2-5 hexyl, 3× CH_2 Ada), 1.50–1.44 (m, 2 H, CH_2-2 hexyl), 1.44–1.39 (m, 4 H, 2× CH_2 hexyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 72.8 (C-3), 72.7 (CH_2-6 hexyl), 70.4 (C-2), 69.5 (C-4), 59.5 (C-5), 58.6 (C-6), 55.3 (C-1), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.7 (CH_2-5 hexyl), 30.5 (CH_2 hexyl), 29.9 (CH Ada), 27.6 (CH_2-1 hexyl), 27.3 (CH_2 hexyl), 27.2 (CH_2-2 hexyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3328, 2901, 2848, 1593, 1452, 1361, 1096, 1046 cm^{-1}. $[\alpha]_D^{20}$ = 9.2 (*c* = 0.7, MeOH). HRMS: found 412.3055 $[M + H]^+$, calcd. for $[C_{23}H_{41}NO_5 + H]^+$ 412.3057.

(1*R*)-1-*C*-[4-(Adamant-1-ylmethoxy)butyl]-1,5-dideoxy-1,5-imino-D-xylitol (79): Compound **69** (111 mg, 147 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **79** (41 mg, 116 μmol) as a colourless oil in 79% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 25% B → 11.5 min: 45% B → 12.5 min: 100% B, 15 min: isocratic 100% B; t_R = 9.2 min). R_f = 0.30 (MeOH/$CHCl_3$, 1:4 + 2% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.96 (dd, *J* = 3.3 Hz, 1 H, 3-H), 3.92–3.89 (m, 1 H, 4-H), 3.86–3.83 (m, 1 H, 2-H), 3.44–3.38 (m, 4 H, 1-H, C*H*H-5, CH_2-4 butyl), 3.19 (d, *J* = 13.1 Hz, 1 H, CH*H*-5), 2.98 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3× CH Ada), 1.91–1.84 (m, 1 H, C*H*H-1 butyl), 1.72 (dd, *J* = 11.6, 49.2 Hz, 6 H, 3× CH_2 Ada), 1.66–1.59 (m, 3 H, CH*H*-1 butyl, CH_2-3 butyl), 1.56 (d, *J* = 2.3 Hz, 6 H, 3× CH_2 Ada), 1.55–1.49 (m, 1 H, C*H*H-2 butyl), 1.49–1.42 (m, 1 H, CH*H*-2 butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.3 (OCH_2-Ada), 72.2 (CH_2-4 butyl), 69.6 (C-2), 68.3 (C-4), 68.0 (C-3), 56.5 (C-1), 47.5 (C-5), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.6 (CH_2-3 butyl), 29.9 (CH Ada), 29.6 (CH_2-1 butyl), 22.9 (CH_2-2 butyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3368, 2903, 2849, 1451, 1203, 1139, 1060 cm^{-1}. $[\alpha]_D^{20}$ = –13.4 (*c* = 0.2, MeOH). HRMS: found 354.2639 $[M + H]^+$, calcd. for $[C_{20}H_{35}NO_4 + H]^+$ 354.2639.

