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The Development of an Aza-C-Glycoside Library Based on a Tandem Staudinger/Aza-Wittig/Ugi Three-Component Reaction

Tom Wennekes,[a][‡] Kimberly M. Bonger,[a][‡‡] Katrin Vogel,[a] Richard J. B. H. N. van den Berg,[a] Anneke Strijland,[b] Wilma E. Donker-Koopman,[b] Johannes M. F. G. Aerts,[b] Gijsbert A. van der Marel,[a] and Herman S. Overkleeft*[a]

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We report the tandem Staudinger/aza-Wittig/Ugi three-component reaction mediated synthesis of a 64-member compound library of aza-C-glycosides. The library is composed of four pyrrolidine and three piperidine scaffolds, onto which a number of functional groups is grafted to form seven sublibraries. Variation in the library is achieved by transformation of two pentoses and a hexose into the corresponding 4-azidopentanal and 5-azidohexanal derivatives as precursors for the Staudinger/aza-Wittig process. Further variation is achieved by using different isocyanides as well as protective- and functional-group manipulations on the fully protected Ugi-3CR intermediates. Preliminary biological evaluation of the compound library revealed several low micromolar inhibitors of human acid glucosylceramidase.

Introduction

Aza-C-glycosides, also known as iminosugar C-glycosides, are iminosugars that have a carbon substituent at the position corresponding to the anomeric carbon of the parent glycoside.[1] This distinguishing feature can be designed such that it resembles the aglycon of the target glycoconjugate, thereby potentially endowing the structure with enhanced enzyme inhibitory potency and/or specificity. Moreover, appending a bulky substituent at the carbon next to the nitrogen of an iminosugar may profoundly affect its conformational behavior, potentially locking the compound in its bioactive conformer. Aza-C-glycosides have therefore become important targets in the quest for iminosugar-type glycosidase and glycosyl transferase inhibitors for medicinal chemistry purposes.[2] A number of potent and selective inhibitors of various glycoprocessing enzymes from various biological origins have been described in recent years, however, the search for such compounds is somewhat compromised by the relatively complex synthetic routes towards aza-C-glycosides. Indeed, although many effective and attractive synthetic routes have been described in recent years,[1,3] transposing such a given synthetic strategy towards a configurational or functional group isomer of the original target compound is not always straightforward (in fact this intrinsic difficulty is experienced for the construction of iminosugar-type alkaloids in general). A straightforward and flexible route towards aza-C-glycosides would therefore be desirable, especially when preparing compound libraries.[3j–3m,5b] We have previously reported on a route that transforms carbohydrate-derived azido aldehydes into cyclic dipeptides that are, in effect, aza-C-glycosides.[4,5] The azido aldehyde is transformed into an intermediate cyclic imine through a Staudinger/aza-Wittig cyclization, after which a Ugi three-component reaction (Ugi-3CR) yields the product. In this study we further investigate the efficiency and versatility of this route in constructing aza-C-glycosides.

Our interest in aza-C-glycosides, and in iminosugar alkaloids in general, is related to our research on human glycolipid metabolism, in particular on the glycoprocessing enzymes involved in the biosynthesis and degradation of glucosylceramide.[6] The lysosomal enzyme responsible for degradation of this glycolipid, acid glucosylceramidase (GBA), exists in genetically disabled isoforms, leading to partially impaired degradation – and thereby accumulation – of glucosylceramide. Such genetic deficiency in GBA activity causes the lysosomal storage disorder

[a] Leiden Institute of Chemistry, Leiden University, Gorlaeus Laboratories,
Einsteinweg 55, 2300 RA Leiden, The Netherlands
E-mail: h.s.overkleeft@chem.leidenuniv.nl
Homepage: http://biosyn.lic.leidenuniv.nl
[b] Department of Medical Biochemistry, Academic Medical Center, University of Amsterdam,
Amsterdam, The Netherlands
[‡] Current address: Laboratory of Organic Chemistry, Wageningen University,
Dreijenplein 8, 6703 HB Wageningen, The Netherlands
[‡‡]T. Wennekes and K. M. Bonger contributed equally to this work.

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Gaucher disease. GBA inhibitors that bind tightly to the enzyme active site have been proposed as a conceptually new therapy known as chemical chaperone therapy for the treatment of Gaucher.[7] Two intrinsically different therapies are already in clinical practice: enzyme replacement therapy[8] is based on administering to Gaucher patients recombinant GBA, whereas substrate reduction therapy[9] is based on inhibition of glucosylceramide synthase (GCS), the enzyme responsible for the synthesis of glucosylceramide through condensing ceramide with UDP-glucose. A second, non-lysosomal glucosylceramidase (GBA2) exists,[10] and in the design of GBA and/or GCS inhibitors of this enzyme (which has itself recently emerged as a drug target in relation to Parkinsonism[11]) has to be taken into account. In our work on the development of potent and selective inhibitors of each of these glucosylceramide-processing enzymes, we have discovered deoxynojirimycin derivatives equipped with a large hydrophobic group as valuable leads. Relevant examples (see Figure 1) are compounds **1**–**3**. *N*-Adamantanemethoxypentyldeoxynojirimycin (**1**)[6b,6c] is a highly potent (IC_{50} 200 nM) GCS inhibitor that is remarkably more potent than the marketed substrate reduction therapy drug, Zavesca (*N*-butyldeoxynojirimycin, IC_{50} 25–50 μM). Both compounds, however, feature broad-spectrum inhibition towards other glucosylceramide-processing enzymes [Zavesca: IC_{50}(GBA) 400 μM, IC_{50}(GBA2) 230 nM; **1**: IC_{50}(GBA) 200 nM, IC_{50}(GBA2) 1 nM] and also towards intestinal glycosidases (maltase, lactase, sucrase). The L-*ido*-configurational isomer of **1**, compound **2**,[6d] is at least as potent in inhibiting GCS (IC_{50} 100 nM) and is significantly more selective. With this compound, GBA (IC_{50} 2 μM) and GBA2 (IC_{50} 30 nM), and especially the intestinal glycosidases (no inhibition up to 1 mM), are much less strongly inhibited. More recently, we have worked on aza-C-glycosides having related structural features. Interestingly, although aza-C-glycoside **3**[6f] structurally resembles the natural GCS product and GBA/GBA2 substrate, glucosylceramide, much closer, it is a considerably weaker inhibitor of all three enzymes when compared to **1** [**3**: IC_{50}(GBA) 3 μM, IC_{50}(GBA2) 40 nM, IC_{50}(GCS) 3 μM].

With the aim of exploring the positioning and nature of the lipophilic group in more detail, while also considering the configuration and ring size of the iminosugar core, we set out to apply the Staudinger/aza-Wittig/Ug-3CR sequence of events to generate a concise library of aza-C-glycosides. The general strategy (Figure 1 right) is as follows. A partially protected, carbohydrate-derived azidoaldehyde **I** can be made to react with trimethylphosphane to generate cyclic imine **III**, via phosphazene **II**, after a Staudinger/aza-Wittig sequence.[12] In this process, the nature of azido aldehyde **I** is translated into that of imine **III**, and in addition to configurational aspects (that is, the nature of the parent sugar) the ring size can be readily varied: 4-azido aldehydes give rise to 1-pyrroline precursors whereas 5-azido aldehydes give 1-piperideine precursors. In the next step, imine **III** is reacted with a variety of isocyanides and pentenoic acid to give Ugi-3CR[13] products **IV**, in which R^1 can be a variety of lipophilic groups. The pentenoyl moiety in **IV** can be selectively removed and the resulting secondary amine functionalized through reductive amination to install R^2, which again denotes a series of lipophilic moieties. We have previously experienced[6b] that *N*-acyl deoxynojirimycin derivatives are poor inhibitors of the human glucosylceramide-processing enzymes and, therefore, opted to pursue diversity through tertiary amines rather than the corresponding amides. Global deprotection provides aza-C-glycosides **VI** for ensuing biological evaluation. In this work we divulge the results of our efforts in the generation and preliminary evaluation as GBA inhibitors of a 64 compound library based on seven iminosugar scaffolds and with a bulky hydrophobic group, positioned either at the ring nitrogen (corresponding to compounds **1** and **2**) or at C1 (the anomeric carbon when related to the parent sugars, in analogy to aza-C-glycoside **3**).

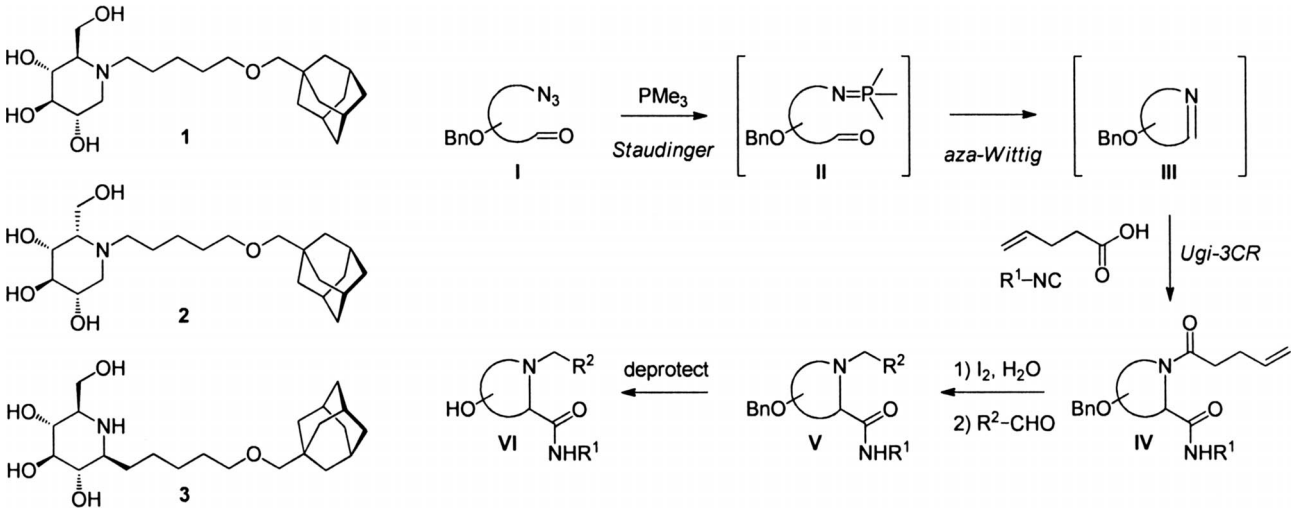


Figure 1. (Left) Previously reported relevant inhibitors of enzymes involved in glucosylceramide metabolism. (Right) General strategy for library synthesis through a tandem Staudinger/aza-Wittig/Ugi three-component reaction.

Results

The results of our library synthesis are summarized in Schemes 1, 2, 3, and 4, with Schemes 1 and 2 outlining the assembly of pyrrolidine aza-C-glycosides starting from L-ribose (Scheme 1) and D-xylose (Scheme 2) and Schemes 3 and 4 outlining the construction of piperidine aza-C-glycosides starting from D-glucose. As hydrophobic isocyanide reagents for the Ugi-3CR, we opted for adamantanemethoxypentane derivative **10** (readily available in a four-step sequence from 5-adamantanemethoxy-1-bromopentane **6** as depicted in Scheme 1), 1,1,3,3-tetramethylbutyl isocyanide **11** and pentyl isocyanide **12**. L-Ribose **4** was transformed into 4-azidopentanal **5** according to our previous report.[4b] In our previous work[4c] we had also found that the outcome in stereochemical terms of an Ugi-3CR involving the D-*lyxo*-pyrroline that emerges upon treatment of **5** with trimethylphosphane can be influenced by including indium trichloride in the reaction mixture. In agreement with our previous[6c] finding, performing the Ugi-3CR in methanol in the absence of $InCl_3$ yields predominantly the 2,3-*cis* adducts (**13**, **15** and **17**).[14] As we had also observed before,[4a] tertiary isocyanide **11** gives higher yields in comparison with primary isocyanides (**10**, **12**), but in all cases useful quantities of the Ugi-3CR products could be obtained. Including $InCl_3$ (1.1 equiv.) in the reaction and switching from methanol to acetonitrile as the solvent led to partial inversion of stereochemistry, with the 2,3-*trans* adducts (**14**, **16** and **18**) being obtained as the major products. The diastereomeric product mixtures were readily separated by silica gel chromatography in all instances, giving two sets of fully protected aza-C-glycosides. In the next step, the *N*-pentenoyl group was selectively removed by treatment with iodine according to the procedure developed by Madsen and Fraser-Reid[15] and the resulting secondary amines **19**–**24** were either globally deprotected or employed in a reductive amination event with butanal or adamantanemethoxypentanal[6c] followed by global deprotection to provide the first two sets of aza-C-glycosides: the 2,3-*cis*-fused D-*lyxo*-pyrrolidine derivatives **25**–**27**, **31**–**33** and **37**–**39** and the 2,3-*trans*-fused D-*lyxo*-pyrrolidine derivatives **28**–**30**, **34**–**36** and **40**–**42**.

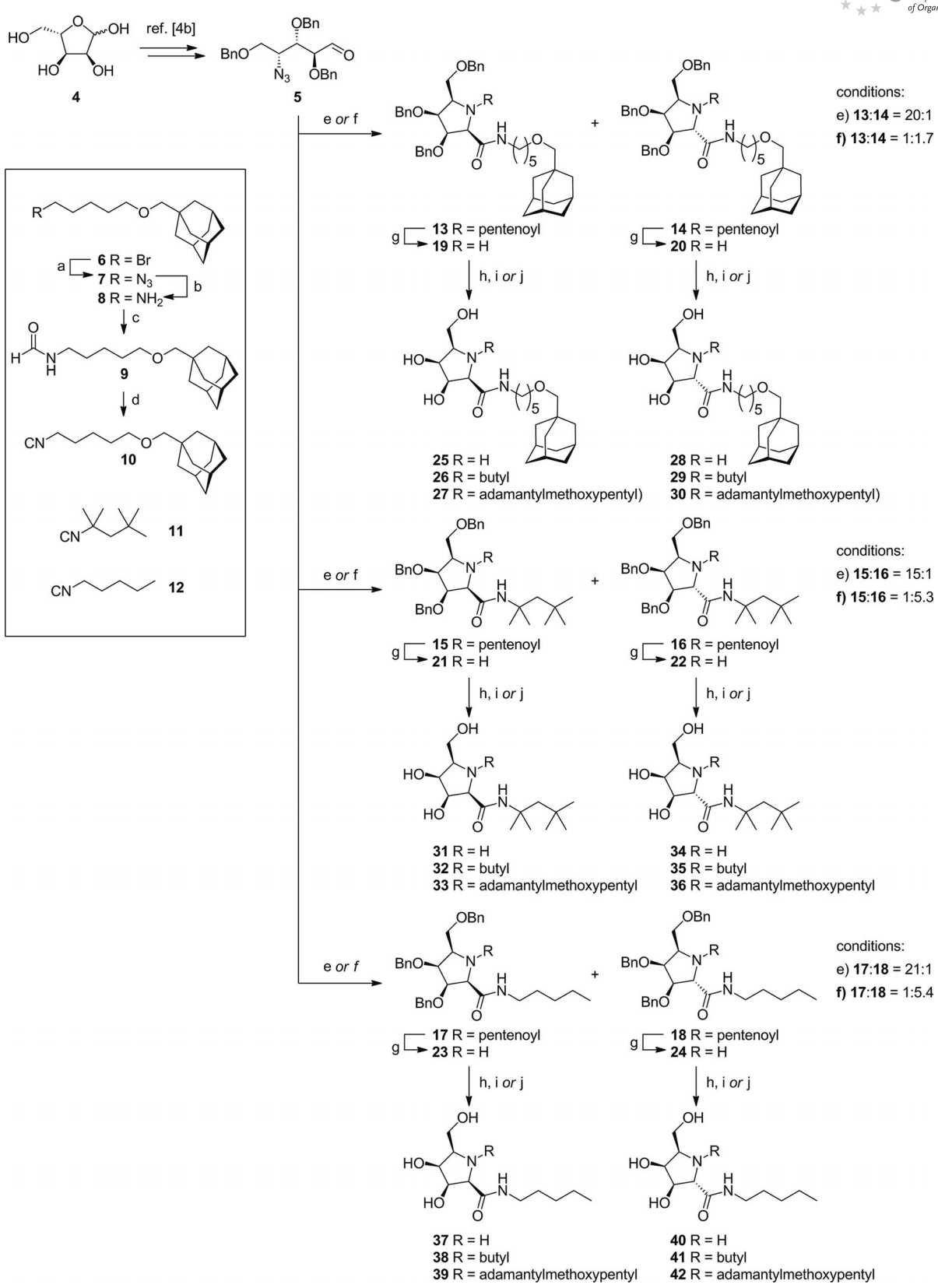
4-Azido aldehyde **50**, a configurational isomer of **5**, was prepared through standard functional group manipulations starting from fully protected D-xylofuranose **43** (Scheme 2). Subjection of **50** to a trimethylphosphane-mediated Staudinger/aza-Wittig event led to the generation of tri-*O*-benzyl-L-*arabino*-pyrroline, which was treated with 1-pentenoic acid and isocyanides **10**–**12** to give the series of fully protected 2,3-*trans*-L-*arabino*-pyrrolidines **51**, **53** and **55** and 2,3-*cis*-L-*arabino*-pyrrolidines **52**, **54** and **56**. In each case, both diastereomers were formed in roughly equal amounts and were readily separated by column chromatography. In this case, addition of $InCl_3$ had no influence on the stereochemical outcome of the Ugi-3CR reaction. The resulting six scaffolds were elaborated in the same vein as in the D-*lyxo* series to provide the second two sets of aza-C-glycosides: the 2,3-*trans*-fused L-*arabino*-pyrrolidine derivatives **63**–**65**, **69**–**71** and **75**–**77** and the 2,3-*cis*-fused L-*arabino*-pyrrolidine derivatives **66**–**68**, **72**–**74** and **78**–**80**.

2,3,4,6-Tetra-*O*-benzyl-D-glucitol (**81**) served as the starting compound for both the L-*ido*-piperidine series (Scheme 3) and D-*gluco*-piperidine series (Scheme 4) of compounds. The requisite 5-azido aldehydes **85** (Scheme 3) and **120** (Scheme 4) were readily prepared by using established procedures,[3h,3n] with, as distinguishing feature between the two routes, introduction of the azide at C5 with inversion of configuration (**82** to **83**; Scheme 3) and with retention of configuration involving first Mitsunobu-based inversion (**82** to **115**; Scheme 4)[16] followed by a second inversion (**117** to **118**; Scheme 4). Staudinger/aza-Wittig reactions under the agency of trimethylphosphane on 5-azido aldehyde **85** provided 2,3,4,6-tetra-*O*-benzyl-L-*ido*-1-piperideine, which was subjected to an Ugi-3CR with 1-pentenoic acid and isocyanides **10**–**12** (Scheme 1) to give 2,3-*trans*-L-*ido*-piperidines **86**, **88** and **90** and 2,3-*cis*-L-*ido*-piperidines **87**, **89** and **91** in about equal amounts as separable mixtures. As before, and following the same procedure, these scaffolds were brought forwards to give the third two sets of aza-C-glycosides: the 2,3-*trans*-fused L-*ido*-piperidine derivatives **98**–**100**, **103**–**105** and **109**–**111** and the 2,3-*cis*-fused L-*ido*-piperidine derivatives **101** and **102**, **106**–**108** and **112**–**114** (reductive amination of 2,3-*cis*-fused secondary amine **93** with adamantanemethoxypentanal did not yield any product). Finally, treatment of azido aldehyde **120** with trimethylphosphane led to the formation of 2,3,4,6-tetra-*O*-benzyl-D-*gluco*-1-piperideine. The stereochemical outcome of an ensuing Ugi-3CR could not be influenced by adding $InCl_3$ and we therefore took this cyclic imine to produce, again using the procedures discussed above, the seventh and final set of aza-C-glycosides: the 2,3-*cis*-fused D-*gluco*-piperidine derivatives **127**–**129**, **130**–**132** and **133**–**135**.

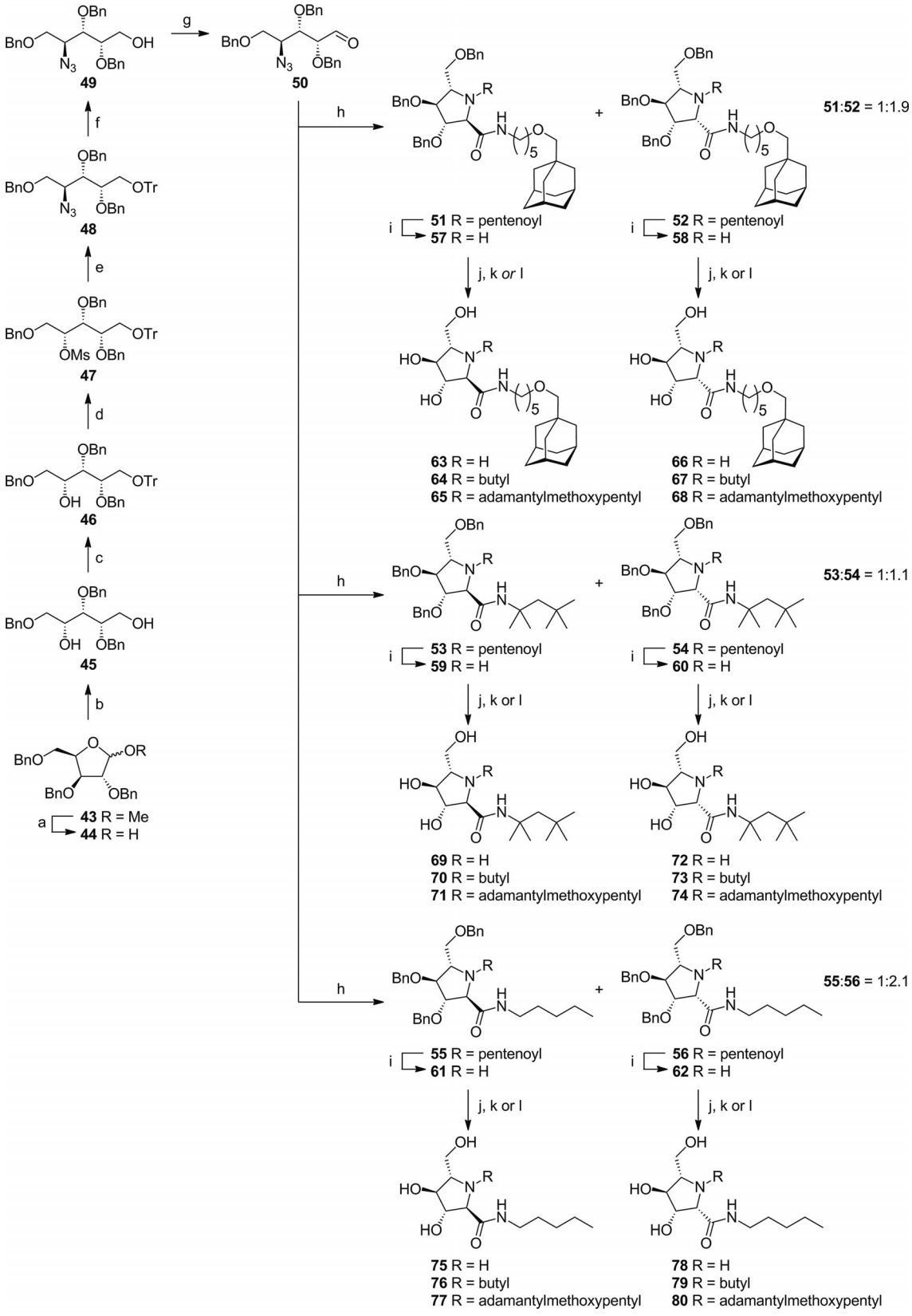
The configuration of the new chiral center, introduced during the Ugi-3CR, was previously reported by us[4b,4c] for D-*lyxo*-pyrrolidine aza-C-glycosides and for the new examples described here it was established by ^{1}H- and NOESY-NMR experiments (Figure 2).