(1*R*)-1-*C*-[5-(Adamant-1-ylmethoxy)pentyl]-1,5-dideoxy-1,5-imino-D-xylitol (80): Compound **70** (140 mg, 182 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **80** (62 mg, 169 μmol) as a colourless oil in 93% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 30% B → 11.5 min: 50% B → 12.5 min: 100% B, 15 min: isocratic 100% B; t_R = 6.5 min). R_f = 0.31 (MeOH/$CHCl_3$, 1:4 + 2% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.96 (dd, *J* = 3.2 Hz, 1 H, 3-H), 3.92–3.89 (m, 1 H, 4-H), 3.86–3.83 (m, 1 H, 2-H), 3.43–3.37 (m, 4 H, 1-H, C*H*H-5, CH_2-5 pentyl), 3.19 (d, *J* = 13.1 Hz, 1 H, CH*H*-5), 2.97 (s, 2 H, OCH_2-Ada), 1.94 (s, 3 H, 3× CH Ada), 1.90–1.83 (m, 1 H, C*H*H-1 pentyl), 1.72 (dd, *J* = 11.9, 49.3 Hz, 6 H, 3× CH_2 Ada), 1.66–1.57 (m, 3 H, CH*H*-1 pentyl, CH_2-4 pentyl), 1.56 (d, *J* = 2.3 Hz, 6 H, 3× CH_2 Ada), 1.52–1.38 (m, 4 H, 2× CH_2 pentyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 72.5 (CH_2-5 pentyl), 69.6 (C-2), 68.4 (C-4), 68.0 (C-3), 56.4 (C-1), 47.4 (C-5), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5 (CH_2-4 pentyl), 29.9 (CH Ada), 29.8 (CH_2-1 pentyl), 27.3 (CH_2 pentyl), 25.8 (CH_2 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3367, 2903, 2849, 1450, 1202, 1139, 1060 cm^{-1}. $[\alpha]_D^{20}$ = –15.8 (*c* = 0.3, MeOH). HRMS: found 368.2796 $[M + H]^+$, calcd. for $[C_{21}H_{37}NO_4 + H]^+$ 368.2795.

(1*R*)-1-*C*-[6-(Adamant-1-ylmethoxy)hexyl]-1,5-dideoxy-1,5-imino-D-xylitol (81): Compound **71** (173 mg, 221 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **81** (75 mg, 197 μmol) as a colourless oil in 89% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 10% B → 12 min: 100% B → 12 min: 100% B, 15 min: isocratic 100% B; t_R = 7.9 min). R_f = 0.33 (MeOH/$CHCl_3$, 1:4 + 2% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.96 (dd, *J* = 3.3 Hz, 1 H, 3-H), 3.92–3.90 (m, 1 H, 4-H), 3.85–3.83 (m, 1 H, 2-H), 3.43–3.36 (m, 4 H, 1-H, C*H*H-5, CH_2-6 hexyl), 3.19 (d, *J* = 13.1 Hz, 1 H, CH*H*-5), 2.97 (s, 2 H, OCH_2-Ada), 1.94 (s, 3 H, 3× CH Ada), 1.89–1.82 (m, 1 H, C*H*H-1 hexyl), 1.79–1.61 (m, 7 H, CH*H*-1 hexyl, 3× CH_2 Ada), 1.61–1.53 (m, 8 H, CH_2-5 hexyl, 3× CH_2 Ada), 1.50–1.43 (m, 1 H, C*H*H-2 hexyl), 1.43–1.37 (m, 5 H, CH*H*-2 hexyl, 2× CH_2 hexyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 72.7 (CH_2-6 hexyl), 69.6 (C-2), 68.3 (C-4), 68.0 (C-3), 56.4 (C-1), 47.4 (C-5), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.7 (CH_2-5 hexyl), 30.4 (CH_2 hexyl), 29.9 (CH Ada), 29.7 (CH_2-1 hexyl), 27.3 (CH_2 hexyl), 26.0 (CH_2 hexyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3370, 2902, 2849, 1449, 1202, 1139, 1061 cm^{-1}. $[\alpha]_D^{20}$ = –13.7 (*c* = 0.6, MeOH). HRMS: found 382.2954 $[M + H]^+$, calcd. for $[C_{22}H_{39}NO_4 + H]^+$ 382.2952.