With the 62 aza-C-glycosides from the seven sub-libraries in hand and their structures established, they were then all evaluated in an in vitro enzyme assay for inhibition of human acid glucosylceramidase (GBA) using pure recombinant enzyme and the artificial substrate 4-methylumbelliferyl-beta-D-glucoside under appropriate conditions.[17] The results are summarized in Table 1.

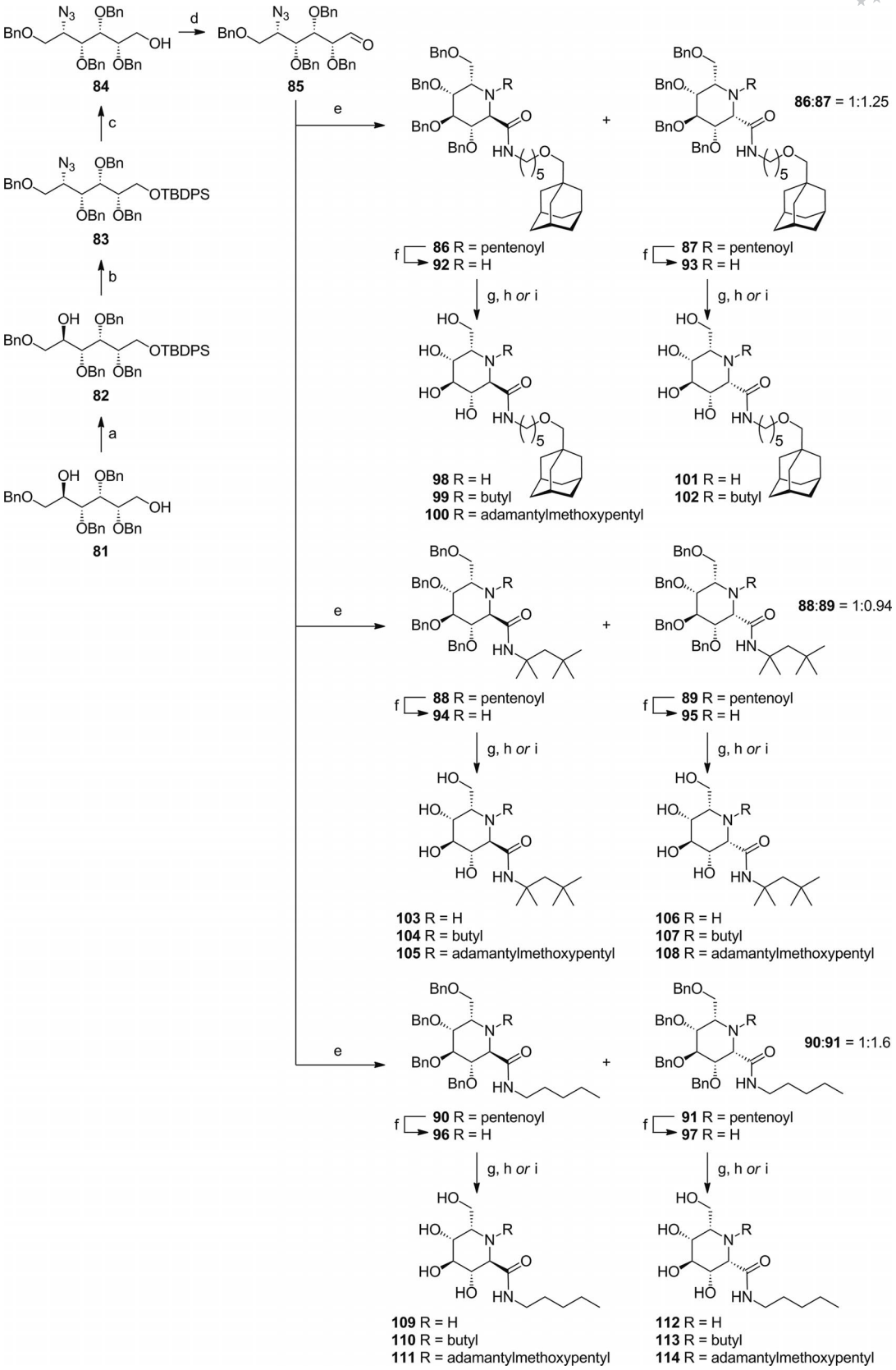
As can be seen, none of the aza-C-glycosides emulate the GBA inhibitory potential of our lead compound, **1** [IC_{50}(GBA) 200 nM]. That said, some interesting trends can be observed. Within the individual sub-libraries, almost without exception, those compounds featuring a single adamantane-containing lipophilic side chain at C2 with no substituent on the ring nitrogen are the most potent GBA inhibitors. Replacing this bulky side chain by either 1,1,3,3-tetramethylbutyl or pentyl gives a considerable drop in inhibition, whereas introducing added bulk on the pyrrolidine/piperidine nitrogen results in comparatively weaker inhibition. The most potent GBA inhibitors within the 62 com-



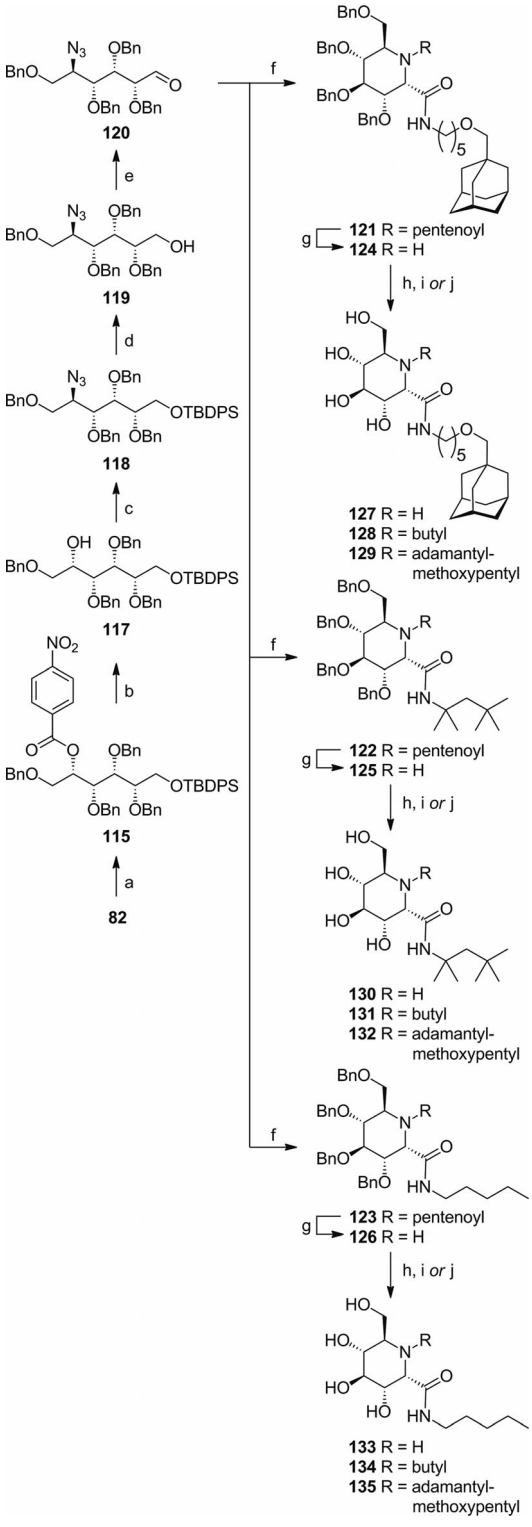
Scheme 1. Preparation of D-*lyxo*-pyrrolidine library entries from azidopentanal **5**. *Reagents and conditions:* (a) NaN_3, DMSO, room temp., 20 h, 95%; (b) PMe_3, H_2O, THF, 0 °C, 3 h, 84%; (c) acetic formic anhydride, CH_2Cl_2, 0 °C→room temp., 20 h, 82%; (d) $POCl_3$, Et_3N, CH_2Cl_2, 30 °C, 1 h, 81%; (e) 1. PMe_3, MeOH, 0 °C, 3 h; 2. acid, isocyanide **10**–**12**, MeOH, 0 °C, 18 h; (f) 1. PMe_3, MeOH, 0 °C, 3 h; 2. pent-4-enoic acid, isocyanide **10**–**12**, $InCl_3$, CH_3CN, 0 °C, 18 h; (g) I_2, H_2O, THF, 0.5 h; (h) Pd/C, H_2, EtOH, 18 h; (i) BCl_3, CH_2Cl_2, 0 °C, 18 h; (j) 1. Aldehyde, $NaCNBH_3$, Na_2SO_4, AcOH, EtOH, 18 h; 2. (h) or (i). For yields of library synthesis steps, e–j, see Exp. Section.



Scheme 2. Preparation of azidopentanal **50** and L-*arabino*-pyrrolidine library entries. *Reagents and conditions:* (a) aq. HCl, dioxane, reflux, 5 h, 70%; (b) $NaBH_4$, MeOH, 0 °C, 3 h, 87%; (c) TrCl, pyridine, 40 °C, 20 h, 94%; (d) MsCl, Et_3N, CH_2Cl_2, 85%; (e) NaN_3, 15-crown-5, DMF, 90 °C, 48 h, 88%; (f) $BF_3{\cdot}OEt_2$, MeOH toluene, 3 h, 98%; (g) Dess–Martin periodinane, CH_2Cl_2, 0 °C→room temp., 1.5 h, 76%; (h) 1. PMe_3, MeOH, 0 °C, 3 h; 2. pent-4-enoic acid, isocyanide **10**–**12**, MeOH, 0 °C, 18 h; (i) I_2, H_2O, THF, 0.5 h; (j) Pd/C, H_2, EtOH, 18 h; (k) BCl_3, CH_2Cl_2, 0 °C, 18 h; (l) 1. Aldehyde, $NaCNBH_3$, Na_2SO_4, AcOH, EtOH, 18 h; 2. (j) or (k). For yields of library synthesis steps, h–l, see Exp. Section.



Scheme 3. Preparation of azidohexanal **85** and L-*ido*-piperidine library entries. *Reagents and conditions*: (a) TBDPSCl, imidazole, DMF, 20 h, 99%; (b) DPPA, DIAD, PPh_3, THF, 0 °C→room temp., 20 h, 66%; (c) TBAF, THF, 20 h, 71%; (d) Dess–Martin periodinane, CH_2Cl_2, 0 °C→room temp., 1.5 h, 89%; (e) 1. PMe_3, MeOH, 0 °C, 3 h; 2. pent-4-enoic acid, isocyanide **10**–**12**, MeOH, 0 °C, 18 h; (f) I_2, H_2O, THF, 0.5 h·(g) Pd/C, H_2, EtOH, 18 h; (h) BCl_3, CH_2Cl_2, 0 °C, 18 h; (i) 1. Aldehyde, $NaCNBH_3$, Na_2SO_4, AcOH, EtOH, 18 h; 2. (g) or (h). For yields of library synthesis steps, e–i, see experimental section.



Scheme 4. Preparation of azidohexanal **120** and D-*gluco*-piperidine library entries. *Reagents and conditions*: (a) *p*-NO_2-benzoic acid, DIAD, PPh_3, 0 °C→room temp., 20 h, by-product[16] **116**: 46%; (b) LiOH, H_2O/THF/EtOH, 2 h, 38% 2 steps; (c) DPPA, DIAD, PPh_3, THF, 0 °C→room temp., 20 h, 63%; (d) TBAF, THF, 20 h, 74%; (e) Dess–Martin periodinane, CH_2Cl_2, 0 °C→room temp., 1.5 h, 96%; (f) 1. PMe_3, MeOH, 0 °C, 3 h; 2. pent-4-enoic acid, isocyanide **10**–**12**, MeOH, 0 °C, 18 h; (g) I_2, H_2O, THF, 0.5 h; (h) Pd/C, H_2, EtOH, 18 h; (i) BCl_3, CH_2Cl_2, 0 °C, 18 h; (j) 1. Aldehyde, $NaCNBH_3$, Na_2SO_4, AcOH, EtOH, 18 h; 2. (h) or (i). For yields of library synthesis steps, f–j, see experimental section.

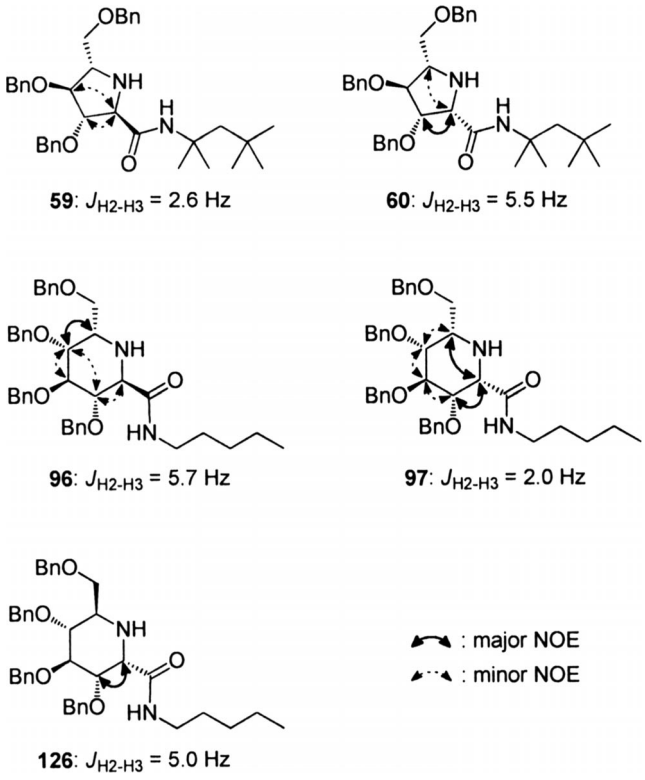


Figure 2. Configuration of the new chiral center as determined by ^{1}H- and NOESY-NMR for representative examples of L-*arabino*-pyrrolidine (**59** and **60**); L-*ido*-piperidine (**96** and **97**) and D-*gluco*-piperidine (**126**)[14] libraries.

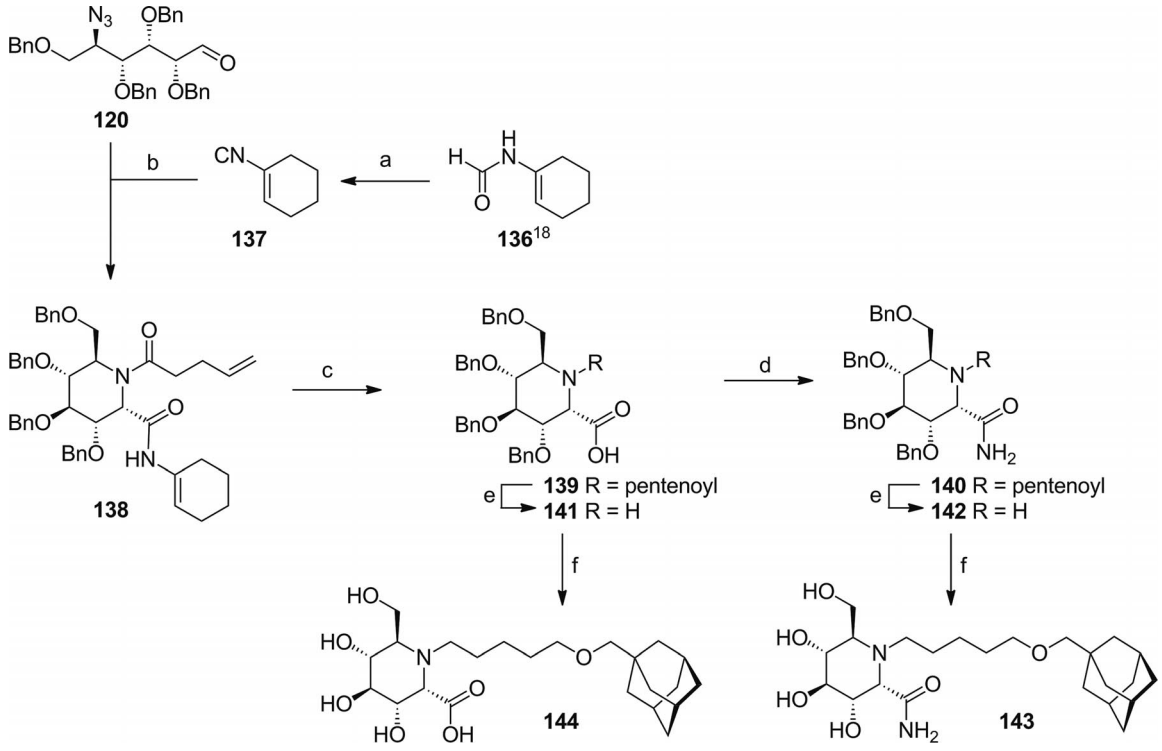
pound library are 2,3-*trans*-D-*lyxo*-pyrrolidine **28**, 2,3-*cis*-L-*arabino*-pyrrolidine **66** and 2,3-*cis*-D-*gluco*-piperidine **127**. Although weaker than **1**, these compounds for instance inhibit GBA rather more potently than *N*-butyldeoxynojirimycin [Zavesca: IC_{50}(GBA) 400 μM] and the archetypal iminosugar glycosidase inhibitor, deoxynojirimycin [IC_{50}(GBA) 250 μM].

When comparing the general structures of the library of aza-C-glycosides with those of leads **1**–**3**, several differences become apparent. Arguably, compound **127** is the closest analogue of aza-C-glycoside **3**, with the major difference, apart from the way the side chain is appended (amide vs. alkyl), being the configuration at the anomeric carbon: "beta" in **3** as opposed to "alpha" in **127**. This difference may be the cause of the slight decrease [**127**: IC_{50}(GBA) 7 μM, **3**: IC_{50}(GBA) 3 μM] in observed inhibitory activity. As mentioned above, the stereochemical outcome in the D-*gluco* series could not be influenced through manipulation (addition of a Lewis acid) of the Ugi-3CR conditions and we therefore had no access to the corresponding "beta" isomer by means of the chemistry described here. When comparing the compounds with N-alkylated deoxynojirimycin derivatives **1** and **2**, it is clear that the compound series do not contain close analogues; all compounds contain a rather bulky side chain at the anomeric carbon. With the aim of arriving at the closest analogues of **1** available through the Staudinger/aza-Wittig/Ugi-3CR sequence of reactions, we turned our attention to the use of isocyanide

Table 1. GBA inhibition assay results with apparent IC_{50} values (IC_{50} values in μM, NI indicates no inhibition up to 1 mM). NT: library entry not synthesized.

2,3-*cis* D-lyxo IC_{50}		2,3-*trans* D-lyxo IC_{50}		2,3-*trans* L-arabino IC_{50}		2,3-*cis* L-arabino IC_{50}		2,3-*trans* L-ido IC_{50}		2,3-*cis* L-ido IC_{50}		2,3-*cis* D-gluco IC_{50}	
25	80	**28**	4	**63**	45	**66**	4	**98**	30	**101**	150	**127**	7
26	200	**29**	20	**64**	50	**67**	40	**99**	40	**102**	20	**128**	45
27	100	**30**	15	**65**	25	**68**	20	**100**	50	NT	–	**129**	30
31	NI	**34**	400	**69**	NI	**72**	100	**103**	NI	**106**	NI	**130**	400
32	NI	**35**	150	**70**	100	**73**	500	**104**	NI	**107**	NI	**131**	NI
33	800	**36**	50	**71**	100	**74**	300	**105**	250	**108**	250	**132**	40
37	NI	**40**	350	**75**	NI	**78**	450	**109**	NI	**112**	NI	**133**	NI
38	NI	**41**	650	**76**	NI	**79**	NI	**110**	NI	**113**	NI	**134**	NI
39	140	**42**	50	**77**	40	**80**	500	**111**	70	**114**	130	**135**	70

137 (available from cyclohexanone following the literature procedure,[18] see Scheme 5). Treatment of **120** with trimethylphosphane, followed by Ugi-3CR of the resulting piperideine with 1-pentenoic acid and isocyanide **137**, gives α-aza-C-glycoside **138**. Acid-mediated hydrolysis gives carboxylate **139**, which can be transformed into the corresponding carboxamide **140** and further elaborated into *N*-adamantanemethoxypentyl derivative **143**. Alternatively, the pentenoyl group in carboxylic acid **139** can be removed and secondary amine **141** *N*-alkylated and globally deprotected to give compound **144**; both close analogues of **1** (essentially the same structure but with either a carboxylate or a primary carboxamide appended in an alpha fashion to the anomeric carbon) were assayed in a preliminary study as inhibitor of the three enzymes involved in glucosylceramide metabolism, GBA, GBA2 and GCS. Of the two new analogues, carboxylate **144** is the most potent inhibitor against all three enzymes [IC_{50}(GBA) 5 μM, IC_{50}(GBA2) 100 nM, IC_{50}(GCS) 20 μM]; in all cases however, **144** is a considerably weaker inhibitor than **1** [IC_{50}(GBA) 200 nM, IC_{50}(GBA2) 1 nM, IC_{50}(GCS) 200 nM]. Carboxamide **143**, in contrast, is a relatively poor inhibitor of the two hydrolases [IC_{50}(GBA) 200 μM, IC_{50}(GBA2) 7 μM] and has no significant inhibitory activity against GCS.



Scheme 5. Preparation of D-*gluco*-piperidine library entries **143** and **144**. *Reagents and conditions:* (a) $POCl_3$, Et_3N, CH_2Cl_2, 30 °C, 1 h, 65%; (b) PMe_3, MeOH, 0 °C, 3 h; 2. pent-4-enoic acid, isocyanide **137**, MeOH, 0 °C, 18 h, 80%; (c) aq. HCl, THF, 20 h, 82%; (d) 1. ClC(O)OEt, Et_3N, THF, 0 °C; 2. 25% aq. NH_3, 0 °C, 1 h, 64%; (e) I_2, H_2O, THF, 0.5 h, **141**: 35%, **142**: 79%; (f) 1. Adamantanemethoxypenanal, $NaCNBH_3$, Na_2SO_4, AcOH, EtOH, 18 h; 2. Pd/C, H_2, EtOH, 18 h, **143**: 39%, **144**: 30%.

Discussion

This paper reports the synthesis of a 64-member aza-C-glycoside library in a combinatorial approach based on our previously reported Staudinger/aza-Wittig/Ugi-3CR methodology. From a synthetic point of view, we believe our approach has value specifically in terms of the numbers of structural and configurational analogues that can be prepared with relative ease. The number of compounds we prepared may appear at a first glance unspectacular. However, we believe that within the field of aza-C-glycosides, and in general in the field of iminosugars, the number is in fact quite substantial, the more so when taking into consideration the potential to diversify at several points in the synthetic strategy. Carbohydrate-derived azido aldehydes are readily available in various configurational and structural isomers. The Ugi-3CR may, or may not, proceed stereoselectively (in some cases the stereochemical outcome can be partially controlled by tuning the conditions) and in all the examples we investigated the diastereoisomers could be readily separated, leading to productive amounts of Ugi-3CR products. Furthermore, both carboxylic acid and isocyanide reaction partners can be selected such that they end up in the Ugi-3CR product as protective groups that can be removed selectively for further functionalisation. On the downside, we recognize that our combinatorial approach brings limitations, or rather introduces obligatory structural features into the library members, which can be avoided in target-oriented approaches. In our initial biological assays we found that these constraints, that is, the appended carboxylate/carboxamide, brings a partial dampening of the activity towards the enzymes assayed (compare lead structure **1** with aza-C-glycoside **144**). A more in-depth analysis of our compounds in assays including a broader panel of glycoprocessing enzymes is required to assess the value of our aza-C-glycoside library, which may then be expanded by including a more diverse set of azido aldehydes, carboxylic acids and isocyanides in the tandem Staudinger/aza-Wittig/Ugi-3CR sequence of reactions.