(1*R*)-1,5-Dideoxy-1,5-imino-1-*C*-nonyl-D-xylitol (82): Compound **72** (305 mg, 461 μmol) was subjected to hydrogenolysis at 4 bar H_2 (see general procedure H) to furnish **82** (113 mg, 438 μmol) as a colourless oil in 95% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 10% B → 12 min: 100% B → 12 min: 100% B, 15 min: isocratic 100% B; t_R = 6.7 min). R_f = 0.25 (MeOH/$CHCl_3$, 1:4 + 2% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 3.97–3.96 (m, 1 H, 3-H), 3.93–3.89 (m, 1 H, 4-H), 3.85–3.82 (m, 1 H, 2-H), 3.41 (dd, *J* = 1.7, 13.1 Hz, 1 H, 5a-H), 3.37 (d, *J* = 7.4 Hz, 1 H, 1-H), 3.19 (d, *J* = 13.1 Hz, 1 H, 5b-H), 1.88–1.81 (m, 1 H, C*H*H-1 nonyl), 1.63 (ddd, *J* = 5.0, 10.5, 18.5 Hz, 1 H, C*H*H-1 nonyl), 1.48–1.41 (m, 1 H, CH*H*-2), 1.41–1.25 (m, 13 H, C*H*H-2 nonyl, 6× CH_2 nonyl), 0.90 (t, *J* = 7.0 Hz, 3 H, CH_3-9 nonyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 69.6 (C-2), 68.3 (C-4), 68.0 (C-3), 56.5 (C-1), 47.4 (C-6), 33.2, 30.7, 30.6, 30.5, 30.4 (5× CH_2 nonyl), 29.8 (CH_2-1 nonyl), 26.0 (CH_2-1 nonyl), 23.9 (CH_2 nonyl), 14.6 (CH_3-9 nonyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3367, 2927, 2857, 1438, 1200, 1139, 1061 cm^{-1}. $[\alpha]_D^{20}$ = –19.6 (*c* = 0.4, MeOH). HRMS: found 260.2222 $[M + H]^+$, calcd. for $[C_{14}H_{29}NO_3 + H]^+$ 260.2220.

(1*R*)-1-*C*-[(*E*/*Z*)-5-(Adamant-1-ylmethoxy)pent-2-enyl]-1-deoxy-L-*ido*-nojirimycin (83): Compound **64** (95 mg, 107 μmol) was subjected to a Birch reduction (see general procedure G) to furnish **83** (30 mg, 75 μmol) as a colourless oil in 70% yield as a 1.3:2 mixture of (*E*)/(*Z*) isomers after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (30% B → 11 min: 100% B, 15 min: isocratic 100% B; t_R = 3.8 min). R_f = 0.41/0.45 (MeOH/$CHCl_3$, 1:4 + 2% NH_4OH). ^1H NMR [600 MHz, MeOD, (*E*)/(*Z*) isomers, integrals for (*Z*) isomer]: δ = 5.72 [dt, *J* = 6.7, 15.4 Hz, =CH-3 (*E*) pentenyl], 5.67 [dt, *J* = 7.3, 10.9 Hz, 1 H, =CH-3 (*Z*) pentenyl], 5.52–5.39 [m, 1 H, =CH-2 (*E*)/(*Z*) pentenyl], 4.01 [dd, *J* = 3.3 Hz, 1 H, 3-H (*E*)/(*Z*)], 3.93–3.89 [m, 1 H, 4-H (*E*)/(*Z*)], 3.89–3.81 [m, 5 H, 2-H (*E*)/(*Z*), CH_2-6 (*E*)/(*Z*)], 3.55–3.50 [m, 1 H, 5-H (*E*)/(*Z*)], 3.47–3.39 [m, 5 H, 1-H (*E*)/(*Z*), CH_2-5 (*E*)/(*Z*) pentenyl], 3.00 [s, 2 H, OCH_2-Ada (*Z*)], 2.99 [s, OCH_2-Ada (*E*)], 2.80–2.74 [m, 1 H, C*H*H-1 (*Z*) pentenyl], 2.64–2.58 [m, C*H*H-1 (*E*) pentenyl], 2.50–2.43 [m, 1 H, CH*H*-1 (*Z*) pentenyl, CH*H*-1 (*E*) pentenyl], 2.43–2.37 [m, 2 H, CH_2-4 (*Z*) pentenyl], 2.31–2.28 [m, CH_2-4 (*E*) pentenyl], 1.94 (s, 3 H, 3× CH Ada), 1.72 (dd, *J* = 11.9, 47.0 Hz, 6 H, 3× CH_2 Ada), 1.56 (d, *J* = 1.8 Hz, 6 H, 3× CH_2 Ada) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 134.0 [=CH-3 (*E*) pentenyl], 132.5 [=CH-3 (*Z*) pentenyl], 126.0 [=CH-2 (*E*) pentenyl], 124.9 [=CH-2 (*Z*) pentenyl], 83.3 [OCH_2-Ada (*Z*)], 83.2 [OCH_2-Ada (*E*)], 72.3 [CH_2-5 (*E*) pentenyl], 72.2 [CH_2-5 (*Z*) pentenyl], 69.3 [C-4 (*E*)], 69.2 [C-4 (*Z*)], 69.1 [C-2 (*Z*)], 69.0 [C-2 (*E*)], 68.2 [C-3 (*E*)/(*Z*)], 60.7 [C-6 (*Z*)], 60.6 [C-6 (*E*)], 58.9 [C-5 (*Z*)], 58.8 [C-5 (*E*)], 56.8 [C-1 (*E*)], 56.7 [C-1 (*Z*)], 41.0 [CH_2 Ada (*E*)], 40.9 [CH_2 Ada (*Z*)], 38.5 [CH_2 Ada (*E*)], 38.4 [CH_2 Ada (*Z*)], 35.3 [C_q Ada (*Z*)], 35.2 [C_q Ada (*E*)], 34.1 [CH_2-4 (*E*) pentenyl], 32.5 [CH_2-1 (*E*) pentenyl], 29.9 [CH Ada (*E*)], 29.8 [CH Ada (*Z*)], 29.2 [CH_2-4 (*Z*) pentenyl], 27.3 [CH_2-1 (*Z*) pentenyl] ppm. 432IR (thin film): $\tilde{\nu}_{max.}$ = 3365, 2903, 2849, 1444, 1203, 1140, 1075, 1011 cm^{-1}. $[a]_D^{20}$ = –10.1 (*c* = 0.3, MeOH). HRMS: found 396.2741 $[M + H]^+$, calcd. for $[C_{22}H_{37}NO_5 + H]^+$ 396.2744.

(1*R*)-1-*C*-[(*E*/*Z*)-5-(Adamant-1-ylmethoxy)pent-2-enyl]-1-deoxynojirimycin (84): Compound **67** (105 mg, 118 μmol) was subjected to a Birch reduction (see general procedure G) to furnish **84** (34 mg, 85 μmol) as a colourless oil in 72% yield as a 3:1 mixture of (*E*)/(*Z*) isomers after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 30% B → 12 min: 100% B → 12 min: 100% B, 15 min: isocratic 100% B; t_R = 4.5 min). R_f = 0.30 (MeOH/$CHCl_3$, 1:4 + 2% NH_4OH). ^1H NMR [600 MHz, MeOD, (*E*)/(*Z*) isomers, integrals for (*E*) isomer]: δ = 5.74 [dt, *J* = 6.8, 15.4 Hz, 1 H, =CH-3 (*E*) pentenyl], 5.73–5.71 [m, =CH-3 (*E*) pentenyl], 5.52–5.44 [m, 1 H, =CH-2 (*E*)/(*Z*) pentenyl], 4.02 [dd, *J* = 7.3, 11.9 Hz, 6a-H (*Z*)], 3.97 [dd, *J* = 7.4, 11.9 Hz, 1 H, 6a-H (*E*)], 3.84–3.78 [m, 2 H, 6b-H (*E*)/(*Z*), 2-H (*E*)/(*Z*)], 3.76 [t, *J* = 6.0 Hz, 3-H (*Z*)], 3.73 [t, *J* = 6.5 Hz, 1 H, 3-H (*E*)], 3.65 [t, *J* = 6.1 Hz, 4-H (*Z*)], 3.62 [t, *J* = 6.6 Hz, 1 H, 4-H (*E*)], 3.54–3.48 [m, 1 H, 1-H (*E*)/(*Z*)], 3.44 [t, *J* = 6.6 Hz, 2 H, CH_2-5 (*E*)/(*Z*) pentenyl], 3.38–3.33 [m, 1 H, 5-H (*E*)/(*Z*)], 3.00 [s, OCH_2-Ada (*Z*)], 2.99 [s, 2 H, OCH_2-Ada (*E*)], 2.77–2.71 [m, C*H*H-1 (*Z*) pentenyl], 2.70–2.64 [m, 1 H, *CHH*-1 (*E*) pentenyl], 2.51–2.45 [m, CH*H*-1 (*Z*) pentenyl], 2.43–2.36 [m, 1 H, CH*H*-1 (*E*) pentenyl], 2.34–2.28 [m, 2 H, CH_2-4 (*E*)/(*Z*) pentenyl], 1.95 [s, 3 H, 3× CH Ada (*E*)/(*Z*)], 1.72 [dd, *J* = 11.9, 47.7 Hz, 6 H, 3× CH_2 Ada (*E*)/(*Z*)], 1.56 [d, *J* = 2.4 Hz, 6 H, 3× CH_2 Ada (*E*)/(*Z*)] ppm. ^{13}C NMR [150 MHz, MeOD, (*E*)/(*Z*) isomer]: δ = 134.3 [=CH-3 (*E*) pentenyl], 132.6 [=CH-3 (*Z*) pentenyl], 126.4 [=CH-2 (*E*) pentenyl], 125.4 [=CH-2 (*Z*) pentenyl], 83.3 [OCH_2-Ada (*Z*)], 83.2 [OCH_2-Ada (*E*)], 72.7 [C-3 (*E*)], 72.5 [C-3 (*Z*)], 72.3 [CH_2-5 pentenyl (*Z*)], 72.1 [CH_2-5 pentenyl (*E*)], 70.1 [C-2 (*E*)], 70.1 [C-2 (*Z*)], 69.6 [C-4 (*E*)], 69.4 [C-4 (*Z*)], 59.5 [C-5 (*E*)/(*Z*)], 58.6 [C-6 (*E*)], 58.5 [C-6 (*Z*)], 54.7 [C-1 (*E*)/(*Z*)], 41.0 (CH_2 Ada), 38.4 (CH_2 Ada), 35.3 [C_q Ada (*E*)/(*Z*)], 34.1 [CH_2-4 pentenyl (*E*)], 30.7 [CH_2-1 pentenyl (*E*)], 29.9 (CH Ada), 29.2 [CH_2-4 pentenyl (*Z*)], 25.8 [CH_2-1 pentenyl (*Z*)] ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3351, 2903, 2849, 1443, 1203, 1139, 1050 cm^{-1}. $[a]_D^{20}$ = 5.5 (*c* = 0.3, MeOH). HRMS: found 396.2741 $[M + H]^+$, calcd. for $[C_{22}H_{37}NO_5 + H]^+$ 396.2744.