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 an argon atmosphere. Residual water was removed from starting compounds by repeated coevaporation with dioxane, toluene or dichloroethane. All solvents were removed by evaporation under reduced pressure. Reaction grade acetonitrile, *n*-propanol and methanol were stored on 3 Å molecular sieves. Other reaction grade solvents were stored on 4 Å molecular sieves. Methanol used in the Staudinger/aza-Wittig/Ugi-3CR sequence was distilled from magnesium (5 g/L)/molecular iodine (0.5 g/L) and stored on activated 3 Å molecular sieves under argon. Ethanol was purged of acetaldehyde contamination by distillation from zinc/KOH. CH_2Cl_2 was distilled prior to use from P_2O_5. R_F values were determined from TLC analysis 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. Visualisation of all deprotected iminosugar compounds during TLC analysis was accomplished by exposure to iodine vapor. Column chromatography was performed on silica gel (40–63 μm). ^1H and ^{13}C-APT NMR spectra were recorded with a Bruker DMX 600 (600/150 MHz), Bruker DMX 500 (500/125 MHz), or Bruker AV 400 (400/100 MHz) spectrometer in $CDCl_3$ or MeOD. Chemical shifts are given in ppm (δ) 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 on the basis of 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) into the mass spectrometer (Thermo Finnigan LTQ Orbitrap), which was equipped with an electrospray ion source operated in the positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 250 °C) with resolution R = 60000 at m/z 400 (mass range m/z = 150–2000) and dioctylphthalate (m/z 391.28428) as a "lock mass". The high-resolution mass spectrometer was calibrated prior to measurements with a calibration mixture (Thermo Finnigan). Optical rotations were measured with a Propol automatic polarimeter (Sodium D-line, λ = 589 nm). ATR-IR spectra are reported in cm^{-1} and were recorded with a Shimadzu FTIR-8300 fitted with a single bounce Durasample IR diamond crystal ATR-element.

Enzyme Assays: The enzyme assays used to determine the inhibition of activity of glucosylceramide synthase (GCS), human acid glucosylceramidase (GBA1) and non-lysosomal glucosylceramidase (GBA2) were performed as reported previously.[6c] All compounds were stored (–20 °C) and tested as their hydrochloric acid salt.

General Procedure A. Dess–Martin Periodinane-Mediated Oxidation of Azido Alcohols 49, 84 and 119: Dess–Martin periodinane (1.5 equiv.) was added to a cooled (0 °C), anhydrous solution of azido alcohol (1 equiv.) in CH_2Cl_2 (0.2 M). The reaction mixture was stirred for 30 min at 0 °C and for a further hour at room temp. The reaction mixture was quenched by the addition of satd. aq. $NaHCO_3$ (5 mL/mmol) and 1M aq. $Na_2S_2O_3$ (5 mL/mmol). The resulting two-phase mixture was rapidly stirred/mixed for 15 min. The mixture was diluted with additional CH_2Cl_2 and washed successively with satd. $NaHCO_3$ and brine. The organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column 923 to provide the aldehyde, which should preferably be used immediately but can be stored for 20 h at –20 °C under argon.

General Procedure B. The Tandem Staudinger/Aza-Wittig/Ugi Three-Component Reaction of Azido Aldehydes 5,[4b] 50, 85 and 120: Trimethylphosphane (2 equiv., 1 M in toluene) was added to a cooled (0 °C), anhydrous solution of the appropriate azido aldehyde (1 equiv.) in anhydrous MeOH (0.2 M). The reaction mixture was stirred for 3 h at 0 °C until TLC analysis indicated complete consumption of the azido aldehyde and the appearance of the intermediate phosphazene [R_f = 0 (EtOAc/toluene, 1:2)]. The reaction mixture was concentrated and coevaporated with toluene (3×), concomitant TLC analysis showed complete disappearance of the baseline phosphazene intermediate and emergence of the cyclic imine [R_f of imine from **5** = 0.34 (EtOAc/toluene, 1:4); imine from **50** = 0.38 (EtOAc/PE, 1:1); imine from **85** = 0.15 (EtOAc/toluene, 1:4); imine from **120** = 0.33 (EtOAc/toluene, 1:3)]. The crude cyclic imine was dissolved in anhydrous MeOH (0.3 M) or CH_3CN (0.3 M for

reactions with $InCl_3$), divided into the appropriate amount of portions and cooled to 0 °C. Where appropriate, $InCl_3$ (1.1 equiv.) was added to the CH_3CN solutions of cyclic imine. The appropriate carboxylic acid (1.1 equiv.) and isocyanide (1.3 equiv.) were then successively added and the reaction mixture was stirred for 20 h at 0–5 °C. Saturated aq. $NaHCO_3$ was added to the mixture, which was warmed to room temperature whilst stirring. Ethyl acetate was added and the organic phase was washed with aq. sat. $NaHCO_3$. The organic phase was dried (Na_2SO_4), concentrated and the product was isolated by silica gel column chromatography (EtOAc in toluene, 5 to 50%) to afford the product as a light-yellow oil.

General Procedure C. Acid-Mediated Isomerization and Hydrolysis of 1-Cyclohexenecarboxamides: The 1-cyclohexenecarboxamide-containing iminosugar was dissolved in THF (0.05 M) containing 1.6% aq. HCl (from 36% aq. HCl). The reaction mixture was stirred for 20 h during which it became brown. Sodium carbonate was added to quench the reaction mixture and subsequently removed by filtration. The filtrate was concentrated and the resulting residue was purified by silica gel column chromatography (EtOAc/toluene, 0→100%; 5% AcOH was added to the eluent if the hydrolysis produced a carboxylic acid) to provide the product as a colorless oil.

General Procedure D. Iodine-Mediated Deprotection of Pent-4-enamides: Molecular iodine (3 equiv.) was added to a solution of the pent-4-enamide (1 equiv.) in THF/H_2O (0.05 M; 3:1, v/v). The reaction mixture was stirred for 30–60 min until TLC analysis indicated complete conversion into a lower running product. Aqueous 1 M $Na_2S_2O_3$ was added and the mixture was vigorously stirred for 30 min. The suspension was poured into a mixture of 1 M aq. $Na_2S_2O_3$/sat aq. NaCl (1:1, v/v) and extracted with EtOAc (3×). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography [25% EtOAc in toluene until (*R*/*S*)-γ-iodomethyl-gamma-butyrolactone has eluted, then 25 to 100% EtOAc in toluene; then optional isocratic 10% MeOH in EtOA + 2% NH_4OH for low running products] to yield the deprotected secondary amine as a colorless oil. R_f (*R*/*S*)-γ-iodomethyl-gamma-butyrolactone = 0.70 (EtOAc/toluene, 2:1).

General Method E. *N*-Alkylation of Benzyl-Protected Iminosugars by Reductive Amination: Sodium sulfate (10 equiv.) was added to an anhydrous solution of the iminosugar (1 equiv.) and either butyraldehyde (5 equiv.) or 5-(adamantane-1-ylmethoxy)-1-pentanal (3 equiv.)[6c] in a mixture of EtOH and AcOH (0.05 M, 20:1, v/v). Subsequently, $NaBH_3CN$ (4 equiv.) was added to the mixture and the reaction mixture was stirred for 20 h, then Et_2O (2-fold reaction volume) and satd. aq. $NaHCO_3$ (2-fold reaction volume) were added and vigorously mixed with the reaction mixture. The organic phase was isolated and the aqueous phase was extracted with Et_2O (2×). The combined organic layers were dried (Na_2SO_4) and concentrated. The crude *N*-alkylated compound was used in the ensuing benzyl ether deprotection reaction.

General Procedure F. Deprotection of Benzyl Ethers: All 5-(adamantane-1-yl-methoxy)-1-pentyl moiety containing iminosugars were deprotected by Pd/C catalyzed hydrogenation. *Hydrogenolysis at atmospheric H_2 pressure:* A solution of compound (ca. 50–250 μmol) in EtOH (4 mL) was acidified to pH ca. 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.-% on act. carbon) was added. Hydrogen was passed through the reaction mixture for 15 min and the reaction was stirred for 20 h under atmospheric hydrogen pressure. 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 at higher H_2 pressure (ca. 5 bar) in a Parr apparatus. The obtained residue was purified by silica gel column chromatography (MeOH/CH_2Cl_2, 5→20% + 2% NH_4OH) to yield the deprotected iminosugar as a colorless oil.

All iminosugars that do not contain a 5-(adamantane-1-yl-methoxy)-1-pentyl moiety were deprotected by a BCl_3-mediated debenzylatyion. *Boron-trichloride-mediated debenzylation:* Boron trichloride (10 equiv., 1 M in CH_2Cl_2) was added to a cooled (0 °C) solution of the benzylated iminosugar (1 equiv.) in CH_2Cl_2 (0.05 M). The reaction mixture was stirred for 20 h at 0–5 °C after which MeOH (0.5 mL) was carefully added. The reaction mixture was concentrated and coevaporated with toluene (3×). The obtained residue was purified by silica gel column chromatography (MeOH/CH_2Cl_2, 5→20% + 2% NH_4OH) to yield the deprotected iminosugar as a colorless oil.

General Method G. *N*-Alkylation of Deprotected Iminosugars by Reductive Amination: Sodium cyanoborohydride (5 equiv.) was added to an anhydrous solution of the iminosugar (1 equiv.) and either butyraldehyde (5 equiv.) or 5-(adamantane-1-ylmethoxy)-1-pentanal (3 equiv.)[6c] in a mixture of anhydrous MeOH and AcOH (0.05 M, 100:1, v/v). The reaction mixture was stirred for 20 h and subsequently 4 M HCl (0.5 mL; in dioxane/H_2O) was added. The mixture was stirred for 3 h and subsequently concentrated and coevaporated with toluene (3×). The obtained residue was purified by silica gel column chromatography (5→20% MeOH in CH_2Cl_2 + 2% NH_4OH) to yield the deprotected iminosugar as a colorless oil.

5-(Adamantan-1-yl-methoxy)pentyl Azide (7): Sodium azide (1.56 g, 240 mmol) was added to an anhydrous solution of 5-(adamantan-1-yl-methoxy)pentyl bromide (**6**; 6.0 g, 191 mmol)[6c] in DMSO (20 mL). The reaction mixture was stirred for 20 h. The mixture was diluted with Et_2O (500 mL) and washed successively with H_2O (2 × 500 mL) and satd. aq. NaCl (200 mL). The organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography (toluene/PE, 10→70%) to give **7** (5.14 g, 185 mmol, 95%) as a colorless oil. R_f (**6**) = 0.60 (4% EtOAc/PE); R_f (**7**) = 0.70 (1:4; EtOAc/PE). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.38 (t, J = 6.3 Hz, 2 H, CH_2-5 pentyl), 3.27 (t, J = 7.0 Hz, 2 H, CH_2-1 pentyl), 2.95 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.77–1.54 (m, 12 H, 3×CH_2 Ada, CH_2-2, CH_2-4 pentyl), 1.53 (d, J = 2.7 Hz, 6 H, 3×CH_2 Ada), 1.49–1.39 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.2 (OCH_2-Ada), 71.4 (CH_2-5 pentyl), 51.6 (CH_2-1 pentyl), 39.9 (CH_2 Ada), 37.4 (CH_2 Ada), 34.3 (C_q Ada), 29.3 (CH_2-4 pentyl), 28.9 (CH_2-2 pentyl), 28.5 (CH Ada), 23.7 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2902, 2848, 2093, 1727, 1453, 1358, 1259, 1158, 1112 cm^{-1}. HRMS: calcd. for $[C_{16}H_{27}N_3O + H]^+$ 278.2227 [M + H]$^+$; found 278.2228.

5-(Adamantan-1-yl-methoxy)pentan-1-amine (8): Trimethylphosphane (33 mL, 33 mmol, 1 M in THF) was added over a 2 min period to a cooled (0 °C) solution of **7** (4.57 g, 16.5 mmol) in THF (83 mL) and H_2O (7 mL). The reaction mixture stirred for 3 h at 0 °C after which it was concentrated and coevaporated three times with toluene. The residue was purified by silica gel column chromatography (MeOH/EtOAc, 10→70% + 5% NH_4OH). Purified **8** contained some dissolved silica gel that could be removed by redissolving **8** in CH_2Cl_2 and passing it over a glassfibre filter to provide **8** (3.48 g, 13.86 mmol, 84%) after concentration as a colorless oil. R_f = 0.10 (25% MeOH/EtOAc). ^1H NMR (200 MHz, $CDCl_3$): δ = 3.38 (t, J = 6.4 Hz, 1 H, CH_2-5 pentyl), 2.95 (s, 2 H,

OCH_2-Ada), 2.70 (t, J = 6.7 Hz, 1 H, CH_2-1 pentyl), 1.94 (s, 3 H, 3×CH Ada), 1.73–1.44 (m, 18 H, 6×CH_2 Ada, 3×CH_2 pentyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 81.8 (OCH_2-Ada), 71.3 (CH_2-5 pentyl), 41.9 (CH_2-1 pentyl), 39.6 (CH_2 Ada), 37.2 (CH_2 Ada), 34.0 (C_q Ada), 29.4, 29.3 (2×CH_2 pentyl), 28.2 (CH Ada), 23.4 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3358, 2899, 2847, 1575, 1453, 1297, 1156, 1111, 945, 860, 745 cm^{-1}. HRMS: calcd. for $[C_{16}H_{29}NO + H]^+$ 252.2322 $[M + H]^+$; found 252.2321.

***N*-[5-(Adamantan-1-yl-methoxy)pentyl]formamide (9):** Acetic formic anhydride was prepared by heating a mixture of acetic anhydride (1.51 mL, 16.0 mmol) and formic acid (0.66 mL, 17.6 mmol) at 55 °C for 2 h. The prepared acetic formic anhydride (16.0 mmol) was cooled to 0 °C and added to a cooled (0 °C) solution of **8** (2.01 g, 8.0 mmol) in CH_2Cl_2 (22 mL). The reaction mixture was stirred at room temp. for 20 h, after which it was concentrated. The residue was purified by silica gel column chromatography (EtOAc/PE, 30→90%) to afford **9** (1.84 g, 6.6 mmol, 82%) as a colorless oil. R_f = 0.39 (EtOAc); $KMnO_4$ staining. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 [s, 1 H, HC(O)N], 5.56–5.41 [m, 1 H, C(O)NH], 3.38 (t, J = 6.3 Hz, 2 H, CH_2-5 pentyl), 3.32 (dd, J = 6.7, 13.4 Hz, 1 H, C*H*H-1 pentyl), 3.25 (dd, J = 7.0, 13.0 Hz, 1 H, CH*H*-1 pentyl), 2.95 (s, 2 H, OCH_2-Ada), 1.96 (s, 3 H, 3×CH Ada), 1.68 (dd, J = 12.0, 34.5 Hz, 6 H, 3×CH_2 Ada), 1.62–1.53 (m, 4 H, CH_2-2, CH_2-4 pentyl), 1.52 (d, J = 2.3 Hz, 6 H, 3×CH_2 Ada), 1.45–1.32 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 161.5 (C=O), 81.9 (OCH_2-Ada), 71.3 (CH_2-5 pentyl), 39.7 (CH_2 Ada), 38.1 (CH_2-1 pentyl), 37.2 (CH_2 Ada), 34.0 (C_q Ada), 29.1, 29.1 (2×CH_2 pentyl), 28.2 (CH Ada), 23.5 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3288, 2899, 2847, 1666, 1540, 1452, 1382, 1232, 1157, 110, 753 cm^{-1}. HRMS: calcd. for $[C_{17}H_{29}NO_2 + H]^+$ 280.2271 $[M + H]^+$; found 280.2272.

***N*-[5-(Adamantan-1-yl-methoxy)pentyl] Isocyanide (10):** Phosphoryl chloride (0.51 mL, 5.49 mmol) was added dropwise to an anhydrous and cooled (–30 °C) solution of **9** (1.02 g, 3.66 mmol) and Et_3N (2.54 mL, 18.3 mmol) in CH_2Cl_2 (19 mL). The reaction mixture was stirred for 1 h at –30 °C, after which TLC analysis indicated complete consumption of **9**. The dark-brown reaction mixture was quenched by addition of satd. aq. $NaHCO_3$ (5 mL). The reaction mixture was diluted with Et_2O (100 mL) and washed successively with satd. aq. $NaHCO_3$ (2× 100 mL) and brine (50 mL). The organic phase was dried (Na_2SO_4) and concentrated. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/hexane, 20→100%) to afford **10** (773 mg, 2.96 mmol, 81%) as a colorless oil. Isocyanide **10** was preferably used immediately but was stable when stored at –20 °C under argon. R_f = 0.90 (EtOAc); 0.40 (EtOAc/PE, 1:9); $KMnO_4$ staining. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.43–3.34 (m, 4 H, CH_2-1 pentyl, CH_2-5 pentyl), 2.95 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.76–1.45 (m, 18 H, 6×CH_2 Ada, 3×CH_2 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9 (t, J_{CN} = 5.5 Hz, NC), 81.9 (OCH_2-Ada), 71.0 (CH_2-5 pentyl), 41.5 (t, J_{N-Cl} = 6.4 Hz, CH_2-1), 39.7 (CH_2 Ada), 37.2 (CH_2 Ada), 34.0 (C_q Ada), 28.9, 28.6, 28.3 (CH Ada), 23.2 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2900, 2847, 2146, 1453, 1358, 1157, 1102, 2929, 1652, 1460, 1058 cm^{-1}.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-D-*galacto*-hexonamide (13): Subjecting azido aldehyde **5** (200 μmol) to the tandem SAWU-3CR (General Procedure B in MeOH) produced a separable 1:20 mixture of **14** (4 mg, 5 μmol) and **13** (91 mg, 119 μmol) in a combined yield of 62%. R_f = 0.15 (EtOAc/toluene, 2:3). ^{1}H NMR (600 MHz, $CDCl_3$, 2:1 mixture of rotamers; major rotamer): δ = 7.41–7.12 (m, 15 H, H_{Ar} Bn), 6.22 [t, J = 5.7 Hz, 1 H, C(O)NH], 5.84–5.72 (m, 1 H, =CH pentenyl), 5.06–4.89 (m, 2 H), 4.85–4.66 (m, 2 H, =CH_2 pentenyl), 4.85–4.66 (m, 2 H), 4.64 (d, J = 6.0 Hz, 1 H, 2-H), 4.60–4.46 (m, 3 H), 4.44–4.40 (m, 1 H, 4-H), 4.39–4.33 (m, 1 H, 5-H), 4.14 (t, J = 10.1 Hz, 1 H, 6a-H), 3.88 (dd, J = 5.0, 6.7 Hz, 1 H, 3-H), 3.82 (dd, J = 3.3, 10.1 Hz, 1 H, 6b-H), 3.29–3.20 (m, 2 H, CH_2-5 pentyl), 3.18–2.97 (m, 1 H, NCH_2-1 pentyl), 2.90 (s, 2 H, OCH_2-Ada), 2.87–2.72 (m, 2 H, NCH_2 pentenyl), 2.45–2.27 (m, 2 H, CH_2 pentenyl), 1.95 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 12.7, 38.4 Hz, 6 H, 3×CH_2 Ada), 1.59–0.97 (m, 12 H, 3×CH_2 Ada, 3×CH_2 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, major rotamer): δ = 173.7 (NC=O pentenyl), 167.7 [NHC(O)-1], 138.3, 137.7, 137.4 (3×C_q Bn), 137.2 (=CH pentenyl), 128.6–127.5 (CH_{Ar} Bn), 115.2 (=CH_2 pentenyl), 81.8 (OCH_2-Ada), 78.8 (C-3), 76.7 (C-4), 74.8, 73.5, 72.4 (3×CH_2 Bn), 71.3 (CH_2-5 pentyl), 69.3 (C-6), 64.3 (C-2), 58.5 (C-5), 39.7 (CH_2 Ada), 39.4 (NCH_2-1 pentyl), 37.3 (CH_2 Ada), 34.0 (C_q Ada), 33.4 (NCH_2 pentenyl), 29.3, 29.2, 28.9 (CH_2 pentenyl, CH_2-2, CH_2-4 pentyl), 28.3 (CH Ada), 23.4 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3316, 2901, 2848, 1653, 1532, 1453, 1407, 1359, 1212, 1097, 911, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = 6.3 (c = 9.0, $CHCl_3$). HRMS: calcd. for $[C_{48}H_{62}O_6N_2 + H]^+$ 763.4681 $[M + H]^+$; found 763.4683.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-D-*talo*-hexonamide (14): Subjecting azido aldehyde **5** (750 μmol) to the tandem SAWU-3CR (General Procedure B in the presence of $InCl_3$ in CH_3CN) produced a separable 1.7:1 mixture of **14** (170 mg, 223 μmol) and **13** (100 mg, 131 μmol) in a combined yield of 47%. R_f = 0.49 (EtOAc/toluene, 2:3). ^{1}H NMR (600 MHz, $CDCl_3$, 10:1 mixture of rotamers; major rotamer): δ = 7.36–7.23 (m, 15 H, H_{Ar} Bn), 6.63 [t, J = 5.6 Hz, 1 H, C(O)NH], 5.76 (ddt, J = 6.5, 10.2, 16.8 Hz, 1 H, =CH pentenyl), 5.00–4.91 (m, 2 H, =CH_2 pentenyl), 4.67 (d, J = 12.0 Hz, 1 H, C*H*H Bn), 4.61 (d, J = 11.6 Hz, 1 H, C*H*H Bn), 4.59–4.55 (m, 2 H, 2×CH*H* Bn), 4.48 (d, J = 11.9 Hz, 1 H, C*H*H Bn), 4.46 (dd, J = 4.3, 7.8 Hz, 1 H, 4-H), 4.42 (d, J = 11.9 Hz, 1 H, CH*H* Bn), 4.39 (s, 1 H, 2-H), 4.38–4.35 (m, 1 H, 5-H), 4.13 (dd, J = 3.5, 10.6 Hz, 1 H, 6a-H), 4.06 (d, J = 4.3 Hz, 1 H, 3-H), 3.70 (dd, J = 6.1, 10.6 Hz, 1 H, 6b-H), 3.35 (t, J = 6.6 Hz, 2 H, CH_2-5 pentyl), 3.20 (dt, J = 7.1, 13.5 Hz, 1 H, NC*H*H-1 pentyl), 3.07 (dt, J = 7.1, 12.7 Hz, 1 H, NCH*H*-1 pentyl), 2.94 (s, 2 H, OCH_2-Ada), 2.75 (ddd, J = 6.3, 8.8, 15.4 Hz, 1 H, NC*H*H pentenyl), 2.53 (ddd, J = 6.4, 8.9, 15.6 Hz, 1 H, NCH*H* pentenyl), 2.40–2.25 (m, 2 H, CH_2 pentenyl), 1.95 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 12.1, 36.2 Hz, 6 H, 3×CH_2 Ada), 1.59–1.49 (m, 8 H, 3×CH_2 Ada, CH_2-4 pentyl), 1.49–1.42 (m, 2 H, CH_2-2 pentyl), 1.36–1.29 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, major rotamer): δ = 174.3 (NC=O pentenyl), 169.6 [NHC(O)-1], 138.2, 137.9, 137.9 (3×C_q Bn), 137.6 (=CH pentenyl), 128.6, 128.5, 128.0, 128.0, 127.9, 127.8, 127.7 (CH_{Ar} Bn), 115.2 (=CH_2 pentenyl), 82.1 (OCH_2-Ada), 78.9 (C-4), 78.4 (C-3), 73.5, 72.7 (3×CH_2 Bn), 71.7 (C-6), 71.6 (CH_2-5 pentyl), 65.4 (C-2), 59.3 (C-5), 39.9 (CH_2 Ada), 39.8 (NCH_2-1 pentyl), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 33.8 (NCH_2 pentenyl), 29.4, 29.3, 29.3 (CH_2 pentenyl, CH_2-2, CH_2-4 pentyl), 28.4 (CH Ada), 23.7 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3308, 2901, 2848, 1651, 1622, 1545, 1452, 1360, 1146, 1097, 1054, 1027, 911, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = 25.5 (c = 2.4, $CHCl_3$). HRMS: calcd. for $[C_{48}H_{62}O_6N_2 + H]^+$ 763.4681 $[M + H]^+$; found 763.4684.