(1*R*)-1-*C*-[(*E*/*Z*)-5-(Adamant-1-ylmethoxy)pent-2-enyl]-1,5-dideoxy-1,5-imino-D-xylitol (85): Compound **70** (110 mg, 143 μmol) was subjected to a Birch reduction (see general procedure G) to furnish **85** (34 mg, 93 μmol) as a colourless oil in 65% yield as a 1.2:1 mixture of (*E*)/(*Z*) isomers after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 10% B → 12 min: 100% B → 12 min: 100% B, 15 min: isocratic 100% B; t_R = 7.3 min). R_f = 0.39/0.45 (MeOH/$CHCl_3$, 1:4 + 2% NH_4OH). ^1H NMR [600 MHz, MeOD, (*E*)/(*Z*) isomers, integrals for (*E*) isomer]: δ = 5.75–5.67 [m, 2 H, =CH-3 (*E*)/(*Z*) pentenyl], 5.52–5.42 [m, 2 H, =CH-2 (*E*)/(*Z*) pentenyl], 3.96 (dd, *J* = 3.6 Hz, 2 H, 3-H), 3.93–3.90 (m, 2 H, 4-H), 3.84–3.82 [m, 1 H, 2-H (*E*)], 3.82–3.80 [m, 2-H (*Z*)], 3.46–3.37 [m, 4 H, 1-H (*E*)/(*Z*), C*H*H-5 (*E*)/(*Z*), CH_2-5 pentenyl (*E*)/(*Z*)], 3.23–3.21 [m, 1 H, CH*H*-5 (*E*)], 3.21–3.19 [m, CH*H*-5 (*Z*)], 3.00 [s, OCH_2-Ada (*Z*)], 2.99 [s, 2 H, OCH_2-Ada (*E*)], 2.67–2.61 [m, C*H*H-1 (*Z*) pentenyl], 2.56–2.49 [m, 1 H, C*H*H-1 (*E*) pentenyl], 2.49–2.43 [m, CH*H*-1 (*Z*) pentenyl], 2.43–2.35 [m, 1 H, CH*H*-1 (*E*) pentenyl, CH_2-4 (*Z*) pentenyl], 2.35–2.28 [m, 2 H, CH_2-4 (*E*) pentenyl], 1.94 [s, 3 H, 3× CH Ada (*E*)/(*Z*)], 1.72 [dd, *J* = 11.8, 47.5 Hz, 6 H, 3× CH_2 Ada (*E*)/(*Z*)], 1.56 [d, *J* = 2.6 Hz, 6 H, 3× CH_2 Ada (*E*)/(*Z*)] ppm. ^{13}C NMR [150 MHz, MeOD, (*E*)/(*Z*) isomers]: δ = 134.2 [=CH-3 (*E*)/(*Z*) pentenyl], 132.8 [=CH-3 (*Z*) pentenyl], 125.9 [=CH-2 (*E*) pentenyl], 124.9 [=CH-2 (*Z*) pentenyl], 83.3 [OCH_2-Ada (*Z*)], 83.2 [OCH_2-Ada (*E*)], 72.2 [CH_2-5 (*E*) pentenyl], 72.1 [CH_2-5 (*Z*) pentenyl], 69.7 [C-2 (*E*)], 69.7 [C-2 (*Z*)], 68.4 [C-4 (*E*)], 68.3 [C-4 (*Z*)], 68.0 [C-3 (*E*)/(*Z*)], 56.4 [C-1 (*Z*)], 56.4 [C-1 (*E*)], 47.5 [C-5 (*E*)/(*Z*)], 40.9 [CH_2 Ada (*E*)/(*Z*)], 38.4 [CH_2 Ada (*E*)/(*Z*)], 35.3 [C_q Ada (*Z*)], 35.2 [C_q Ada (*E*)], 34.1 [CH_2-4 (*E*) pentenyl], 33.3 [CH_2-1 (*E*) pentenyl], 29.9 [CH Ada (*E*)/(*Z*)], 29.2 [CH_2-4 (*Z*) pentenyl], 28.0 [CH_2-1 (*Z*) pentenyl] ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3367, 2902, 2849, 1444, 1200, 1137, 1064, 1012, 940 cm^{-1}. $[a]_D^{20}$ = 12.0 (*c* = 0.5, MeOH). HRMS: found 366.2639 $[M + H]^+$, calcd. for $[C_{21}H_{35}NO_4 + H]^+$ 366.2639.