1,1,3,3-Tetramethylbutyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-D-*galacto*-hexonamide (15): Subjecting azido aldehyde **5** (500 μmol) to the tandem SAWU-3CR (General Procedure B in MeOH) produced a separable 1:15 mixture of **16** (15 mg, 23 μmol) and **15** (216 mg, 338 μmol) in a combined yield of 72%. R_f = 0.24 (EtOAc/toluene, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 2:1 mixture of rotamers; major rotamer): δ = 7.32–7.25 (m, 15 H, H_{Ar} Bn), 6.02

[s, 1 H, C(O)NH], 5.85–5.73 (m, 1 H, =CH pentenyl), 5.06–4.91 (m, 2 H, =CH_2 pentenyl), 4.75 (d, *J* = 11.5 Hz, 1 H, C*H*H Bn), 4.69 (d, *J* = 11.6 Hz, 1 H, CH*H* Bn), 4.58 (d, *J* = 11.6 Hz, 1 H, C*H*H Bn), 4.53–4.47 (m, 3 H, 2-H, C*H*H Bn, CH*H* Bn), 4.44–4.36 (m, 2 H, 4-H, CH*H* Bn), 4.34–4.27 (m, 1 H, 5-H), 4.11 (dd, *J* = 10.2 Hz, 1 H, 6-Ha), 3.87 (d, *J* = 9.9 Hz, 1 H, 6-Hb), 3.83 (dd, *J* = 4.8 Hz, 1 H, 3-H), 2.89–2.84 (m, 1 H, NC*H*H pentenyl), 2.46–2.31 (m, 3 H, NCH*H* pentenyl, CH_2 pentenyl), 1.61 (d, *J* = 14.8 Hz, 1 H, C*H*2-H tMB), 1.46 (d, *J* = 15.2 Hz, 1 H, CH2-H tMB), 1.00 (d, *J* = 5.6 Hz, 6 H, 2×CH_3 tMB), 0.87 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ = 173.8 (NC=O pentenyl), 166.3 [NHC(O)-1], 138.0, 137.5 (2×C_q Bn), 137.1 (=CH pentenyl), 137.0 (C_q Bn), 128.3–127.1 (CH_{Ar} Bn), 114.9 (=CH_2 pentenyl), 78.7 (C-4), 76.6 (C-3), 74.6, 73.3, 72.0 (3×CH_2 Bn), 69.8 (C-6), 64.7 (C-2), 59.0 (C-5), 55.6 (NHC_q-1 tMB), 53.3 (CH_2-2 tMB), 33.3 (CH_2 pentenyl), 31.4 (C_q-3 tMB), 31.3, 31.2 (2×CH_3-2 tMB), 31.1 (3×CH_3 tMB), 28.6 (CH_2 pentenyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3323, 2951, 1666, 1521, 1400, 1098, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = 11.4 (*c* = 9.0, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{52}O_5N_2 + H]^+$ 641.3949 $[M + H]^+$; found 641.3949.

1,1,3,3-Tetramethylbutyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-D-*talo*-hexonamide (16): Subjecting azido aldehyde **5** (600 μmol) to the tandem SAWU-3CR (General Procedure B in the presence of $InCl_3$ in CH_3CN) produced a separable 5.3:1 mixture of **16** (204 mg, 318 μmol) and **15** (38 mg, 60 μmol) in a combined yield of 63%. R_f = 0.72 (EtOAc/toluene, 2:3). ^{1}H NMR (400 MHz, $CDCl_3$, 6:1 mixture of rotamers; major rotamer): δ = 7.33–7.22 (m, 15 H, H_{Ar}), 6.28 [s, 1 H, C(O)NH], 5.81–5.74 (m, 1 H, =CH pentenyl), 4.97 (ddd, *J* = 1.2, 16.8, 37.2 Hz, 2 H, =CH_2 pentenyl), 4.65 (d, *J* = 12.0 Hz, 1 H, C*H*H Bn), 4.63 (d, *J* = 12.0 Hz, 1 H, C*H*H Bn), 5.58 (d, *J* = 12.0 Hz, 1 H, CH*H* Bn), 4.55 (d, *J* = 12.0 Hz, 1 H, CH*H* Bn), 4.47 (d, *J* = 12.0 Hz, 1 H, C*H*H Bn), 4.44 (dd, *J* = 4.2, 7.8 Hz, 1 H, 4-H), 4.41 (d, *J* = 12.0 Hz, 1 H, CH*H* Bn), 4.34–4.32 (m, 2 H, 2-H, 5-H), 4.16 (dd, *J* = 3.6, 10.8 Hz, 1 H, 6a-H), 4.08 (d, *J* = 4.2 Hz, 1 H, 3-H), 3.69 (dd, *J* = 5.4, 10.8 Hz, 1 H, 6b-H), 2.76–2.71 (m, 1 H, NC*H*H pentenyl), 2.56–2.51 (m, 1 H, NCH*H* pentenyl), 2.41–2.31 (m, 2 H, CH_2 pentenyl), 1.71 (d, *J* = 15.0 Hz, 1 H, C*H*H-2 tMB), 1.60 (d, *J* = 15.0 Hz, 1 H, CH*H*-2 tMB), 1.32 (d, *J* = 14.4 Hz, 6 H, 2×CH_3 tMB), 0.95 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ = 174.1 (NC=O pentenyl), 168.1 [NHC(O)-1], 137.8, 137.7, 137.6 (3×C_q Bn), 137.3 (=CH pentenyl), 128.4, 128.3, 128.2, 128.0, 127.6, 127.5, 127.4 (CH_{Ar} Bn), 114.9 (=CH_2 pentenyl), 78.7 (C-4), 77.9 (C-3), 73.2, 72.4 (3×CH_2 Bn), 71.5 (C-6), 65.8 (C-2), 59.1 (C-5), 55.2 (NHC_q-1 tMB), 51.4 (CH_2-2 tMB), 33.6 (NCH_2 pentenyl), 31.4 (C_q-3 tMB), 31.3 (CH_3-4, 2×CH_3 tMB), 29.0 (CH_2 pentenyl), 28.8, 28.6 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3329, 2950, 1679, 1624, 1544, 1422, 1096, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = 22.3 (*c* = 6.1, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{52}O_5N_2 + H]^+$ 641.3949 $[M + H]^+$; found 641.3949.

Pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-D-*galacto*-hexonamide (17): Subjecting azido aldehyde **5** (194 μmol) to the tandem SAWU-3CR (General Procedure B in MeOH) produced a separable 1:21 mixture of **18** (5 mg, 8 μmol) and **17** (104 mg, 174 μmol) in a combined yield of 94%. R_f = 0.40 (EtOAc/toluene, 2:1). ^{1}H NMR (600 MHz, $CDCl_3$, 2:1 mixture of rotamers; major rotamer): δ = 7.38–7.20 (m, 15 H, H_{Ar} Bn), 6.19 [t, *J* = 5.5 Hz, 1 H, C(O)NH], 5.84–5.74 (m, 1 H, =CH pentenyl), 5.07–4.91 (m, 2 H, =CH_2 pentenyl), 4.86–4.46 (m, 7 H, 2-H, 3×CH_2 Bn), 4.44–4.41 (m, 1 H, 4-H), 4.39–3.34 (m, 1 H, 5-H), 4.14 (dd, *J* = 10.2 Hz, 1 H, 6a-H), 3.88 (dd, *J* = 5.0, 6.7 Hz, 1 H, 3-H), 3.83 (dd, *J* = 3.6, 10.3 Hz, 1 H, 6b-H), 3.19–2.97 (m, 2 H, NCH_2-1 pentyl), 2.97–2.69 (m, 2 H, NCH_2 pentenyl), 2.46–2.29 (m, 2 H, CH_2 pentenyl), 1.35–0.94 (m, 6 H, 3×CH_2 pentyl), 0.80–0.73 (m, 6 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, major rotamer): δ = 173.8 (NC=O pentenyl), 167.7 [NHC(O)-1], 138.4, 137.8, 137.5 (3×C_q Bn), 137.2 (=CH pentenyl), 128.7–127.5 (CH_{Ar} Bn), 115.2 (=CH_2 pentenyl), 78.8 (C-4), 76.8 (C-3), 74.9, 73.6, 72.4 (3×CH_2 Bn), 69.4 (C-6), 64.4 (C-2), 58.6 (C-5), 39.4 (NCH_2-1 pentyl), 33.5 (NCH_2 pentenyl), 29.0, 22.3, 14.1 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3320, 2939, 2868, 1652, 1532, 1454, 1406, 1212, 1142, 1096, 1025, 911, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = 8.9 (*c* = 4.2, $CHCl_3$). HRMS: calcd. for $[C_{37}H_{46}O_5N_2 + H]^+$ 599.3479 $[M + H]^+$; found 599.3478.

Pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-D-*talo*-hexonamide (18): Subjecting azido aldehyde **5** (750 μmol) to the tandem SAWU-3CR (General Procedure B in the presence of $InCl_3$ in CH_3CN) produced a separable 5.4:1 mixture of **18** (128 mg, 215 μmol) and **17** (24 mg, 40 μmol) in a combined yield of 34%. R_f = 0.72 (EtOAc/toluene, 2:3). ^{1}H NMR (600 MHz, $CDCl_3$, 5.5:1 mixture of rotamers; major rotamer): δ = 7.35–7.24 (m, 15 H, H_{Ar} Bn), 6.76 [t, *J* = 5.6 Hz, 1 H, C(O)NH], 5.76 (ddt, *J* = 6.5, 10.2, 16.8 Hz, 1 H, =CH pentenyl), 4.99–4.89 (m, 2 H, =CH_2 pentenyl), 4.67–4.52 (m, 4 H, 2×CH_2 Bn), 4.50–4.45 (m, 2 H, 4-H, C*H*H Bn), 4.43 (s, *J* = 12.2 Hz, CH*H* Bn), 4.42 (s, 1 H, H2), 4.40–4.36 (m, 1 H, 5-H), 4.13 (dd, *J* = 3.5, 10.6 Hz, 1 H, 6a-H), 4.04 (d, *J* = 4.3 Hz, 1 H, 3-H), 3.70 (dd, *J* = 6.2, 10.6 Hz, 1 H, 6b-H), 3.20 (dt, *J* = 7.1, 13.5 Hz, 1 H, NC*H*H-1 pentyl), 3.04 (dt, *J* = 7.2, 12.7 Hz, 1 H, NCH*H*-1 pentyl), 2.75 (ddd, *J* = 6.2, 8.9, 15.5 Hz, 1 H, NC*H*H pentenyl), 2.54 (ddd, *J* = 6.3, 9.0, 15.6 Hz, 1 H, NCH*H* pentenyl), 2.44–2.26 (m, 2 H, CH_2 pentenyl), 1.46–1.39 (m, 2 H, CH_2-2 pentyl), 1.33–1.21 (m, 4 H, CH_2-3, CH_2-4 pentyl), 0.88 (t, *J* = 7.2 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, major rotamer): δ = 174.3 (NC=O pentenyl), 169.6 [NHC(O)-1], 138.2, 137.9, 137.8 (3×C_q Bn), 137.6 (=CH pentenyl), 129.0, 128.6, 128.6, 128.5, 128.4, 128.3, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6 (CH_{Ar} Bn), 115.2 (=CH_2 pentenyl), 78.8 (C-4), 78.4 (C-3), 73.4, 72.6, 72.5 (3×CH_2 Bn), 71.7 (C-6), 65.4 (C-2), 59.2 (C-5), 39.7 (NCH_2-1 pentyl), 33.8 (NCH_2 pentenyl), 29.3 (CH_2 pentenyl), 29.2, 29.1, 22.5 (3×CH_2 pentyl), 14.2 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3312, 2956, 2929, 2869, 1652, 1622, 1557, 1453, 1434, 1361, 1143, 1097, 1027, 1000, 911, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = 26.6 (*c* = 2.5, $CHCl_3$). HRMS: calcd. for $[C_{37}H_{46}O_5N_2 + H]^+$ 599.3479 $[M + H]^+$; found 599.3478.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-D-*galacto*-hexonamide (19): Compound **19** (385 mg, 0.57 mmol) was synthesized in 97% yield from **13** (0.58 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.25 (EtOAc/toluene, 2:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 [t, *J* = 5.5 Hz, 1 H, C(O)NH], 7.38–7.18 (m, 15 H, H_{Ar} Bn), 5.91–5.73 (s, NH), 4.95 (dd, *J* = 4.1, 5.8 Hz, 1 H, 3-H), 4.84 (d, *J* = 6.0 Hz, 1 H, 2-H), 4.74 (d, *J* = 11.3 Hz, 1 H, C*H*H Bn), 4.70 (d, *J* = 11.3 Hz, 1 H, CH*H* Bn), 4.62–4.46 (m, 4 H, 2×CH_2 Bn), 4.35 (dd, *J* = 3.8, 6.4 Hz, 1 H, 4-H), 4.16 (dt, *J* = 5.4, 10.8 Hz, 1 H, 5-H), 3.96 (dd, *J* = 10.4 Hz, 1 H, 6a-H), 3.70 (dd, *J* = 4.6, 10.4 Hz, 1 H, 6b-H), 3.37 (t, *J* = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.32–3.16 (m, 2 H, CH_2-1 pentyl), 2.91 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.67 (dd, *J* = 12.4, 40.4 Hz, 6 H, 3×CH Ada), 1.61–1.54 (m, 2 H, CH_2-4 pentyl), 1.52 (d, *J* = 6.6 Hz, 6 H, 3×CH Ada), 1.47–1.36 (m, 3 H, CH_2-2, C*H*H-3 pentyl), 1.31–1.23 (m, 1 H, CH*H*-3 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.8 [C(O)-1], 137.3, 137.1, 136.9 (3×C_q Bn), 128.7, 128.7, 128.6, 128.3, 128.1, 128.1, 127.7, 127.7 (CH_{Ar} Bn), 82.1 (C-3), 82.0 (C-4), 78.7, 78.4, 74.7, 73.7, 73.7, 71.4, 71.4 (3×CH_2 Bn), 66.1 (C-6), 59.9 (C-2), 58.5 (C-5), 40.5 (CH_2-1 pentyl), 39.9 (CH_2 Ada), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 29.3 (CH_2 pentyl), 29.2, 29.0 (CH_2 pentyl), 28.4 (CH Ada), 23.7, 23.7 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3242,

2900, 2847, 1686, 1544, 1453, 1359, 1153, 1097, 1026, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = 13.5 (c = 1.8, $CHCl_3$). HRMS: calcd. for $[C_{43}H_{56}O_5N_2 + H]^+$ 681.4262 $[M + H]^+$; found 681.4262.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-D-*talo*-hexonamide (20): Compound **20** (75 mg, 0.11 mmol) was synthesized in 75% yield from **14** (0.15 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.46 (EtOAc/toluene, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 [t, J = 5.8 Hz, 1 H, C(O)NH], 7.38–7.24 (m, 15 H, H_{Ar} Bn), 4.73 (d, J = 12.2 Hz, 1 H, C*H*H Bn), 4.65 (d, J = 12.2 Hz, 1 H, CH*H* Bn), 4.63 (d, J = 11.8 Hz, 1 H, C*H*H Bn), 4.53 (d, J = 11.9 Hz, 1 H, C*H*H Bn), 4.50 (d, J = 11.9 Hz, 1 H, CH*H* Bn), 4.45 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.10 (dd, J = 4.0 Hz, 1 H, 3-H), 3.95 (dd, J = 5.1 Hz, 1 H, 4-H), 3.79 (d, J = 3.4 Hz, 1 H, 2-H), 3.77 (dd, J = 9.2 Hz, 1 H, 6a-H), 3.72 (dd, J = 5.0, 9.5 Hz, 1 H, 6b-H), 3.55–3.48 (m, 1 H, 5-H), 3.35 (t, J = 6.5 Hz, 2 H, CH_2-5 pentyl), 3.27–3.21 (m, 1 H, NC*H*H-1 pentyl), 3.21–3.09 (m, 1 H, NCH*H*-1 pentyl), 2.94 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 12.1, 37.4 Hz, 6 H, 3×CH_2 Ada), 1.58–1.49 (m, 8 H, 3×CH_2 Ada, CH_2-4 pentyl), 1.49–1.41 (m, 2 H, CH_2-2 pentyl), 1.38–1.29 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.5 [C(O)-1], 138.4, 138.3, 138.2 (3×C_q Bn), 128.7, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8 (CH_{Ar} Bn), 82.1 (OCH_2-Ada), 81.7 (C-3), 78.9 (C-4), 73.5, 72.9, 72.0 (3×CH_2 Bn), 71.5 (CH_2-5 pentyl), 70.6 (C-6), 64.3 (C-2), 59.2 (C-5), 39.9 (CH_2 Ada), 39.3 (NCH_2-1 pentyl), 37.4 (CH_2 Ada), 34.3 (C_q Ada), 29.6 (CH_2-2 pentyl), 29.4 (CH_2-4 pentyl), 28.5 (CH Ada), 23.8 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3328, 2900, 2848, 1667, 1653, 1519, 1453, 1360, 1096, 1058, 1027, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = –4.2 (c = 0.6, $CHCl_3$). HRMS: calcd. for $[C_{43}H_{56}O_5N_2 + H]^+$ 681.4262 $[M + H]^+$; found 681.4261.

1,1,3,3-Tetramethylbutyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-D-*galacto*-hexonamide (21): Compound **21** (301 mg, 0.54 mmol) was synthesized in 92% yield from **15** (0.58 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.40 (EtOAc/toluene, 1:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 [s, 1 H, C(O)NH], 7.37–7.25 (m, 15 H, H_{Ar} Bn), 5.56–5.19 (s, 1 H, NH), 4.76 (d, J = 11.4 Hz, 1 H, C*H*H Bn), 4.73 (d, J = 11.4 Hz, 1 H, CH*H* Bn), 4.64 (d, J = 11.7 Hz, 1 H, C*H*H Bn), 4.61 (dd, J = 3.8, 6.1 Hz, 1 H, 3-H), 4.57 (d, J = 11.7 Hz, 1 H, C*H*H Bn), 4.55–4.49 (m, 2 H, 2×CH*H* Bn), 4.28 (d, J = 6.3 Hz, 1 H, 2-H), 4.18 (dd, J = 3.8, 6.2 Hz, 1 H, 4-H), 3.89–3.84 (m, 1 H, 5-H), 3.81 (dd, J = 9.2 Hz, 1 H, 6a-H), 3.76 (dd, J = 4.6, 9.7 Hz, 1 H, 6b-H), 1.66–1.57 (m, 2 H, CH_2-2 tMB), 1.33 (d, J = 29.4 Hz, 6 H, 2×CH_3 tMB), 0.95 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.1 [C(O)-1], 137.8, 137.7, 137.5 (3×C_q Bn), 128.3, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4 (CH_{Ar} Bn), 79.2 (C-3), 78.7 (C-4), 73.7, 73.2, 73.0 (3×CH_2 Bn), 69.2 (C-6), 60.9 (C-2), 57.9 (C-5), 55.2 (NHC_q-1 tMB), 52.4 (CH_2-2 tMB), 31.6 (C_q-3 tMB), 31.4 (2×CH_3, CH_3-4 tMB), 28.4 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3274, 2951, 1681, 1668, 1530, 1093, 732, 696 cm^{-1}. $[\alpha]_D^{20}$ = 4.2 (c = 6.0, $CHCl_3$). HRMS: calcd. for $[C_{35}H_{46}O_4N_2 + H]^+$ 559.3530 $[M + H]^+$; found 559.352.

1,1,3,3-Tetramethylbutyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-D-*talo*-hexon-amide (22): Compound **22** (212 mg, 0.38 mmol) was synthesized in 69% yield from **16** (0.55 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.59 (EtOAc/toluene, 1:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 [s, 1 H, C(O)NH], 7.39–7.21 (m, 15 H, H_{Ar} Bn), 4.73 (d, J = 12.0 Hz, 1 H, C*H*H Bn), 4.65–4.59 (m, 2 H, CH*H* Bn, C*H*H Bn), 4.52 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.48 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.42 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.08 (dd, J = 3.2, 4.7 Hz, 1 H, 3-H), 3.91 (dd, J = 4.7, 6.0 Hz, 1 H, 4-H), 3.78 (dd, J = 9.3 Hz, 1 H, 6a-H), 3.72 (dd, J = 4.8, 9.6 Hz, 1 H, 6b-H), 3.67 (d, J = 3.2 Hz, 1 H, 2-H), 3.52 (ddd, J = 4.8, 5.9, 8.9 Hz, 1 H, 5-H), 2.55 (s, 1 H, NH), 1.72 (d, J = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.63 (d, J = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.36 (d, J = 17.3 Hz, 6 H, 2×CH_3 tMB), 0.94 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.0 [C(O)-1], 138.1, 138.0, 137.8 (3×C_q Bn), 128.3, 128.2, 127.8, 127.7, 127.6, 127.4 (CH_{Ar} Bn), 81.1 (C-3), 78.2 (C-4), 73.2, 73.4, 71.5 (3×CH_2 Bn), 70.3 (C-6), 64.6 (C-2), 58.8 (C-5), 54.2 (NHC_q-1 tMB), 51.7 (CH_2-2 tMB), 31.5 (C_q-3 tMB), 31.3 (2×CH_3, CH_3-4 tMB), 29.1, 28.6 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3317, 2950, 1668, 1515, 1093, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = –14.6 (c = 3.7, $CHCl_3$). HRMS: calcd. for $[C_{35}H_{46}O_4N_2 + H]^+$ 559.3530 $[M + H]^+$; found 559.3528.

Pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-D-*galacto*-hexonamide (23): Compound **23** (341 mg, 0.66 mmol) was synthesized from **17** (0.86 mmol, 77%) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.15 (EtOAc/toluene, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 [s, 1 H, C(O)NH], 7.38–7.19 (m, 15 H, H_{Ar} Bn), 6.34–6.11 (s, 1 H, NH), 4.74–4.48 (m, 7 H, 3-H, 3×CH_2 Bn), 4.47 (d, J = 5.6 Hz, 1 H, 2-H), 4.20 (dd, J = 3.9, 6.2 Hz, 1 H, 4-H), 3.92–3.86 (m, 1 H, 5-H), 3.83 (dd, J = 9.6 Hz, 1 H, 6a-H), 3.74–3.67 (m, 1 H, 6b-H), 3.16–3.10 (m, 2 H, NCH_2-1 pentyl), 1.39–1.32 (m, 2 H, CH_3-2 pentyl), 1.23–1.13 (m, 4 H, 2×CH_2 pentyl), 0.80 (t, J = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.7 [C(O)-1], 137.8, 137.6, 137.4 (3×C_q Bn), 128.8, 128.4, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 127.2 (CH_{Ar} Bn), 79.1 (C-3), 78.8 (C-4), 74.0, 73.4, 73.2 (3×CH_2 Bn), 68.3 (C-6), 60.6 (C-2), 58.0 (C-5), 39.9 (NCH_2-1 pentyl), 29.0 (CH_2-2 pentyl), 28.8, 22.2 (2×CH_2 pentyl), 14.0 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3231, 2929, 2862, 1682, 1652, 1543, 1454, 1358, 1257, 1210, 1092, 1026, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = 14.4 (c = 5.5, $CHCl_3$). HRMS: calcd. for $[C_{32}H_{40}O_4N_2 + H]^+$ 517.3061 $[M + H]^+$; found 517.3059.

Pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-D-*talo*-hexonamide (24): Compound **24** (81 mg, 0.16 mmol) was synthesized from **18** (0.20 mmol, 80%) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.85 (EtOAc/toluene, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43–7.21 [m, 16 H, C(O)NH, H_{Ar} Bn], 4.73 (d, J = 12.0 Hz, 1 H, C*H*H Bn), 4.65 (d, J = 12.0 Hz, 1 H, CH*H* Bn), 4.63 (d, J = 11.8 Hz, 1 H, C*H*H Bn), 4.53 (d, J = 11.7 Hz, 1 H, C*H*H Bn), 4.50 (d, J = 11.7 Hz, 1 H, CH*H* Bn), 4.45 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.10 (dd, J = 3.6, 4.5 Hz, 1 H, 3-H), 3.95 (dd, J = 4.9, 5.5 Hz, 1 H, 4-H), 3.79 (d, J = 3.6 Hz, 1 H, 2-H), 3.77–3.71 (m, 2 H, CH_2-6), 3.52 (dt, J = 5.3, 8.8 Hz, 1 H, 5-H), 3.26–3.11 (m, 2 H, NCH_2-1 pentyl), 1.48–1.41 (m, 2 H, CH_2-2 pentyl), 1.34–1.28 (m, 2 H, CH_2 pentyl), 1.28–1.21 (m, 2 H, CH_2 pentyl), 0.88 (t, J = 7.2 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.5 [C(O)-1], 138.4, 138.3, 138.2 (3×C_q Bn), 128.6, 128.5, 128.2, 128.0, 127.9, 127.9, 127.8 (CH_{Ar} Bn), 81.7 (C-3), 78.9 (C-4), 73.6, 72.9, 72.0 (3×CH_2 Bn), 70.6 (C-6), 64.3 (C-2), 59.2 (C-5), 39.2 (NCH_2-1 pentyl), 29.5 (CH_2-2 pentyl), 29.2, 22.5 (2×CH_2 pentyl), 14.2 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3325, 2929, 2867, 1667, 1521, 1454, 1360, 1209, 1096, 1027, 735, 698 cm^{-1}. $[\alpha]_D^{20}$ = –4.0 (c = 0.8, $CHCl_3$). HRMS: calcd. for $[C_{32}H_{40}O_4N_2 + H]^+$ 517.3061 $[M + H]^+$; found 517.3059.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-Dideoxy-2,5-imino-D-*galacto*-hexonamide (25): Compound **25** (20 mg, 49 μmol) was synthesized from **19** (131 μmol, 37%) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.14 ($MeOH/CH_2Cl_2$, 1:9 + 2% NH_4OH). ^{1}H NMR (500 MHz, MeOD): δ = 4.27–4.21 (m, 2 H, 3-H, 4-H), 3.75 (d, J = 5.3 Hz, 1

H, 2-H), 3.69 (dd, J = 5.1, 11.1 Hz, 1 H, 6a-H), 3.63 (dd, J = 4.3, 11.1 Hz, 1 H, 6b-H), 3.42–3.35 (m, 4 H, 5-H, CH_2-5 pentyl), 3.24 (dt, J = 1.4, 7.0 Hz, 2 H, NCH_2-1 pentyl), 2.97 (s, 2 H, OCH_2-Ada), 1.94 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 11.7, 38.7 Hz, 6 H, 3×CH_2 Ada), 1.62–1.51 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.45–1.37 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (125 MHz, MeOD): δ = 174.6 [C(O)-1], 83.2 (OCH_2-Ada), 74.4 (C-3), 74.2 (C-4), 72.7 (CH_2-5 pentyl), 63.8 (C-2), 62.7 (C-6), 61.5 (C-5), 41.0 (CH_2 Ada), 40.2 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5, 30.5 (2×CH_2 pentyl), 29.9 (CH Ada), 24.8 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3320, 2902, 2848, 1637, 1543, 1456, 1114 cm^{-1}. $[\alpha]_D^{20}$ = 27.1 (c = 0.3, MeOH). HRMS: calcd. for $[C_{22}H_{38}O_5N_2 + H]^+$ 411.2853 $[M + H]^+$; found 411.2851.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-Butylimino-2,5-dideoxy-D-*galacto*-hexonamide (26): Compound **26** (36 mg, 77 μmol, 48%) was synthesized in two steps from **19** (161 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and a subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.31 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.61 (EtOAc/toluene, 1:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.30 (dd, J = 4.5, 7.9 Hz, 1 H, 4-H), 4.18 (dd, J = 4.9 Hz, 1 H, 3-H), 3.72 (dd, J = 2.8, 11.2 Hz, 1 H, 6a-H), 3.62 (dd, J = 4.3, 11.2 Hz, 1 H, 6b-H), 3.41–3.31 (m, 4 H, 2-H, CH_2-5, NC*H*H-1 pentyl), 3.22–3.15 (m, 1 H, NCH*H*-1 pentyl), 3.04–2.99 (m, 1 H, 5-H), 2.96 (s, 1 H, OCH_2-Ada), 2.68–2.61 (m, 1 H, NC*H*H butyl), 2.57–2.49 (m, 1 H, NCH*H* butyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 11.6, 46.0 Hz, 6 H, 3×CH_2 Ada), 1.62–1.26 (m, 16 H, 3×CH_2 Ada, 5×CH_2 pentyl/butyl), 0.94 (t, J = 7.4 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 174.4 [C(O)-1], 83.2 (OCH_2-Ada), 74.2 (C-3), 73.2 (C-4), 72.7 (CH_2-5 pentyl), 72.3 (C-2), 67.8 (C-5), 61.7 (C-6), 57.4 (NCH_2 butyl), 41.0 (CH_2 Ada), 40.1 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 32.0, 30.6, 30.5, 24.9, 21.7 (5×CH_2 pentyl/butyl), 14.6 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3319, 2902, 2849, 1651, 1637, 1458, 1113 cm^{-1}. $[\alpha]_D^{20}$ = 34.7 (c = 0.7, MeOH). HRMS: calcd. for $[C_{26}H_{46}O_5N_2 + H]^+$ 467.3479 $[M + H]^+$; found 467.3475.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,5-dideoxy-D-*galacto*-hexonamide (27): Compound **27** (56 mg, 87 μmol, 59%) was synthesized in two steps from **19** (148 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.37 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.69 (EtOAc/toluene, 1:1 + 2% Et_3N). ^{1}H NMR (500 MHz, MeOD): δ = 4.29 (dd, J = 4.5, 7.9 Hz, 1 H, 4-H), 4.18 (dd, J = 4.5, 5.5 Hz, 1 H, 3-H), 3.72 (dd, J = 3.0, 11.2 Hz, 1 H, 6a-H), 3.64 (dd, J = 4.5, 11.2 Hz, 1 H, 6b-H), 3.41–3.36 (m, 2 H, 2×CH_2-5 pentyl), 3.37–3.34 [m, 1 H, C(O)NC*H*H-1 pentyl], 3.33 (d, J = 5.5 Hz, 1 H, 2-H), 3.18 [dt, J = 6.8, 13.5 Hz, 1 H, C(O)NCH*H*-1 pentyl], 3.02 (ddd, J = 3.0, 4.5, 7.6 Hz, 1 H, 5-H), 2.97 (s, 4 H, 2×OCH_2-Ada), 2.70–2.62 (m, 1 H, NC*H*H-1 pentyl), 2.54 (ddd, J = 6.3, 9.3, 12.5 Hz, 1 H, NCH*H*-1 pentyl), 1.95 (s, 6 H, 3×CH_2 Ada), 1.72 (dd, J = 11.8, 39.2 Hz, 12 H, 6×CH_2 Ada), 1.63–1.30 (m, 24 H, 6×CH_2 Ada, 6×CH_2 pentyl) ppm. ^{13}C NMR (125 MHz, MeOD): δ = 174.4 [C(O)-1], 83.2 (2×OCH_2-Ada), 74.2 (C-3), 73.3 (C-4), 72.7, 72.6 (2×CH_2-5 pentyl), 72.3 (C-2), 67.9 (C-5), 61.8 (C-6), 57.6 (NCH_2-1 pentyl), 41.0, 41.0 (2×CH_2 Ada), 40.1 [C(O)N*C*H_2-1 pentyl], 38.5 (2×CH_2 Ada), 35.3, 35.3 (2×C_q Ada), 30.8, 30.6, 30.6, 29.7 (4×CH_2 pentyl), 29.9 (2×CH Ada), 25.3, 24.9 (2×CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3319, 2902, 2848, 1651, 1455, 1361, 1113 cm^{-1}. $[\alpha]_D^{20}$ = 24.3 (c = 0.7, MeOH). HRMS: calcd. for $[C_{38}H_{64}O_6N_2 + H]^+$ 645.4837 $[M + H]^+$; found 645.4834.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-Dideoxy-2,5-imino-D-*talo*-hexonamide (28): Compound **28** (11 mg, 27 μmol, 82%) was synthesized in from **20** (33 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.16 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 4.07 (t, J = 4.1 Hz, 1 H, 4-H), 4.02 (dd, J = 4.3, 7.1 Hz, 1 H, 3-H), 3.77 (dd, J = 5.9, 10.9 Hz, 1 H, 6a-H), 3.65 (dd, J = 6.3, 10.9 Hz, 1 H, 6b-H), 3.52 (d, J = 7.1 Hz, 1 H, 2-H), 3.38 (t, J = 6.3 Hz, 2 H, CH_2-5 pentyl), 3.30–3.27 (m, 1 H, 5-H), 3.23 (t, J = 7.0 Hz, 2 H, NCH_2-1 pentyl), 2.96 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 11.9, 45.9 Hz, 6 H, 3×CH_2 Ada), 1.61–1.51 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.44–1.36 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 175.5 [C(O)-1], 83.2 (OCH_2-Ada), 78.6 (C-3), 74.3 (C-4), 72.6 (CH_2-5 pentyl), 65.9 (C-2), 62.7 (C-5), 62.5 (C-6), 41.0 (CH_2 Ada), 40.5 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5, 30.5 (2×CH_2 pentyl), 29.9 (CH Ada), 24.8 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3319, 2902, 2849, 1652, 1543, 1454, 1112. $[\alpha]_D^{20}$ = –1.0 (c = 0.2, MeOH). HRMS: calcd. for $[C_{22}H_{38}O_5N_2 + H]^+$ 411.2853 $[M + H]^+$; found 411.2851.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-Butylimino-2,5-dideoxy-D-*talo*-hexonamide (29): Compound **29** (11 mg, 24 μmol, 67%) was synthesized in two steps from **20** (36 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and a subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.30 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.85 (EtOAc/toluene, 1:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.31 (dd, J = 5.7, 6.5 Hz, 1 H, 4-H), 3.87 (dd, J = 1.0, 5.7 Hz, 1 H, 3-H), 3.80 (d, J = 8.2 Hz, 1 H, 6a-H), 3.70 (dd, J = 1.4, 11.6 Hz, 1 H, 6b-H), 3.39–3.37 (m, 3 H, 2-H, CH_2-5 pentyl), 3.35–3.32 (m, 1 H, 5-H), 3.28–3.20 (m, 1 H, NC*H*H-1 pentyl), 3.20–3.11 (m, 1 H, NCH*H*-1 pentyl), 2.96 (s, 2 H, OCH_2-Ada), 2.93–2.85 (m, 1 H, NC*H*H butyl), 2.60–2.47 (m, 1 H, NCH*H* butyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 12.1, 46.3 Hz, 8 H, 3×CH_2 Ada), 1.62–1.27 (m, 16 H, 3×CH_2 Ada, 5×CH_2 pentyl/butyl), 0.94 (t, J = 7.4 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 175.8 [C(O)-1], 83.2 (OCH_2-Ada), 76.2 (C-3), 76.2 (C-2), 72.7 (C-4), 72.6 (CH_2-5 pentyl), 64.9 (C-5), 58.3 (C-6), 50.7 (NCH_2 butyl), 41.0 (CH_2 Ada), 40.0 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 32.2, 30.6, 30.5 (3×CH_2 pentyl/butyl), 29.9 (CH Ada), 25.0 (CH_2-3 pentyl), 21.9 (CH_2 butyl), 14.6 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3328, 2903, 2850, 1652, 1456, 1097, 1016 cm^{-1}. $[\alpha]_D^{20}$ = –29.7 (c = 0.2, MeOH). HRMS: calcd. for $[C_{26}H_{46}O_5N_2 + H]^+$ 467.3479 $[M + H]^+$; found 467.3475.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,5-dideoxy-D-*talo*-hexonamide (30): Compound **30** (17 mg, 26 μmol, 72%) was synthesized in two steps from **20** (36 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and a subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.37 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.88 (EtOAc/toluene, 1:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.31 (dd, J = 6.0, 7.1 Hz, 1 H, 4-H), 3.88 (dd, J = 1.5, 5.8 Hz, 1 H, 3-H), 3.81 (dd, J = 3.5, 11.7 Hz, 1 H, 6a-H), 3.71 (dd, J = 1.9, 11.7 Hz, 1 H, 6b-H), 3.41–3.36 (m, 5 H, 2-H, 2×CH_2-5 pentyl), 3.35–3.32 (m, 1 H, 5-H), 3.26 [dt, J = 7.0, 13.8 Hz, 1 H, C(O)NC*H*H-1 pentyl], 3.16 [dt, J = 6.9, 13.5 Hz, 1 H, C(O)NCH*H*-1 pentyl], 2.98–2.95 (m, 4 H, 2×OCH_2-Ada), 2.94–2.87 (m, 1 H, NC*H*H pentyl), 2.53 (ddd, J = 7.1, 9.3, 12.3 Hz, 1 H, NCH*H* pentyl), 1.95 (s, 6 H, 6×CH Ada), 1.72 (dd, J = 11.9, 46.7 Hz, 12 H, 6×CH_2 Ada), 1.63–1.47 (m, 20 H, 6×CH_2 Ada, 4×CH_2 pentyl), 1.47–1.31 (m, 4 H, 2×CH_2-3 pentyl) ppm. ^{13}C NMR

(150 MHz, MeOD): δ = 175.8 [C(O)-1], 83.3, 83.2 (2×OCH_2-Ada), 76.3 (C-3), 76.2 (C-2), 72.7 (C-4), 72.6, 72.5 (2×CH_2-5 pentyl), 64.8 (C-5), 58.3 (C-6), 50.9 (NCH_2-1 pentyl), 41.0, 41.0 (2×CH_2 Ada), 40.1 [C(O)N*C*H_2-1 pentyl], 38.5 (2×CH_2 Ada), 35.3, 35.3 (2×C_q Ada), 29.9 (2×CH Ada), 30.8, 30.6, 30.5, 29.8 (4×CH_2 pentyl), 25.4, 25.0 (2×CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3332, 2902, 2848, 1652, 1454, 1361, 1158, 1112 cm^{-1}. $[\alpha]_D^{20}$ = –14.6 (*c* = 0.3, MeOH). HRMS: calcd. for $[C_{38}H_{64}O_6N_2 + H]^+$ 645.4837 [M + H]$^+$; found 645.4834.

1,1,3,3-Tetramethylbutyl 2,5-Dideoxy-2,5-imino-D-*galacto*-hexonamide (31): Compound **31** (14 mg, 47 μmol, 53%) was synthesized in from **21** (90 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.15 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 4.25–4.18 (m, 2 H, 3-H, 4-H), 3.71–3.61 (m, 2 H, CH_2-6), 3.59 (d, *J* = 5.9 Hz, 1 H, 2-H), 3.37–3.32 (m, 1 H, 5-H), 1.87 (d, *J* = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.65 (d, *J* = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.41 (d, *J* = 20.5 Hz, 6 H, 2×CH_3 tMB), 1.03 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 173.8 [C(O)-1], 74.6, 74.2 (C-3, C-4), 63.9 (C-2), 62.8 (C-6), 61.3 (C-5), 55.9 (NHC_q-1 tMB), 53.1 (CH_2-2 tMB), 32.6 (C_q-3 tMB), 32.1 (CH_3-4, 2×CH_3 tMB), 29.7, 29.4 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3325, 2952, 1651, 1537, 1452, 1390, 1366, 1227, 1120, 1034 cm^{-1}. $[\alpha]_D^{20}$ = 33.1 (*c* = 0.3, MeOH). HRMS: calcd. for $[C_{14}H_{28}O_4N_2 + H]^+$ 289.2122 [M + H]$^+$; found 289.2123.

1,1,3,3-Tetramethylbutyl 2,5-Butylimino-2,5-dideoxy-D-*galacto*-hexonamide (32): Compound **32** (27 mg, 78 μmol, 87%) was synthesized in two steps from **21** (90 μmol) through reductive amination with the the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.31 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.82 (EtOAc/toluene, 1.5:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.27 (dd, *J* = 4.5, 7.7 Hz, 1 H, 4-H), 4.20–4.12 (m, 1 H, 3-H), 3.71 (dd, *J* = 2.6, 10.8 Hz, 1 H, 6a-H), 3.63 (dd, *J* = 4.8, 10.8 Hz, 1 H, 6b-H), 3.18 (d, *J* = 5.7 Hz, 1 H, 2-H), 3.03–2.99 (m, 1 H, 5-H), 2.66–2.59 (m, 1 H, NC*H*H butyl), 2.57–2.49 (m, 1 H, NCH*H* butyl), 1.93 (d, *J* = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.63 (d, *J* = 14.9 Hz, 1 H, CH*H*-2 tMB), 1.55–1.26 (m, 10 H, 2×CH_2 butyl, 2×CH_3 tMB), 1.04 (s, 9 H, 2×CH_3, CH_3-4 tMB), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 173.5 [C(O)-1], 74.4 (C-3), 73.3 (C-4), 72.5 (C-2), 67.5 (C-5), 61.9 (C-6), 57.4 (NCH_2 butyl), 56.2 (NHC_q-1 tMB), 53.6 (CH_2-2 tMB), 32.6 (C_q-3 tMB), 32.3 (CH_2 butyl), 32.2 (CH_3-4, 2×CH_3 tMB), 29.4, 29.3 (2×CH_3 tMB), 21.8 (CH_2 butyl), 14.6 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3292, 2957, 2928, 1639, 1461, 1440, 1366, 1229, 1149, 1128, 1034 cm^{-1}. $[\alpha]_D^{20}$ = 37.8 (*c* = 0.5, MeOH). HRMS: calcd. for $[C_{18}H_{36}O_4N_2 + H]^+$ 345.2748 [M + H]$^+$; found 345.2748.

1,1,3,3-Tetramethylbutyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]-imino-2,5-dideoxy-D-*galacto*-hexonamide (33): Compound **33** (35 mg, 67 μmol, 74%) was synthesized in two steps from **21** (90 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and a subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.35 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.84 (EtOAc/toluene, 1.5:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.28 (dd, *J* = 4.5, 7.7 Hz, 1 H, 4-H), 4.17 (t, *J* = 5.0 Hz, 1 H, 3-H), 3.72 (dd, *J* = 1.6, 10.5 Hz, 1 H, 6a-H), 3.64 (dd, *J* = 4.5, 10.5 Hz, 1 H, 6b-H), 3.39 (t, *J* = 6.3 Hz, 2 H, CH_2-5 pentyl), 3.20 (d, *J* = 3.4 Hz, 1 H, 2-H), 3.07–3.01 (m, 1 H, 5-H), 2.96 (s, 2 H, OCH_2-Ada), 2.70–2.61 (m, 1 H, NC*H*H-1 pentyl), 2.60–2.48 (m, 1 H, NCH*H*-1 pentyl), 1.98–1.91 (m, 4 H, 3×CH Ada, C*H*H-2 tMB), 1.80–1.65 (m, 7 H, 3×CH_2 Ada, CH*H* tMB), 1.65–1.31 (m, 18 H, 3×CH_2 Ada, 3×CH_2 pentyl, 2×CH_3 tMB), 1.04 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 173.3 [C(O)-1], 83.2 (OCH_2-Ada), 74.3 (C-3), 73.3 (C-4), 72.5 (C-2), 72.5 (CH_2-5 pentyl), 67.5 (C-5), 61.9 (C-6), 57.7 (NCH_2-1), 56.2 (NHC_q-1 tMB), 53.6 (CH_2-2 tMB), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 32.6 (C_q-3 tMB), 32.3 (CH_3-4, 2×CH_3 tMB), 30.8 (CH_2 pentyl), 29.9 (CH Ada), 29.5, 29.4 (2×CH_3 tMB, CH_2 pentyl), 25.4 (CH_2-1 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3325, 2903, 2850, 1651, 1454, 1366, 1228, 1110, 1055 cm^{-1}. $[\alpha]_D^{20}$ = 28.4 (*c* = 0.7, MeOH). HRMS: calcd. for $[C_{30}H_{54}O_5N_2 + H]^+$ 523.4105 [M + H]$^+$; found 523.4101.

1,1,3,3-Tetramethylbutyl 2,5-Dideoxy-2,5-imino-D-*talo*-hexonamide (34): Compound **34** (15 mg, 52 μmol, 93%) was synthesized from **22** (56 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.16 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 4.06 (m, 1 H, 4-H), 4.02 (dd, *J* = 4.2, 6.8 Hz, 1 H, 3-H), 3.76 (dd, *J* = 5.9, 10.9 Hz, 1 H, 6a-H), 3.65 (dd, *J* = 6.1, 10.9 Hz, 1 H, 6b-H), 3.45 (d, *J* = 6.8 Hz, 1 H, 2-H), 3.24 (dd, *J* = 5.8, 10.1 Hz, 1 H, 5-H), 1.83 (d, *J* = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.75 (d, *J* = 14.9 Hz, 1 H, CH*H*-2 tMB), 1.40 (d, *J* = 8.2 Hz, 6 H, 2×CH_3 tMB), 1.02 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 174.4 [C(O)-1], 78.2 (C-3), 74.4 (C-4), 66.3 (C-2), 62.6 (C-5), 62.4 (C-6), 55.9 (NHC_q-1 tMB), 52.4 (CH_2-2 tMB), 32.7 (C_q-3 tMB), 32.1 (CH_3-4, 2×CH_3 tMB), 29.8, 29.7 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3309, 2970, 2904, 1652, 1529, 1391, 1366, 1227, 1050 cm^{-1}. $[\alpha]_D^{20}$ = –7.1 (*c* = 0.3, MeOH). HRMS: calcd. for $[C_{14}H_{28}O_4N_2 + H]^+$ 289.2122 [M + H]$^+$; found 289.2123.

1,1,3,3-Tetramethylbutyl 2,5-Butylimino-2,5-dideoxy-D-*talo*-hexonamide (35): Compound **35** (23 mg, 67 μmol, 85%) was synthesized in two steps from **22** (79 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and a subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.29 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.93 (EtOAc/toluene, 1.5:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.23 (dd, *J* = 5.8, 6.8 Hz, 1 H, 4-H), 3.92 (d, *J* = 5.3 Hz, 1 H, 3-H), 3.83 (dd, *J* = 3.5, 11.9 Hz, 1 H, 6a-H), 3.75 (d, *J* = 10.9 Hz, 1 H, 6b-H), 3.41 (s, 1 H, 5-H), 3.31 (s, 1 H, 1-H), 3.03–2.95 (m, 1 H, NC*H*H butyl), 2.61–2.51 (m, 1 H, NCH*H* butyl), 1.83 (d, *J* = 14.9 Hz, 1 H, C*H*H-2 tMB), 1.73 (d, *J* = 14.9 Hz, 1 H, CH*H*-2 tMB), 1.61–1.27 (m, 10 H, 2×CH_2 butyl, 2×CH_3 tMB), 1.02 (s, 9 H, 2×CH_3, CH_3-4 tMB), 0.96 (t, *J* = 7.4 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (150 MHz, MeOD, collapsed iminosugar signals): δ = 76.7 (C-2), 75.9 (C-3), 72.7 (C-4), 65.1 (C-5), 57.9 (C-6), 56.0 (NHC_q-1 tMB), 52.8 (CH_2-2 tMB), 50.9 (NCH_2 butyl), 32.6 (C_q-3 tMB), 32.1 (CH_3-4, 2×CH_3 tMB), 30.9 (CH_2 butyl), 29.9, 29.1 (2×CH_3 tMB), 22.0 (CH_2 butyl), 14.6 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3328, 2957, 2929, 1652, 1432, 1366, 1227, 1166, 1046 cm^{-1}. $[\alpha]_D^{20}$ = –33.6 (*c* = 0.5, MeOH). HRMS: calcd. for $[C_{18}H_{36}O_4N_2 + H]^+$ 345.2748 [M + H]$^+$; found 345.2748.