(1*R*)-1,5-Dideoxy-1,5-imino-1-*C*-[(*E*)-non-2-enyl]-D-xylitol (86): Compound **72** (110 mg, 166 μmol) was subjected to a Birch reduction (see general procedure G) to furnish **86** (30 mg, 115 μmol) as a colourless oil in 69% yield after purification (silica gel, 0% → 20% MeOH in $CHCl_3$ with 0.5% NH_4OH). Additional HPLC purification was required for removal of minor 5–10% impurities (1 min: isocratic 20% B → 11.5 min: 40% B → 12.5 min: 100% B, 20 min: isocratic 100% B; t_R = 7.6 min). R_f = 0.32 (MeOH/$CHCl_3$, 1:4 + 2% NH_4OH). ^1H NMR (600 MHz, MeOD): δ = 5.69 (dt, *J* = 6.8, 15.2 Hz, 1 H, =CH-2 nonenyl), 5.40 (dt, *J* = 7.2, 15.2 Hz, 1 H, =CH-3 nonenyl), 3.97–3.93 (m, 1 H, 3-H), 3.93–3.89 (m, 1 H, 4-H), 3.84–3.80 (m, 1 H, 2-H), 3.42–3.36 (m, 2 H, 1-H, 5a-H), 3.20 (d, *J* = 13.2 Hz, 1 H, 5b-H), 2.55–2.48 (m, 1 H, C*H*H-1 nonenyl), 2.38 (dt, *J* = 6.8, 13.7 Hz, 1 H, CH*H*-1 nonenyl), 2.09–2.02 (m, 2 H, CH_2-4 nonenyl), 1.43–1.36 (m, 2 H, CH_2-5 nonenyl), 1.36–1.26 (m, 6 H, 3× CH_2 nonenyl), 0.90 (t, *J* = 7.0 Hz, 3 H, CH_3-9 nonenyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 137.7 (=CH-3 nonenyl), 124.0 (=CH-2 nonenyl), 69.7 (C-2), 68.4 (C-4), 68.0 (C-3), 56.4 (C-1), 47.5 (C-6), 33.8 (CH_2-4 nonenyl), 33.2 (CH_2-1 nonenyl), 33.0 (CH_2 nonenyl), 30.4 (CH_2-5 nonenyl), 30.1 (CH_2 nonenyl),

23.8 (CH_2 nonenyl), 14.6 (CH_3-9 nonenyl) ppm. IR (thin film): $\tilde{\nu}_{max.}$ = 3366, 2928, 2857, 1436, 1199, 1139, 1062, 1007, 971 cm^{-1}. $[\alpha]_D^{20}$ = 13.2 (c = 0.4, MeOH). HRMS: found 258.2065 $[M + H]^+$, calcd. for $[C_{14}H_{27}NO_3 + H]^+$ 258.2064.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C APT NMR spectra for all synthetic intermediates and iminosugars reported in the Experimental Section.

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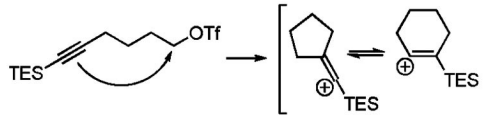

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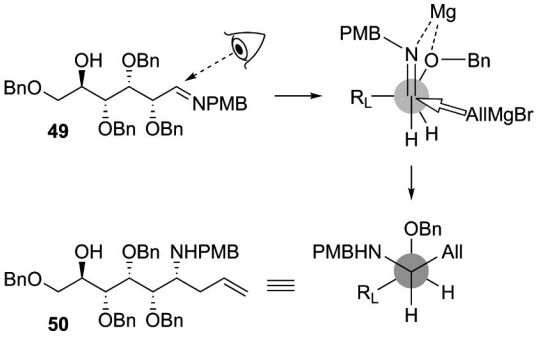

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