1,1,3,3-Tetramethylbutyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]-imino-2,5-dideoxy-D-*talo*-hexonamide (36): Compound **36** (34 mg, 65 μmol, 72%) was synthesized in two steps from **22** (90 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.32 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.89 (EtOAc/toluene, 1:2 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.22 (dd, *J* = 5.9, 7.2 Hz, 1 H, 4-H), 3.89 (dd, *J* = 1.6, 5.8 Hz, 1 H, 3-H), 3.83 (dd, *J* = 3.4, 11.8 Hz, 1 H, 6a-H), 3.72 (dd, *J* = 2.1, 11.8 Hz, 1

H, 6b-H), 3.39 (t, J = 6.2 Hz, 2 H, CH_2-5 pentyl), 3.37–3.33 (m, 1 H, 5-H), 3.25 (d, J = 1.6 Hz, 1 H, 2-H), 3.00–2.94 (m, 3 H, OCH_2-Ada, NC*H*H-1 pentyl), 2.49 (dt, J = 8.2, 12.5 Hz, 1 H, NCH*H*-1 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.86 (d, J = 14.9 Hz, 1 H, C*H*H-2 tMB), 1.79–1.66 (m, 7 H, 3×CH_2 Ada, CH*H*-2 tMB), 1.64–1.45 (m, 11 H, 3×CH_2 Ada, 2×CH_2 pentyl, C*H*H-3 pentyl), 1.44–1.37 (m, 7 H, CH*H*-3pentyl, 2×CH_3 tMB), 1.03 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 174.3 [C(O)-1], 83.2 (OCH_2-Ada), 77.2 (C-2), 75.9 (C-3), 72.7 (C-4), 72.4 (CH_2-5 pentyl), 64.3 (C-5), 57.9 (C-6), 56.0 (NHC_q-1 tMB), 52.8 (CH_2-2 tMB), 50.9 (NCH_2-1 pentyl), 41.1 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 32.7 (C_q-3 tMB), 32.1 (CH_3-4, 2×CH_3 tMB), 30.8, 30.0 (2×CH_2 pentyl), 29.9 (CH Ada), 30.1, 29.2 (2×CH_3 tMB), 25.7 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3328, 2903, 2849, 1652, 1429, 1366, 1228, 1159, 1109 cm^{-1}. $[\alpha]_D^{20}$ = –34.2 (c = 0.5, MeOH). HRMS: calcd. for $[C_{30}H_{54}O_5N_2 + H]^+$ 523.4105 $[M + H]^+$; found 523.4100.

Pentyl 2,5-Dideoxy-2,5-imino-D-*galacto*-hexonamide (37): Compound **37** (22 mg, 89 μmol, 66%) was synthesized from **23** (135 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.08 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH). ^{1}H NMR (500 MHz, MeOD): δ = 4.28–4.21 (m, 2 H, 3-H, 4-H), 3.76 (d, J = 5.4 Hz, 1 H, 2-H), 3.69 (dd, J = 5.2, 11.1 Hz, 1 H, 6a-H), 3.63 (dd, J = 4.4, 11.1 Hz, 1 H, 6b-H), 3.37 (dd, J = 5.1, 11.6 Hz, 1 H, 5-H), 3.28–3.17 (m, 2 H, NCH_2-1 pentyl), 1.58–1.50 (m, 2 H, CH_2-2 pentyl), 1.39–1.30 (m, 4 H, 2×CH_2 pentyl), 0.92 (t, J = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (151 MHz, MeOD): δ = 174.4 [C(O)-1], 74.3 (C-3), 74.1 (C-4), 63.8 (C-2), 62.6 (C-6), 61.5 (C-5), 40.3 (NCH_2-1 pentyl), 30.3, 23.6 (3×CH_2 pentyl), 14.5 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3325, 2959, 2930, 1636, 1543, 1456, 1408, 1251, 1118, 1048 cm^{-1}. $[\alpha]_D^{20}$ = 53.6 (c = 0.3, MeOH). HRMS: calcd. for $[C_{11}H_{22}O_4N_2 + H]^+$ 247.1652 $[M + H]^+$; found 247.1654.

Pentyl 2,5-Butylimino-2,5-dideoxy-D-*galacto*-hexonamide (38): Compound **38** (55 mg, 182 μmol, 86%) was synthesized in two steps from **23** (212 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.24 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.56 (EtOAc/toluene, 1:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.32 (dd, J = 4.6, 8.0 Hz, 1 H, 4-H), 4.20 (dd, J = 4.6, 5.4 Hz, 1 H, 3-H), 3.75 (dd, J = 2.9, 11.2 Hz, 1 H, 6a-H), 3.64 (dd, J = 4.4, 11.2 Hz, 1 H, 6b-H), 3.37–3.30 (m, 2 H, H-2, NC*H*H-1 pentyl), 3.25–3.16 (m, 1 H, NCH*H*-1 pentyl), 3.06–3.00 (m, 1 H, 5-H), 2.72–2.62 (m, 1 H, NC*H*H butyl), 2.59–2.50 (m, 1 H, NCH*H* butyl), 1.60–1.29 (m, 10 H, 5×CH_2 pentyl/butyl), 0.99–0.90 (m, 6 H, 2×CH_3 pentyl/butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 174.4 [C(O)-1], 74.2 (C-3), 73.2 (C-4), 72.4 (C-2), 67.8 (C-5), 61.7 (C-6), 57.4 (NCH_2 butyl), 40.1 (NCH_2-1 pentyl), 32.0, 30.4, 30.4, 23.6, 21.7 (5×CH_2 pentyl/butyl), 14.6, 14.5 (2×CH_3 pentyl/butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3327, 2957, 2930, 2862, 1650, 1636, 1539, 1463, 1141, 1030, 1011 cm^{-1}. $[\alpha]_D^{20}$ = 60.6 (c = 0.9, MeOH). HRMS: calcd. for $[C_{15}H_{30}O_4N_2 + H]^+$ 303.2278 $[M + H]^+$; found 303.2279.

Pentyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,5-dideoxy-D-*galacto*-hexonamide (39): Compound **39** (71 mg, 148 μmol, 69%) was synthesized in two steps from **23** (213 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and a subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.26 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.62 (EtOAc/toluene, 1:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD, collapsed iminosugar signals): δ = 4.50–4.03 (m, 2 H), 4.03–3.55 (m, 2 H), 3.38 (t, J = 6.3, 2 H, CH_2-5 pentyl AMP), 3.27–3.00 (m, 2 H), 2.96 (s, 2 H, OCH_2-Ada), 2.84–2.48 (m, 1 H), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 12.1, 48.0, 6 H, 3×CH_2 Ada), 1.63–1.32 (m, 18 H, 3×CH_2 Ada, 6×CH_2 pentyl/pentyl AMP), 0.93 (t, J = 7.0, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, MeOD, collapsed iminosugar signals): δ = 83.2 (OCH_2-Ada), 72.4 (CH_2-5 pentyl AMP), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 30.6, 30.5, 30.4, 30.3, 25.3, 23.6 (6×CH_2 pentyl/pentyl AMP), 14.6 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3280, 1638, 1471, 1360, 1114, 1010 cm^{-1}. $[\alpha]_D^{20}$ = 22.2 (c = 0.2, MeOH). HRMS: calcd. for $[C_{27}H_{48}O_5N_2 + H]^+$ 481.3636 $[M + H]^+$; found 481.3631.

Pentyl 2,5-Dideoxy-2,5-imino-D-*talo*-hexonamide (40): Compound **40** (10 mg, 41 μmol, 89%) was synthesized from **24** (46 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.09 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH). ^{1}H NMR (600 MHz, MeOD): δ = 4.10 (dd, J = 4.0 Hz, 1 H, 4-H), 4.05 (dd, J = 4.2, 7.2 Hz, 1 H, 3-H), 3.79 (dd, J = 5.8, 11.0 Hz, 1 H, 6a-H), 3.69 (dd, J = 6.4, 11.0 Hz, 1 H, 6b-H), 3.58 (d, J = 7.2 Hz, 1 H, 2-H), 3.39–3.33 (m, 1 H, 5-H), 3.22 (t, J = 7.1 Hz, 2 H, NCH_2-1 pentyl), 1.57–1.49 (m, 2 H, CH_2-2 pentyl), 1.41–1.28 (m, 4 H, 2×CH_2 pentyl), 0.92 (t, J = 6.9 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 174.7 [C(O)-1], 78.4 (C-3), 74.1 (C-4), 65.5 (C-2), 63.0 (C-5), 62.1 (C-6), 40.6 (NCH_2-1 pentyl), 30.3, 23.6 (3×CH_2 pentyl), 14.5 (CH_3-5 pentyl). IR (thin film): $\tilde{\nu}_{max}$ = 3350, 2930, 2857, 1652, 1544, 1464, 1317, 1127 cm^{-1}. $[\alpha]_D^{20}$ = –2.0 (c = 0.2, MeOH). HRMS: calcd. for $[C_{11}H_{22}O_4N_2 + H]^+$ 247.1652 $[M + H]^+$; found 247.1654.

Pentyl 2,5-Butylimino-2,5-dideoxy-D-*talo*-hexonamide (41): Compound **41** (7 mg, 23 μmol, 44%) was synthesized in two steps from **24** (52 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.23 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.83 (EtOAc/toluene, 1:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.32 (dd, J = 5.8, 7.2 Hz, 1 H, 4-H), 3.87 (dd, J = 1.7, 5.8 Hz, 1 H, 3-H), 3.80 (dd, J = 3.6, 11.6 Hz, 1 H, 6a-H), 3.71 (dd, J = 2.1, 11.6 Hz, 1 H, 6b-H), 3.39 (d, J = 1.4 Hz, 1 H, 2-H), 3.35–3.32 (m, 1 H, 5-H), 3.26–3.19 (m, 1 H, NC*H*H-1 pentyl), 3.19–3.11 (m, 1 H, NCH*H*-1 pentyl), 2.88 (ddd, J = 4.8, 9.5, 12.6 Hz, 1 H, NC*H*H butyl), 2.54 (ddd, J = 6.8, 9.8, 12.5 Hz, 1 H, NCH*H* butyl), 1.56–1.26 (m, 10 H, 5×CH_2 pentyl/butyl), 0.96–0.90 (m, 6 H, 2×CH_3 pentyl/butyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 175.8 [C(O)-1], 76.2 (C-3), 76.0 (C-2), 72.7 (C-4), 65.0 (C-5), 58.4 (C-6), 50.7 (NCH_2 butyl), 40.1 (NCH_2-1 pentyl), 32.2, 30.5, 30.4, 23.6, 21.9 (5×CH_2 pentyl/butyl), 14.6, 14.5 (2×CH_3 pentyl/butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3312, 2927, 2856, 1652, 1528, 1461, 1167 cm^{-1}. $[\alpha]_D^{20}$ = –32.3 (c = 0.1, MeOH). HRMS: calcd. for $[C_{15}H_{30}O_4N_2 + H]^+$ 303.2278 $[M + H]^+$; found 303.2279.

Pentyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,5-dideoxy-D-*talo*-hexonamide (42): Compound **42** (17 mg, 35 μmol, 73%) was synthesized in two steps from **24** (48 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and a subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.29 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.87 (EtOAc/toluene, 1:1 + 2% Et_3N). ^{1}H NMR (600 MHz, MeOD): δ = 4.31 (dd, J = 5.8, 7.4 Hz, 1 H, 4-H), 3.87 (dd, J = 1.6, 5.8 Hz, 1 H, 3-H), 3.81 (dd, J = 3.4, 11.5 Hz, 1 H, 6a-H), 3.70 (d, J = 11.5 Hz, 1 H, 6b-H), 3.39–3.37 (m, 3 H, H-2, CH_2-5 pentyl AMP), 3.36–3.32 (m, 1 H, 5-H), 3.27–3.20 (m, 1 H, NC*H*H-1 pentyl AMP), 3.19–3.11 (m, 1 H, NCH*H*-1 pentyl AMP), 2.96 (s, 2 H, OCH_2-Ada), 2.94–2.85 (m, 1 H, NC*H*H

pentyl), 2.58–2.50 (m, 1 H, NCH*H* pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, *J* = 12.1, 48.4 Hz, 6 H, 3×CH_2 Ada), 1.60–1.27 (m, 18 H, 3×CH_2 Ada, 6×CH_2 pentyl/pentyl AMP), 0.93 (t, *J* = 7.1 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, MeOD): δ = 175.8 [C(O)-1], 83.2 (OCH_2-Ada), 76.3 (C-3), 76.2 (C-2), 72.7 (C-4), 72.6 (CH_2-5 pentyl AMP), 64.9 (C-5), 58.3 (C-6), 50.9 (NCH_2 pentyl), 41.0 (CH_2 Ada), 40.1 (NCH_2 pentyl AMP), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 30.7, 30.5, 30.4, 29.7, 25.4, 23.6 (6×CH_2 pentyl/pentyl AMP), 14.6 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3319, 2902, 2849, 1652, 1458, 1112 cm^{-1}. $[\alpha]_D^{20}$ = –17.3 (*c* = 0.3, MeOH). HRMS: calcd. for $[C_{27}H_{48}O_5N_2 + H]^+$ 481.3636 $[M + H]^+$; found 481.3631.

Mixture of 2,3,5-Tri-*O*-benzyl-1-*O*-methyl-α/β-D-xylofuranoside (43): An anhydrous solution of HCl [prepared by careful addition of AcCl (2 mL) to MeOH (100 mL)] was added to an anhydrous solution of D-xylose (20.07 g, 133.7 mmol) in MeOH (340 mL). The reaction mixture was stirred for 20 h at room temp., then the reaction was quenched by adjusting the pH of the reaction mixture to ca. pH 7 by addition of 3 M aq. NaOH. The mixture was concentrated and coevaporated with toluene (4× 100 mL). The crude residue was dissolved in DMF (500 mL) and cooled to 0 °C. Subsequently, NaH (60% in mineral oil, 30.04 g, 751 mmol), tetrabutylammonium iodide (32.312 g, 88 mmol) and benzyl bromide (52 mL, 437 mmol) were added. After stirring the reaction mixture for 48 h at room temp., MeOH (10 mL) was added and the mixture was concentrated. The residue was dissolved in ethyl acetate (100 mL) and washed successively with H_2O (4× 50 mL) and satd. aq. NaCl (50 mL). The organic layer was dried ($MgSO_4$), concentrated, and the resulting residue was purified by silica gel column chromatography (EtOAc/toluene, 5→20%) to provide **43** (53.9 g, 124.1 mmol, 93%) as a colorless oil. R_f = 0.58 (β-anomer), 0.42 (α-anomer) (EtOAc/PE, 5:1). ^{1}H NMR ($CDCl_3$, 200 MHz): δ (β-anomer) = 7.28–7.26 (m, 15 H, H_{Ar} Bn), 4.91 (d, *J* = 1.8 Hz, 1 H, 1-H), 4.56–4.40 (m, 7 H), 4.04 (dd, *J* = 2.5, 2.6 Hz, 1 H), 3.97 (m, 1 H), 3.77–3.71 (m, 2 H), 3.37 (s, 3 H, OMe) ppm; δ (α-anomer) = 7.29–7.25 (m, 15 H, H_{Ar} Bn), 4.80 (d, *J* = 4.0 Hz, 1 H, 1-H), 4.67–4.46 (m, 6 H, 3×CH_2 Bn), 4.43–4.26 (m, 2 H, 3-H, 4-H), 4.03–4.01 (m, 1 H, 2-H), 3.74–3.53 (m, 2 H, CH_2-5), 3.39 (s, 3 H, OMe) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ (β-anomer) = 139.1, 138.6, 138.1 (3×C_q Bn), 129.0, 128.6, 128.4, 127.7, 127.5 (CH_{Ar} Bn), 108.1 (C-1), 87.0, 82.0, 80.0 (C-2, C-3, C-4), 73.3, 72.1, 71.8 (3×CH_2 Bn), 69.9 (C-5), 55.9 (OMe) ppm; δ (α-anomer) = 138.4, 138.2, 137.9 (3×C_q Bn), 127.9, 127.5, 127.4 (CH_{Ar} Bn), 100.5 (C-1), 84.0, 81.5, 76.0 (C-2, C-3, C-4), 73.2, 72.3 (3×CH_2 Bn), 69.3 (C-5), 54.9 (OMe) ppm.

Mixture of 2,3,5-Tri-*O*-benzyl-α/β-D-xylose (44): The combined α/β-anomers of **43** (25.11 g, 57.8 mmol) in dioxane (200 mL) and 4 M aq. HCl (200 mL) were heated to reflux for 5 h until TLC analysis indicated complete conversion of the starting material. The reaction mixture was cooled to room temp., diluted with Et_2O (200 mL) and washed successively with satd. aq. $NaHCO_3$ (100 mL), H_2O (3× 50 mL) and satd. aq. NaCl (50 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography (EtOAc/toluene, 5→20%) to provide **44** (16.9 g, 40.2 mmol, 70%) as a colorless oil. R_f = 0.38 (EtOAc/toluene, 1:1). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.34–7.17 (m, 15 H, H_{Ar} Bn), 5.46 (d, *J* = 4.4 Hz, 1 H, 1α-H), 5.23 (s, 1 H, 1β-H), 4.65–4.46 (m, 6 H, 3×CH_2 Bn), 4.42–4.33 (m, 1 H), 4.10–3.90 (m, 2 H), 3.79–3.60 (m, 2 H), 2.34 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 137.3, 136.8, 136.6, 136.1 (3×C_q Bn α/β), 128.2, 127.6, 127.3, 127.1, 127.0, 126.9, 126.5, 126.0 (CH_{Ar} Bn α/β), 100.8 (C-1 β), 95.1 (C-1 α), 85.8, 80.6, 80.4, 80.2, 78.9, 72.7, 72.5, 71.9, 71.6, 71.4, 71.9, 67.9, 67.6, 64.0 ppm.

2,3,5-Tri-*O*-benzyl-D-xylitol (45): Sodium borohydride (10.78 g, 285 mmol) was added to a cooled solution (0 °C) of **44** (20 g, 48.0 mmol) in MeOH (240 mL). The reaction mixture was stirred for 3 h at room temp., then the pH was adjusted to pH 5 by addition of acetic acid. The mixture was concentrated, dissolved in Et_2O (500 mL), and washed successively with water (200 mL), 1 M aq. HCl (300 mL), 10% aq. $NaHCO_3$ (300 mL), and satd. aq. NaCl (200 mL). The organic phase was dried ($MgSO_4$), concentrated, and the residue was purified by silica gel column chromatography (EtOAc/PE, 20→60%) to give **45** (17.6 g, 41.6 mmol, 87%) as a colorless oil. R_f = 0.45 (EtOAc/PE, 1:1). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.26–7.19 (m, 15 H, H_{Ar} Bn), 4.94–4.37 (m, 6 H, 3×CH_2 Bn), 4.15–4.01 (m, 1 H), 3.77–3.70 (m, 4 H), 3.63–3.36 (m, 2 H), 2.94 (br. s, 2 H, OH-1, OH-4) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 137.9, 137.8, 137.7 (3×C_q Bn), 128.1, 127.6, 127.5, 127.4 (CH_{Ar} Bn), 78.7, 77.3 (C-2, C-3), 73.9, 72.9, 72.0 (3×CH_2 Bn), 70.9 (C-5), 68.4 (C-4), 60.2 (C-1) ppm.

2,3,5-Tri-*O*-benzyl-1-*O*-trityl-D-xylitol (46): Triphenylmethyl chloride (14.1 g, 50.6 mmol) was added to a solution of **45** (17.6 g, 40.5 mmol) in pyridine (210 mL). The reaction mixture was stirred for 20 h at 40 °C, then excess triphenylmethyl chloride was quenched by addition of H_2O (5 mL) and the mixture was concentrated. The residue was redissolved in Et_2O (100 mL) and washed successively with 0.1 M aq. HCl (2× 100 mL), satd. aq. $NaHCO_3$ (100 mL) and satd. aq. NaCl (50 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified by silica gel column chromatography (EtOAc/toluene, 0→20%) to give **46** (25.3 g, 38.1 mmol, 94%) as a colorless oil. R_f = 0.45 (EtOAc/PE, 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.43 (m, 6 H, H_{Ar} Tr), 7.35–7.13 (m, 24 H, H_{Ar} Bn/Tr), 4.73–4.65 (m, 2 H, 2×C*H*H Bn), 4.55–4.48 (m, 2 H, 2×CH*H* Bn), 4.42 (s, 2 H, CH_2 Bn), 3.91 (dd, *J* = 3.1, 5.6 Hz, 1 H, 3-H), 3.85–3.79 (m, 2 H, 2-H, 4-H), 3.44 (dd, *J* = 4.2, 10.2 Hz, 1 H, 1a-H), 3.38 (d, *J* = 6.0 Hz, 2 H, CH_2-5), 3.32 (dd, *J* = 5.0, 10.2 Hz, 1 H, 1b-H), 2.45 (d, *J* = 6.3 Hz, 1 H, O4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1 (C_q-Ph Tr), 138.5, 138.4, 138.3 (3×C_q Bn), 128.9, 128.5, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 127.8, 127.2 (CH_{Ar} Bn/Tr), 87.0 (C_q Tr), 79.6 (C-2), 78.3 (C-3), 75.0, 73.3, 73.0 (3×CH_2 Bn), 71.2 (C-5), 70.0 (C-4), 63.0 (C-1) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3031, 2956, 1726, 1491, 1452, 1285, 1069, 747, 700 cm^{-1}. $[\alpha]_D^{20}$ = –3.3 (*c* = 2.2, $CHCl_3$). HRMS: calcd. for $[C_{45}H_{44}O_5 + Na]^+$ 687.3080 $[M + Na]^+$; found 687.3080.

2,3,5-Tri-*O*-benzyl-4-methanesulfonyl-1-*O*-trityl-D-xylitol (47): Methanesulfonyl chloride (6.7 mL, 86 mmol) was added to an anhydrous solution of **46** (14.4 g, 21.7 mmol) and Et_3N (10.9 mL, 78.0 mmol) in CH_2Cl_2 (110 mL). The reaction mixture and stirred for 20 h, then quenched by addition of H_2O (5 mL). The reaction mixture was washed successively with 0.1 M aq. HCl (50 mL), satd. aq. $NaHCO_3$ (50 mL) and satd. aq. NaCl (50 mL). The organic phase was dried ($MgSO_4$), concentrated, and the residue was purified by silica gel column chromatography (EtOAc/PE, 5→25%) to produce **47** (13.7 g, 18.5 mmol, 85%) as a colorless oil. R_f = 0.60 (EtOAc/toluene, 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.38 (m, 6 H, H_{Ar} Tr), 7.34–7.08 (m, 26 H, H_{Ar} Bn/Tr), 4.79 (ddd, *J* = 2.8, 5.3, 6.9, 1 H, 4-H), 4.62–4.55 (m, 2 H, 2×C*H*H Bn), 4.52 (d, *J* = 11.2, 1 H, CH*H* Bn), 4.47 (d, *J* = 11.9, 1 H, C*H*H Bn), 4.32–4.27 (m, 2 H, 2×CH*H* Bn), 4.11 (dd, *J* = 3.4, 6.8, 1 H, 3-H), 3.73 (ddd, *J* = 3.5, 5.1, 6.1, 1 H, 2-H), 3.62 (dd, *J* = 2.8, 11.5, 1 H, 6a-H), 3.47 (dd, *J* = 5.1, 9.8, 1 H, 1a-H), 3.39 (dd, *J* = 5.3, 11.5, 1 H, 6b-H), 3.35 (dd, *J* = 6.2, 9.8, 1 H, 1b-H), 2.81 (s, 3 H, CH_3 Ms) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9 (C_q-Ph Tr), 137.9, 137.8, 137.7 (3×C_q Bn), 128.8, 128.7, 128.6, 128.5, 128.5, 128.5, 128.1, 128.0, 127.3 (CH_{Ar} Bn/Tr), 87.3 (C_q Tr), 82.1 (C-4),

77.3 (C-3), 76.9 (C-2), 75.3, 73.4, 72.6 (3×CH_2 Bn), 69.3 (C-5), 62.1 (C-1), 38.3 (CH_3 Ms) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3032, 1492, 1452, 1358, 1213, 1175, 1073, 918, 748, 701 cm^{-1}. $[\alpha]_D^{20}$ = 23.5 (*c* = 1.6, $CHCl_3$). HRMS: calcd. for $[C_{46}H_{46}O_7S + Na]^+$ 765.2862 [M + Na]$^+$; found 765.2860.

4-Azido-2,3,5-tri-*O*-benzyl-4-deoxy-1-*O*-trityl-L-arabinitol (48): Sodium azide (7.80 g, 120 mmol) and 15-crown-5 (0.25 mL, 1.25 mmol) were added to an anhydrous solution of **47** (9.21, 12.4 mmol) in DMF (60 mL). The resulting suspension was stirred at 90 °C for 48 h. The reaction mixture was concentrated and the residue was dissolved in Et_2O (100 mL) and washed successively with water (100 mL) and satd. aq. NaCl (100 mL). The organic layer was dried ($MgSO_4$), concentrated, and the resulting residue was purified by silica gel column chromatography (EtOAc/PE, 5→20%) to produce **48** (7.5 g, 10.9 mmol, 88%) as a colorless oil. R_f = 0.80 (EtOAc/toluene, 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.39 (m, 6 H, H_{Ar} Tr), 7.33–7.02 (m, 24 H, H_{Ar} Bn/Tr), 4.63 (d, *J* = 11.6 Hz, 1 H, C*H*H Bn), 4.49 (d, *J* = 11.6 Hz, 1 H, CH*H* Bn), 4.46–4.38 (m, 4 H, 2×CH_2 Bn), 3.86 (dd, *J* = 3.3, 7.4 Hz, 1 H, 3-H), 3.82–3.78 (m, 1 H, 2-H), 3.77–3.71 (m, 2 H, 4-H, 5a-H), 3.63 (dd, *J* = 6.5, 10.2 Hz, 1 H, 5b-H), 3.45 (dd, *J* = 5.3, 9.8 Hz, 1 H, 1a-H), 3.30 (dd, *J* = 6.5, 9.8 Hz, 1 H, 1b-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1 (C1-Ph Tr), 138.5, 138.1, 138.1 (3×C_q Bn), 128.9, 128.7, 128.6, 128.5, 128.2, 128.0, 128.0, 127.8, 127.4 (CH_{Ar} Bn/Tr), 87.4 (C_q Tr), 78.3 (C-3), 78.2 (C-2), 75.0, 73.5, 73.4 (3×CH_2 Bn), 70.0 (C-5), 62.9 (C-1), 61.3 (C-4) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3032, 2870, 2096, 1492, 1452, 1073, 747, 699 cm^{-1}. $[\alpha]_D^{20}$ = 11.2 (*c* = 1.2, $CHCl_3$). HRMS: calcd. for $[C_{45}H_{43}N_3O_4 + Na]^+$ 712.3151 [M + Na]$^+$; found 712.3147.

4-Azido-2,3,5-tri-*O*-benzyl-4-deoxy-L-arabinitol (49): Boron trifluoride diethyletherate (4.8 mL, 38.0 mmol) was added to a solution of **48** (7.3 g, 10.5 mmol) in a mixture of toluene/MeOH (265 mL, 16:1, v/v). The reaction mixture was stirred for 3 h, after which the reaction was successively washed with satd. aq. $NaHCO_3$ (100 mL) and satd. aq. NaCl (100 mL). The organic phase was dried ($MgSO_4$) and concentrated, and the residue was dissolved in EtOAc, cooled to 0 °C and the triphenylmethoxymethane that precipitated was removed by filtration. Subsequent concentration and purification of the residue by silica gel column chromatography (EtOAc/toluene, 5→50%) afforded **49** (4.6 g, 10.3 mmol, 98%) as a colorless oil. R_f = 0.15 (EtOAc/toluene, 1:19). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.15 (m, 15 H, H_{Ar} Bn), 4.62–4.51 (m, 4 H, 2×CH_2 Bn), 4.49 (s, 2 H, CH_2 Bn), 3.82–3.61 (m, 7 H, CH_2-1, 2-H, 3-H, 4-H, CH_2-5), 2.27 (s, 1 H, OH-1) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 137.7, 137.7 (3×C_q Bn), 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 126.9 (CH_{Ar} Bn), 79.1, 78.0 (C-2, C-3), 74.4, 73.4, 73.1 (3×CH_2 Bn), 69.6 (C-5), 61.3 (C-4), 61.3 (C-1) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3465, 3033, 2868, 2096, 1496, 1454, 1267, 1211, 1093, 1027, 735, 698 cm^{-1}. $[\alpha]_D^{20}$ = 18.5 (*c* = 7.0, $CHCl_3$). HRMS: calcd. for $[C_{26}H_{29}N_3O_4 + Na]^+$ 470.2056 [M + Na]$^+$; found 470.2046.

4-Azido-2,3,5-tri-*O*-benzyl-4-deoxy-L-arabinose (50): Azido alcohol **49** (2.00 g, 4.47 mmol) was subjected to a Dess–Martin mediated oxidation (General Procedure A) to produce **50** (1.51 g, 3.39 mmol, 76%) as a colorless oil. R_f = 0.60 (EtOAc/toluene, 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.66 [d, *J* = 1.1 Hz, 1 H, C(O)H-1], 7.37–7.14 (m, 15 H, H_{Ar} Bn), 4.75 (d, *J* = 11.7 Hz, 1 H, C*H*H Bn), 4.60 (d, *J* = 11.7 Hz, 1 H, CH*H* Bn), 4.53 (s, 2 H, CH_2 Bn), 4.44 (s, 2 H, CH_2 Bn), 4.03 (dd, *J* = 1.2, 3.0 Hz, 1 H, 2-H), 3.96 (dd, *J* = 3.0, 8.1 Hz, 1 H, 3-H), 3.85 (dt, *J* = 2.7, 5.7 Hz, 1 H, 4-H), 3.81 (dd, *J* = 2.7, 9.9 Hz, 1 H, 5a-H), 3.70 (dd, *J* = 5.6, 9.9 Hz, 1 H, 5b-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.2 [C(O)H-1], 137.7, 137.1, 136.9 (3×C_q Bn), 128.8, 128.7, 128.7, 128.6, 128.6, 128.3, 128.3, 128.1, 128.0 (CH_{Ar} Bn), 83.4 (C-2), 78.0 (C-3), 74.5, 73.9, 73.6 (3×CH_2 Bn), 69.3 (C-5), 60.9 (C-4) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2867, 2097, 1728, 1496, 1454, 1315, 1266, 1210, 1093, 1026, 912, 734, 695 cm^{-1}. $[\alpha]_D^{20}$ = 12.6 (*c* = 1.8, $CHCl_3$). HRMS: calcd. for $[C_{26}H_{27}N_3O_4 + Na]^+$ 468.1899 [M + Na]$^+$; found 468.1891.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-L-*gulo*-hexonamide (51): Subjecting azido aldehyde **50** (1.04 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced a separable 1:1.9 mixture of **51** (114 mg, 0.15 mmol) and **52** (213 mg, 0.28 mmol) in a combined yield of 41%. R_f = 0.63 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, 2:1 mixture of rotamers; major rotamer): δ = 7.37–7.20 (m, 15 H, H_{Ar} Bn), 6.17 [t, *J* = 5.8 Hz, 1 H, C(O)NH], 5.84–5.71 (m, 1 H, =CH pentenyl), 5.10–4.92 (m, 2 H, =CH_2 pentenyl), 4.70–4.41 (m, 7 H, 3×CH_2 Bn, 5-H), 4.38 (s, 1 H, 2-H), 4.22 (s, 1 H, 3-H), 4.18 (s, 1 H, 4-H), 3.98 (dd, *J* = 4.4, 8.8 Hz, 1 H), 3.49 (dd, *J* = 8.8, 10.5 Hz, 1 H, 6b-H), 3.27 (t, *J* = 6.5 Hz, 2 H, CH_2-5 pentyl), 3.17–2.92 (m, 2 H, NCH_2-1 pentyl), 2.91 (s, 2 H, OCH_2-Ada), 2.47–2.19 (m, 4 H, 2×CH_2 pentenyl), 1.95 (s, 3 H, 3×CH Ada), 1.68 (dd, *J* = 12.0, 27.2 Hz, 6 H, 3×CH_2 Ada), 1.51 (d, *J* = 2.6 Hz, 6 H, 3×CH_2 Ada), 1.48–1.35 (m, 2 H, CH_2-2 pentyl), 1.35–1.04 (m, 4 H, 2×CH_2 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ = 173.0 (NC=O pentenyl), 169.9 [NHC(O)-1], 138.5, 137.1 (3×C_q Bn), 137.0 (=CH pentenyl), 128.8–127.8 (CH_{Ar} Bn), 115.8 (=CH_2 pentenyl), 85.9 (C-4), 82.1 (OCH_2-Ada), 80.9 (C-3), 73.3, 71.9 (2×CH_2 Bn), 71.5 (CH_2-5 pentyl), 71.4 (CH_2 Bn), 69.1 (C-2), 66.8 (C-6), 64.1 (C-5), 39.9 (CH_2 Ada), 39.8 (NCH_2-1 pentyl), 37.5 (CH_2 Ada), 34.3 (C_q Ada), 34.1 (CH_2 pentenyl), 29.3, 29.1, 29.0 (CH_2 pentenyl, 2×CH_2 pentyl), 28.5 (CH Ada), 23.7 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3338, 2901, 2848, 1654, 1648, 1454, 1407, 1206, 1096, 734, 698 cm^{-1}. $[\alpha]_D^{20}$ = 12.8 (*c* = 2.2, $CHCl_3$). HRMS: calcd. for $[C_{48}H_{62}O_6N_2 + H]^+$ 763.4681 [M + H]$^+$; found 763.4683.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-L-*ido*-hexonamide (52): R_f = 0.50 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, 6:1 mixture of rotamers; major rotamer): δ = 7.65 [t, *J* = 5.9 Hz, 1 H, C(O)NH], 7.45–7.19 (m, 15 H, H_{Ar} Bn), 5.87–5.71 (m, 1 H, =CH pentenyl), 5.09–4.92 (m, 2 H, =CH_2 pentenyl), 4.78 (d, *J* = 11.8 Hz, 1 H, C*H*H Bn), 4.67–4.36 (m, 6 H, 2-H, 6a-H, CH*H* Bn, C*H*H Bn, CH_2 Bn), 4.26–4.20 (m, 3 H, CH*H* Bn, 3-H, 4-H), 3.84–3.79 (m, 1 H, 5-H), 3.48 (dd, *J* = 1.3, 9.6 Hz, 1 H, 6b-H), 3.26 (t, *J* = 6.6 Hz, 2 H, CH_2-5 pentyl), 2.92 (s, 2 H, OCH_2-Ada), 2.68–2.56 (m, 2 H, NCH_2-1 pentyl), 2.41–2.31 (m, 4 H, 2×CH_2 pentenyl), 1.96 (s, 3 H, 3×CH Ada), 1.68 (dd, *J* = 11.8, 27.1 Hz, 6 H, 3×CH_2 Ada), 1.53 (d, *J* = 2.6 Hz, 6 H, 3×CH_2 Ada), 1.46–1.33 (m, 2 H, CH_2-2 pentyl), 1.13–1.01 (m, 4 H, 2×CH_2 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ = 173.3 (NC=O pentenyl), 168.8 [NHC(O)-1], 138.2, 137.7, 137.0 (3×C_q Bn), 137.1 (=CH pentenyl), 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9 (CH_{Ar} Bn), 115.7 (=CH_2 pentenyl), 82.1 (OCH_2-Ada), 82.1, 79.0 (C-3, C-4), 73.8, 73.4, 73.0 (3×CH_2 Bn), 71.7 (CH_2-5 pentyl), 66.6 (C-6), 63.4 (C-2), 60.2 (C-5), 40.0 (CH_2 Ada), 39.2 (NCH_2-1 pentyl), 37.5 (CH_2 Ada), 34.3 (C_q Ada), 33.5 (CH_2 pentenyl), 29.8, 29.5, 29.3, 28.8 (CH_2 pentenyl, 2×CH_2 pentyl), 28.5 (CH Ada), 23.6 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3322, 2902, 2848, 1664, 1560, 1454, 1406, 1095, 1028, 737, 698 cm^{-1}. $[\alpha]_D^{20}$ = 16.8 (*c* = 4.0, $CHCl_3$). HRMS: calcd. for $[C_{48}H_{62}O_6N_2 + H]^+$ 763.4681 [M + H]$^+$; found 763.4684.

1,1,3,3-Tetramethylbutyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-L-*gulo*-hexonamide (53): Subjecting azido aldehyde **50**

(1.59 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced a separable 1:1.1 mixture of **53** (269 mg, 0.42 mmol) and **54** (282 mg, 0.44 mmol) in a combined yield of 54%. R_f = 0.75 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, 4:1 mixture of rotamers; major rotamer): δ = 7.40–7.18 (m, 15 H, H_{Ar} Bn), 6.13 [s, 1 H, C(O)NH], 5.88–5.73 (m, 1 H, =CH pentenyl), 5.08–4.93 (m, 2 H, =CH_2 pentenyl), 4.70–4.39 (m, 7 H, 5-H, 3×CH_2 Bn), 4.24 (s, 1 H, 2-H), 4.21 (s, 1 H, 3-H), 4.16 (s, 1 H, 4-H), 3.99 (dd, J = 4.3, 8.8 Hz, 1 H, 6a-H), 3.45 (dd, J = 8.8, 10.9 Hz, 1 H, 6b-H), 2.43–2.24 (m, 4 H, 2×CH_2 pentenyl), 1.48–1.32 (m, 2 H, CH_2-2 tMB), 1.23 (s, 3 H, CH_3 tMB), 1.18 (s, 3 H, CH_3 tMB), 0.85 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ = 172.9 (NC=O pentenyl), 168.7 [NHC(O)-1], 138.5, 137.2, 136.9 (3×C_q Bn), 137.1 (=CH pentenyl), 128.7, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.8 (CH_{Ar} Bn), 115.8 (=CH_2 pentenyl), 85.9 (C-4), 81.3 (C-3), 73.3, 71.8 (3×CH_2 Bn), 70.0 (C-2), 66.7 (C-6), 64.0 (C-5), 55.8 (NHC_q-1 tMB), 53.4 (CH_2-2 tMB), 34.2 (NCH_2 pentenyl), 31.6 (CH_3-4, 2×CH_3 tMB, C_q-3 tMB), 28.9 (CH_2 pentenyl), 28.3, 27.3 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2952, 1654, 1560, 1458, 1096, 736, 698, 668 cm^{-1}. $[\alpha]_D^{20}$ = 11.2 (c = 2.0, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{52}O_5N_2 + H]^+$ 641.3949 $[M + H]^+$; found 641.3949.

1,1,3,3-Tetramethylbutyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-L-*ido*-hexonamide (54): R_f = 0.65 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, 5:1 mixture of rotamers; major rotamer): δ = 7.41–7.14 (m, 15 H, H_{Ar} Bn), 6.99 [s, 1 H, C(O)NH], 5.83 (ddd, J = 6.3, 12.3, 16.8 Hz, 1 H, =CH pentenyl), 5.09–4.90 (m, 2 H, =CH_2 pentenyl, C*H*H Bn), 4.65 (d, J = 11.7 Hz, 1 H, C*H*H Bn), 4.59–4.41 (m, 5 H, 2-H, CH_2 Bn, 2×CH*H* Bn), 4.26–4.20 (m, 2 H, 3-H, 4-H), 4.17 (dd, J = 4.3, 9.7 Hz, 1 H, 6a-H), 3.95–3.89 (m, 1 H, 5-H), 3.50 (dd, J = 2.3, 9.7 Hz, 1 H, 6b-H), 2.45–2.29 (m, 4 H, 2×CH_2 pentenyl), 1.92 (d, J = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.59 (d, J = 14.5 Hz, 1 H, CH*H*-2 tMB), 1.32 (d, J = 9.6 Hz, 6 H, 2×CH_3 tMB), 0.93 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer): δ = 173.8 (NC=O pentenyl), 167.9 [NHC(O)-1], 138.0, 137.7, 137.6 (3×C_q Bn), 137.1 (=CH pentenyl), 128.7, 128.5, 128.2, 128.2, 128.0, 127.8 (CH_{Ar} Bn), 115.7 (=CH_2 pentenyl), 82.7, 79.3 (C-3, C-4), 73.4, 73.0, 72.8 (3×CH_2 Bn), 66.1 (C-6), 64.5 (C-2), 60.7 (C-5), 55.7 (NHC_q-1 tMB), 51.5 (CH_2-2 tMB), 33.7 (NCH_2 pentenyl), 31.7 (CH_3-4, 2×CH_3 tMB), 31.6 (C_q-3 tMB), 29.4, 28.8 (2×CH_3 tMB), 28.8 (CH_2 pentenyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2952, 2361, 2343, 1668, 1540, 1455, 1398, 1365, 1206, 1096, 1028, 736, 698, 668 cm^{-1}. $[\alpha]_D^{20}$ = 12.1 (c = 2.1, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{52}O_5N_2 + H]^+$ 641.3949 $[M + H]^+$; found 641.3949.

Pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-L-*gulo*-hexonamide (55): Subjecting azido aldehyde **50** (3.39 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced a separable 1:2.1 mixture of **55** (285 mg, 0.48 mmol) and **56** (585 mg, 0.98 mmol) in a combined yield of 43%. R_f = 0.65 (EtOAc/PE, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$, 3.5:1 mixture of rotamers; major rotamer): δ = 7.39–7.20 (m, 15 H, H_{Ar} Bn), 6.16 [t, J = 5.6 Hz, 1 H, C(O)NH], 5.83–5.72 (m, 1 H, =CH pentenyl), 5.07–4.93 (m, 2 H, =CH_2 pentenyl), 4.68–4.39 (m, 7 H, 5-H, 3×CH_2 Bn), 4.38 (s, 1 H, 2-H), 4.22 (s, 1 H, 3-H), 4.18 (s, 1 H, 4-H), 3.98 (dd, J = 4.4, 8.8 Hz, 1 H, 6a-H), 3.49 (dd, J = 9.7 Hz, 1 H, 6b-H), 3.13–3.05 (m, 1 H, NC*H*H-1 pentyl), 2.97–2.86 (m, 1 H, NCH*H*-1 pentyl), 2.48–2.24 (m, 4 H, 2×CH_2 pentenyl), 1.28–1.06 (m, 6 H, 3×CH_2 pentyl), 0.81 (t, J = 7.2 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, major rotamer): δ = 173.0 (NC=O pentenyl), 169.9 [NHC(O)-1], 138.5, 137.7, 137.1 (3×C_q Bn), 137.0 (=CH pentenyl), 128.7, 128.7, 128.6, 128.3, 128.2, 127.9, 127.9, 127.8 (CH_{Ar} Bn), 115.8 (=CH_2 pentenyl), 85.9 (C-4), 80.9 (C-3), 73.3, 71.9, 71.5 (3×CH_2 Bn), 69.1 (C-2), 66.8 (C-6), 64.1 (C-5), 39.8 (NCH_2-1 pentyl), 34.1 (NCH_2 pentenyl), 29.2, 28.9, 22.4 (CH_2 pentyl/pentenyl), 14.1 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3325, 2930, 1652, 1540, 1455, 1366, 1097, 737, 699 cm^{-1}. $[\alpha]_D^{20}$ = 17.3 (c = 0.3, $CHCl_3$). HRMS: calcd. for $[C_{37}H_{46}O_5N_2 + H]^+$ 599.3479 $[M + H]^+$; found 599.3478.

Pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-(pent-4-enimido)-L-*ido*-hexonamide (56): R_f = 0.55 (EtOAc/PE, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$, 9:1 mixture of rotamers; major rotamer): δ = 7.65 [t, J = 5.8 Hz, 1 H, C(O)NH], 7.43–7.15 (m, 15 H, H_{Ar} Bn), 5.83–5.76 (m, 1 H, =CH pentenyl), 5.05–4.97 (m, 3 H, =CH_2 pentenyl, C*H*H Bn), 4.78 (d, J = 11.8 Hz, 1 H, C*H*H Bn), 4.60–4.55 [m, J = 6.9 Hz, 2 H, 2-H (d), CH*H* Bn], 4.53 (d, J = 11.2 Hz, 1 H, CH*H* Bn), 4.45–4.39 (m, 2 H, 6a-H, C*H*H Bn), 4.25–4.21 (m, 3 H, 3-H, 4-H, CH*H* Bn), 3.81 (d, J = 4.4 Hz, 1 H, 5-H), 3.48 (d, J = 10.6 Hz, 1 H, 6b-H), 2.69 (dt, J = 6.4, 13.4 Hz, 1 H, NC*H*H-1 pentyl), 2.60 (dt, J = 6.1, 13.4 Hz, 1 H, NCH*H*-1 pentyl), 2.41–2.32 (m, 3 H, NC*H*H pentenyl, CH_2 pentenyl), 2.23–2.15 (m, 1 H, NC*H*H pentenyl), 1.22–1.12 (m, 2 H, CH_2-2 pentyl), 1.11–0.98 (m, 4 H, 2×CH_2 pentyl), 0.81 (t, J = 7.4 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, major rotamer): δ = 173.4 (NC=O pentenyl), 168.8 [NHC(O)-1], 138.2, 137.7, 137.1 (3×C_q Bn), 137.0 (=CH pentenyl), 128.8, 128.8, 128.6, 128.6, 128.6, 128.6, 128.5, 128.2, 128.1 (CH_{Ar} Bn), 115.7 (=CH_2 pentenyl), 82.1, 79.0 (C-3, C-4), 73.8, 73.4, 73.1 (3×CH_2 Bn), 66.5 (C-6), 63.4 (C-2), 60.2 (C-5), 39.2 (NCH_2-1 pentyl), 33.5 (CH_2 pentenyl), 29.6, 29.1, 28.8, 22.6 (CH_2 pentyl/pentenyl), 14.2 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3330, 2940, 1667, 1538, 1365, 1096, 737, 700 cm^{-1}. $[\alpha]_D^{20}$ = 23.3 (c = 0.3, $CHCl_3$). HRMS: calcd. for $[C_{37}H_{46}O_5N_2 + H]^+$ 599.3479 $[M + H]^+$; found 599.3477.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-L-*gulo*-hexonamide (57): Compound **57** (54 mg, 79 μmol, 55%) was synthesized from **51** (144 μmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.38 (EtOAc/PE, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 [t, J = 5.9 Hz, 1 H, C(O)NH], 7.39–7.18 (m, 15 H, H_{Ar} Bn), 4.77 (d, J = 11.8 Hz, 1 H, C*H*H Bn), 4.62 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.55–4.45 (m, 3 H, C*H*H Bn, CH_2 Bn), 4.41 (d, J = 11.6 Hz, 1 H, CH*H* Bn), 4.36 (dd, J = 2.9 Hz, 1 H, 3-H), 3.88 (dd, J = 3.2, 5.7 Hz, 1 H, 4-H), 3.74 (d, J = 2.3 Hz, 1 H, 2-H), 3.58 (dd, J = 4.0, 9.6 Hz, 1 H, 6a-H), 3.53 (dd, J = 5.6, 9.6 Hz, 1 H, 6b-H), 3.34 (t, J = 6.5 Hz, 2 H, CH_2-5 pentyl), 3.29–3.15 (m, 3 H, 5-H, NCH_2-1 pentyl), 2.93 (s, 2 H, OCH_2-Ada), 2.66 (s, 1 H, NH), 1.95 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 11.6, 36.7 Hz, 6 H, 3×CH_2 Ada), 1.58–1.43 (m, 10 H, 3×CH_2 Ada), 1.39–1.30 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.9 [NHC(O)-1], 138.1, 137.9, 137.9 (3×C_q Bn), 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6 (CH_{Ar} Bn), 87.2 (C-3), 84.9 (C-4), 81.9 (OCH_2-Ada), 73.2, 71.8, 71.6 (3×CH_2 Bn), 71.4 (CH_2-5 pentyl), 68.8 (C-6), 65.7 (C-2), 62.4 (C-5), 39.7 (CH_2 Ada), 39.1 (NCH_2-1 pentyl), 37.3 (CH_2 Ada), 34.1 (C_q Ada), 29.5, 29.2 (2×CH_2 pentyl), 28.3 (CH Ada), 23.6 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2901, 1669, 1513, 1455, 1097, 735, 697 cm^{-1}. $[\alpha]_D^{20}$ = –0.5 (c = 0.8, $CHCl_3$). HRMS: calcd. for $[C_{43}H_{56}O_5N_2 + H]^+$ 681.4262 $[M + H]^+$; found 681.4259.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-L-*ido*-hexonamide (58): Compound **58** (111 mg, 163 μmol, 62%) was synthesized from **52** (262 μmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.16 (EtOAc/PE, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 [t, J = 5.6 Hz, 1 H, C(O)NH], 7.37–7.19 (m, 15 H, H_{Ar} Bn), 4.59 (d, J = 11.7 Hz, 1 H, C*H*H Bn), 4.53–4.39 (m, 5 H, CH*H* Bn, 2×CH_2 Bn), 4.29 (dd, J = 1.7, 5.6 Hz, 1 H, 3-H), 4.16 (d, J = 5.6 Hz, 1 H, 2-H), 3.85 (dd, J =

2.1 Hz, 1 H, 4-H), 3.56–3.47 (m, 3 H, 5-H, CH_2-6), 3.30 (t, J = 6.6 Hz, 2 H, CH_2-5 pentyl), 3.23–3.18 (m, 2 H, NCH_2-1 pentyl), 2.92 (s, 2 H, OCH_2-Ada), 2.55–2.14 (m, 1 H, NH), 1.95 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 11.6, 38.8 Hz, 6 H, 3×CH_2 Ada), 1.54–1.37 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.34–1.26 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.5 [NHC(O)-1], 138.2, 138.0, 137.8 (3×C_q Bn), 128.7, 128.4, 128.4, 128.3, 128.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6 (CH_{Ar} Bn), 83.2 (C-4), 83.0 (C-3), 81.9 (OCH_2-Ada), 73.2, 72.9 (2×CH_2 Bn), 72.0 (C-6), 71.5 (CH_2 Bn), 71.4 (CH_2-5 pentyl), 64.5 (C-2), 62.3 (C-5), 39.8 (CH_2 Ada), 39.1 (NCH_2-1 pentyl), 37.3 (CH_2 Ada), 34.1 (C_q Ada), 29.5, 29.2 (2×CH_2 pentyl), 28.3 (CH Ada), 23.6 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3030, 2903, 1668, 1512, 1454, 1096, 735, 699 cm^{-1}. $[\alpha]_D^{20}$ = –4.6 (c = 2.2, $CHCl_3$). HRMS: calcd. for $[C_{43}H_{56}O_5N_2 + H]^+$ 681.4262 $[M + H]^+$; found 681.4259.

1,1,3,3-Tetramethylbutyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-L-*gulo*-hexon-amide (59): Compound **59** (175 mg, 313 μmol, 95%) was synthesized from **53** (330 μmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.69 (EtOAc/PE, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 [s, 1 H, C(O)NH], 7.39–7.20 (m, 15 H, H_{Ar} Bn), 4.78 (d, J = 11.8 Hz, 1 H, C*H*H Bn), 4.62 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.59–4.41 (m, 4 H, 2×CH_2 Bn), 4.34 (dd, J = 2.8, 3.3 Hz, 1 H, 3-H), 3.90 (dd, J = 3.4, 6.0 Hz, 1 H, 4-H), 3.61 (d, J = 2.6 Hz, 1 H, 2-H), 3.59–3.51 (m, 2 H, CH_2-6), 3.20–3.13 (m, 1 H, 5-H), 2.74–2.61 (m, 1 H, NH), 1.76 (d, J = 14.9 Hz, 1 H, C*H*H-2 tMB), 1.60 (d, J = 13.7 Hz, 1 H, CH*H*-2 tMB), 1.39 (d, J = 12.9 Hz, 6 H, 2×CH_3 tMB), 0.98 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.0 [NHC(O)-1], 138.5, 138.2, 138.1 (3×C_q Bn), 128.6, 128.5, 128.5, 128.1, 128.1, 128.0, 128.0, 127.8, 127.7 (CH_{Ar} Bn), 87.7 (C-3), 85.2 (C-4), 73.4, 72.1, 71.9 (3×CH_2 Bn), 68.8 (C-6), 66.3 (C-2), 62.3 (C-5), 54.5 (NHC_q-1 tMB), 52.8 (CH_2-2 tMB), 31.8 (C_q-3 tMB), 31.7 (CH_3-4, 2×CH_3 tMB), 29.3, 28.6 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3322, 2948, 1670, 1516, 1092, 738, 698 cm^{-1}. $[\alpha]_D^{20}$ = –1.5 (c = 2.0, $CHCl_3$). HRMS: calcd. for $[C_{35}H_{46}O_4N_2 + H]^+$ 559.3530 $[M + H]^+$; found 559.3525.

1,1,3,3-Tetramethylbutyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-L-*ido*-hexonamide (60): Compound **60** (151 mg, 270 μmol, 75%) was synthesized from **54** (360 μmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.47 (EtOAc/PE, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.22 [m, 16 H, C(O)NH, H_{Ar} Bn], 4.62 (d, J = 11.7 Hz, 1 H, C*H*H Bn), 4.56 (d, J = 12.0 Hz, 1 H, C*H*H Bn), 4.53–4.45 (m, 3 H, CH*H* Bn, CH*H* Bn, C*H*H Bn), 4.43 (d, J = 11.9 Hz, 1 H, CH*H* Bn), 4.26 (dd, J = 1.4, 5.5 Hz, 1 H, 3-H), 4.02 (d, J = 5.5 Hz, 1 H, 2-H), 3.88 (dd, J = 1.7 Hz, 1 H, 4-H), 3.57 (dd, J = 5.5, 7.0 Hz, 1 H, 6a-H), 3.53–3.47 (m, 2 H, 5-H, 6b-H), 2.33 (s, 1 H, NH), 1.81 (d, J = 14.9 Hz, 1 H, C*H*H-2 tMB), 1.51 (d, J = 14.9 Hz, 1 H, CH*H*-2 tMB), 1.40 (d, J = 29.5 Hz, 6 H, 2×CH_3 tMB), 0.98 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.5 [NHC(O)-1], 138.3, 138.1, 137.9 (3×C_q Bn), 128.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.7, 127.7, 127.5 (CH_{Ar} Bn), 83.5 (C-4), 83.1 (C-3), 73.2, 72.9 (2×CH_2 Bn), 72.6 (C-6), 71.4 (CH_2 Bn), 65.4 (C-2), 62.5 (C-5), 54.4 (NHC_q-1 tMB), 53.0 (CH_2-2 tMB), 31.6 (C_q-3 tMB), 31.5 (CH_3-4, 2×CH_3 tMB), 28.9, 28.2 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3320, 2950, 1669, 1522, 1096, 738, 698 cm^{-1}. $[\alpha]_D^{20}$ = –6.1 (c = 2.1, $CHCl_3$). HRMS: calcd. for $[C_{35}H_{46}O_4N_2 + H]^+$ 559.3530 $[M + H]^+$; found 559.3525.

Pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-L-*gulo*-hexonamide (61): Compound **61** (220 mg, 0.43 mmol, 95%) was synthesized from **55** (0.45 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.57 (EtOAc/PE, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 [t, J = 5.6 Hz, 1 H, C(O)NH], 7.40–7.19 (m, 15 H, H_{Ar} Bn), 4.77 (d, J = 11.8 Hz, 1 H, C*H*H Bn), 4.62 (d, J = 11.8 Hz, 1 H), CH*H* Bn, 4.54–4.39 (m, 4 H, 2×CH_2 Bn), 4.36 (dd, J = 2.9 Hz, 1 H, 3-H), 3.89 (dd, J = 3.3, 5.6 Hz, 1 H, 4-H), 3.78 (d, J = 2.3 Hz, 1 H, 2-H), 3.58 (dd, J = 4.1, 9.6 Hz, 1 H, 6a-H), 3.55 (dd, J = 5.7, 9.6 Hz, 1 H, 6b-H), 3.28–3.15 (m, 3 H, 5-H, NCH_2-1 pentyl), 1.51–1.42 (m, 2 H, CH_2-2 pentyl), 1.32–1.24 (m, 4 H, 2×CH_2 pentyl), 0.87 (t, J = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.8 [NHC(O)-1], 138.3, 138.1, 138.0 (3×C_q Bn), 128.7, 128.6, 128.5, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9 (CH_{Ar} Bn), 87.3 (C-3), 85.0 (C-4), 73.4, 72.1, 71.9 (3×CH_2 Bn), 68.9 (C-6), 65.8 (C-2), 62.7 (C-5), 39.3 (NCH_2-1 pentyl), 29.5, 29.3, 22.6 (3×CH_2 pentyl), 14.2 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3325, 2930, 2860, 1668, 1526, 1455, 1096, 736, 698 cm^{-1}. $[\alpha]_D^{20}$ = –1.6 (c = 4.4, $CHCl_3$). HRMS: calcd. for $[C_{32}H_{40}O_4N_2 + H]^+$ 517.3061 $[M + H]^+$; found 517.3055.

Pentyl 3,4,6-Tri-*O*-benzyl-2,5-dideoxy-2,5-imino-L-*ido*-hexonamide (62): Compound **62** (410 mg, 0.79 mmol, 83%) was synthesized from **56** (0.95 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.35 (EtOAc/PE, 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 [t, J = 5.7 Hz, 1 H, C(O)NH], 7.35–7.21 (m, 15 H, H_{Ar} Bn), 4.60 (d, J = 11.7 Hz, 1 H, C*H*H Bn), 4.52–4.40 (m, 5 H, CH*H* Bn, 2×CH_2 Bn), 4.30 (dd, J = 1.5, 5.6 Hz, 1 H, 3-H), 4.17 (d, J = 5.7 Hz, 1 H, 2-H), 3.85 (s, 1 H, 4-H), 3.56–3.47 (m, 3 H, 5-H, CH_2-6), 3.26–3.12 (m, 2 H, NCH_2-1 pentyl), 2.44 (s, 1 H, NH), 1.46–1.38 (m, 2 H, CH_2-2 pentyl), 1.29–1.19 (m, 4 H, 2×CH_2 pentyl), 0.84 (t, J = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.7 [NHC(O)-1], 138.3, 138.2, 137.9 (3×C_q Bn), 128.8, 128.6, 128.6, 128.5, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8 (CH_{Ar} Bn), 83.4 (C-4), 83.2 (C-3), 73.4, 73.1 (2×CH_2 Bn), 72.1 (C-6), 71.7 (CH_2 Bn), 64.6 (C-2), 62.6 (C-5), 39.3 (NCH_2-1 pentyl), 29.5, 29.3, 22.5 (3×CH_2 pentyl), 14.2 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3325, 3032, 2929, 2861, 1668, 1532, 1497, 1455, 1363, 1208, 1093, 1028, 735, 698 cm^{-1}. $[\alpha]_D^{20}$ = –5.8 (c = 8.2, $CHCl_3$). HRMS: calcd. for $[C_{32}H_{40}O_4N_2 + H]^+$ 517.3061 $[M + H]^+$; found 517.3056.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-Dideoxy-2,5-imino-L-*gulo*-hexonamide (63): Compound **63** (7 mg, 17 μmol, 85%) was synthesized from **57** (20 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.29 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH). ^{1}H NMR (400 MHz, MeOD): δ = 4.02 (dd, J = 5.2 Hz, 1 H, 3-H), 3.79 (dd, J = 5.7 Hz, 1 H, 4-H), 3.70 (dd, J = 4.1, 11.1 Hz, 1 H, 6a-H), 3.60 (dd, J = 5.8, 11.1 Hz, 1 H, 6b-H), 3.49 (d, J = 5.3 Hz, 1 H, 2-H), 3.38 (t, J = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.22 (t, J = 7.0 Hz, 2 H, NCH_2-1 pentyl), 3.08 (dd, J = 5.8, 10.2 Hz, 1 H, 5-H), 2.97 (s, 2 H, OCH_2-Ada), 1.94 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 11.9, 31.5 Hz, 6 H, 3×CH_2 Ada), 1.63–1.49 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.46–1.35 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 175.0 [C(O)-1], 83.2 (OCH_2-Ada), 82.6 (C-3), 80.0 (C-4), 72.7 (CH_2-5 pentyl), 67.0 (C-2), 66.0 (C-5), 63.3 (C-6), 41.0 (CH_2 Ada), 40.4 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5, 30.4 (2×CH_2 pentyl), 29.9 (CH Ada), 24.8 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3313, 2902, 2849, 1652, 1452, 1109 cm^{-1}. $[\alpha]_D^{20}$ = 1.5 (c = 0.1, MeOH). HRMS: calcd. for $[C_{22}H_{38}O_5N_2 + H]^+$ 411.2853 $[M + H]^+$; found 411.2851.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-Butylimino-2,5-dideoxy-L-*gulo*-hexonamide (64): Compound **64** (7 mg, 15 μmol, 75%) was synthesized in two steps from **57** (20 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.76 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH);

R_f *N*-alkylated penultimate = 0.80 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, MeOD): δ = 3.96 (dd, *J* = 1.7 Hz, 1 H, 4-H), 3.89 (dd, *J* = 1.8 Hz, 1 H, 3-H), 3.79 (dd, *J* = 5.0, 11.4 Hz, 1 H, 6a-H), 3.69 (dd, *J* = 3.2, 11.4 Hz, 1 H, 6b-H), 3.40 (s, 1 H, 2-H), 3.38 (t, *J* = 5.6 Hz, 2 H, CH_2-5 pentyl), 3.28–3.11 [m, 3 H, 5-H, C(O)NCH_2-1 pentyl], 2.97 (s, 2 H, OCH_2-Ada), 2.88–2.79 (m, 1 H, NC*H*H-1 pentyl), 2.65–2.55 (m, 1 H, NCH*H*-1 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, *J* = 11.7, 31.6 Hz, 6 H, 3×CH_2 Ada), 1.64–1.23 (m, 16 H, 3×CH_2 Ada, 3×CH_2 pentyl, 2×CH_2 butyl), 0.94 (t, *J* = 7.3 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.3 (OCH_2-Ada), 82.3 (C-3), 81.5 (C-4), 76.3 (CH_2-5 pentyl), 72.7 (C-2), 70.9 (C-5), 61.0 (C-6), 49.8 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 40.2 [C(O)NCH_2-1 pentyl], 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 32.1, 30.5, 30.5, 24.9, 21.8 (3×CH_2 pentyl, 2×CH_2 butyl), 14.6 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3324, 2904, 2851, 1651, 1457, 1057 cm^{-1}. $[\alpha]_D^{20}$ = 14.3 (*c* = 0.1, MeOH). HRMS: calcd. for $[C_{26}H_{46}O_5N_2 + H]^+$ 467.3479 $[M + H]^+$; found 467.3476.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,5-dideoxy-L-*gulo*-hexonamide (65): Compound **65** (8 mg, 13 μmol, 65%) was synthesized in two steps from **57** (20 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.80 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f *N*-alkylated penultimate = 0.82 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, MeOD): δ = 3.96 (dd, *J* = 1.6 Hz, 1 H, 4-H), 3.89 (dd, *J* = 1.7 Hz, 1 H, 3-H), 3.80 (dd, *J* = 5.0, 11.4 Hz, 1 H, 6a-H), 3.69 (dd, *J* = 3.2, 11.4 Hz, 1 H, 6b-H), 3.42–3.35 (m, 5 H, 2-H, 2×CH_2-5 pentyl), 3.27–3.16 [m, 3 H, 5-H, C(O)NCH_2-1 pentyl], 2.97 (s, 4 H, 2×OCH_2-Ada), 2.88–2.79 (m, 1 H, NC*H*H-1 pentyl), 2.65–2.53 (m, 1 H, NCH*H*-1 pentyl), 1.95 (s, 6 H, 6×CH Ada), 1.72 (dd, *J* = 12.1, 31.4 Hz, 12 H, 6×CH_2 Ada), 1.63–1.52 (m, 20 H, 6×CH_2 Ada, 4×CH_2 pentyl), 1.49–1.34 (m, 4 H, 2×CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.3, 83.3 (2×OCH_2-Ada), 82.4 (C-3), 81.6 (C-4), 76.5 (C-2), 72.7, 72.7 (2×CH_2-5 pentyl), 70.8 (C-5), 61.0 (C-6), 50.0 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 40.2 [C(O)NCH_2-1 pentyl], 38.5 (CH_2 Ada), 35.4, 35.3 (2×C_q Ada), 29.9 (CH Ada), 30.8, 30.5, 30.5, 29.7, 25.4 (CH_2 pentyl), 24.9 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3328, 2902, 2849, 1651, 1454, 1157, 1111 cm^{-1}. $[\alpha]_D^{20}$ = 13.8 (*c* = 0.2, MeOH). HRMS: calcd. for $[C_{38}H_{64}O_6N_2 + H]^+$ 645.4837 $[M + H]^+$; found 645.4834.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-Dideoxy-2,5-imino-L-*ido*-hexonamide (66): Compound **66** (12 mg, 29 μmol, 55%) was synthesized from **58** (53 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.10 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH). ^{1}H NMR (400 MHz, MeOD): δ = 4.17 (dd, *J* = 2.1, 5.1 Hz, 1 H, 3-H), 4.04 (d, *J* = 5.1 Hz, 1 H, 2-H), 3.92 (dd, *J* = 2.4 Hz, 1 H, 4-H), 3.71–3.68 (m, 2 H, CH_2-6), 3.38 (t, *J* = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.27–3.22 (m, 3 H, 5-H, NCH_2-1 pentyl), 2.97 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, *J* = 12.1, 31.7 Hz, 7 H, 3×CH_2 Ada), 1.62–1.52 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.46–1.37 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 175.0 [C(O)-1], 83.2 (OCH_2-Ada), 79.8 (C-4), 79.0 (C-3), 72.7 (CH_2-5 pentyl), 67.9 (C-5), 65.8 (C-2), 63.5 (C-6), 41.0 (CH_2 Ada), 40.4 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5, 30.4 (2×CH_2 pentyl), 29.9 (CH Ada), 24.8 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3326, 2902, 2849, 1652, 1454, 1050 cm^{-1}. $[\alpha]_D^{20}$ = –22.4 (*c* = 0.1, MeOH). HRMS: calcd. for $[C_{22}H_{38}O_5N_2 + H]^+$ 411.2853 $[M + H]^+$; found 411.2851.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-Butylimino-2,5-dideoxy-L-*ido*-hexonamide (67): Compound **67** (18 mg, 39 μmol, 74%) was synthesized in two steps from **58** (53 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.54 (MeOH/CH_2Cl_2. 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.85 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.19–3.49 (m, 5 H), 3.38 (t, *J* = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.22 (s, 1 H), 2.97 (s, 2 H, OCH_2-Ada), 2.91–2.55 (m, 3 H), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, *J* = 12.1, 32.0 Hz, 6 H, 3×CH_2 Ada), 1.64–1.25 (m, 16 H, 3×CH_2 Ada, 3×CH_2 pentyl, 2×CH_2 butyl), 0.94 (t, *J* = 7.3 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD, collapsed iminosugar signals): δ = 83.3 (OCH_2-Ada), 79.3 (CH), 78.4 (CH), 72.7 (CH_2-5 pentyl), 41.0 (CH_2 Ada), 40.3 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5 (CH_2), 29.9 (CH Ada), 24.9 (CH_2), 21.8 (CH_2), 14.5 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3295, 2902, 2849, 1637, 1456, 1360, 1110, 756 cm^{-1}. $[\alpha]_D^{20}$ = –16.7 (*c* = 0.4, MeOH). HRMS: calcd. for $[C_{26}H_{46}O_5N_2 + H]^+$ 467.3479 $[M + H]^+$; found 467.3476.

5-(Adamantan-1-yl-methoxy)pentyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,5-dideoxy-L-*ido*-hexonamide (68): Compound **68** (27 mg, 42 μmol, 79%) was synthesized in two steps from **58** (53 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.56 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.72 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.47–3.50 (m, 5 H), 3.39 (t, *J* = 6.4 Hz, 4 H, 2×CH_2-5 pentyl), 3.27–3.16 (m, 1 H), 2.97 (s, 4 H, 2×OCH_2-Ada), 2.94–2.49 (m, 2 H), 1.95 (s, 6 H, 6×CH Ada), 1.72 (dd, *J* = 12.0, 32.1 Hz, 12 H, 6×CH_2 Ada), 1.65–1.48 (m, 20 H, 6×CH_2 Ada, 4×CH_2 pentyl), 1.48–1.32 (m, 4 H, 2×CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD, collapsed iminosugar signals): δ = 83.3 (OCH_2-Ada), 78.4 (CH), 72.7 (CH_2-5 pentyl), 41.0 (CH_2 Ada), 40.3 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3, 35.3 (2×C_q Ada), 30.7, 30.5, 30.5 (CH_2), 29.9 (CH Ada), 25.2, 24.9 (2×CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3295, 2900, 2848, 1652, 1453, 1361, 1157, 1109, 755 cm^{-1}. $[\alpha]_D^{20}$ = –18.1 (*c* = 0.5, MeOH). HRMS: calcd. for $[C_{38}H_{64}O_6N_2 + H]^+$ 645.4837 $[M + H]^+$; found 645.4835.

1,1,3,3-Tetramethylbutyl 2,5-Dideoxy-2,5-imino-L-*gulo*-hexonamide (69): Compound **69** (10 mg, 35 μmol, 58%) was synthesized from **59** (60 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.43 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH). ^{1}H NMR (400 MHz, MeOD): δ = 4.02 (dd, *J* = 5.2 Hz, 1 H, 3-H), 3.78 (dd, *J* = 5.4, 6.1 Hz, 1 H, 4-H), 3.69 (dd, *J* = 4.1, 11.2 Hz, 1 H, 6a-H), 3.60 (dd, *J* = 5.7, 11.2 Hz, 1 H, 6b-H), 3.39 (d, *J* = 5.2 Hz, 1 H, 2-H), 3.02 (dt, *J* = 4.1, 6.0 Hz, 1 H, 5-H), 1.81 (d, *J* = 14.9 Hz, 1 H, C*H*H-2 tMB), 1.74 (d, *J* = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.41 (s, 6 H, 2×CH_3 tMB), 1.02 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 174.1 [C(O)-1], 82.4 (C-3), 80.0 (C-4), 67.4 (C-2), 65.9 (C-5), 63.2 (C-6), 55.8 (NHC_q-1 tMB), 52.9 (CH_2-2 tMB), 32.6 (C_q-3 tMB), 32.1 (2×CH_3, CH_3-4 tMB), 29.6, 29.4 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3304, 2954, 1652, 1453, 1366, 1227, 1055 cm^{-1}. $[\alpha]_D^{20}$ = 8.0 (*c* = 0.2, MeOH). HRMS: calcd. for $[C_{14}H_{28}O_4N_2 + H]^+$ 289.2122 $[M + H]^+$; found 289.2123.

1,1,3,3-Tetramethylbutyl 2,5-Butylimino-2,5-dideoxy-L-*gulo*-hexonamide (70): Compound **70** (11 mg, 32 μmol, 53%) was synthesized in two steps from **59** (60 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.85 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.95 (EtOAc/PE, 1:1). ^{1}H NMR

(400 MHz, MeOD): δ = 3.97 (s, 1 H, 4-H), 3.89 (s, 1 H, 3-H), 3.81 (dd, J = 5.1, 11.5 Hz, 1 H, 6a-H), 3.69 (dd, J = 3.0, 11.5 Hz, 1 H, 6b-H), 3.29 (s, 2 H, 2-H, 5-H), 2.94–2.82 (m, 1 H, NC*H*H butyl), 2.67–2.51 (m, 1 H, NCH*H* butyl), 1.88 (d, J = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.73 (d, J = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.63–1.25 (m, 10 H, 2×CH_3 tMB, 2×CH_2 butyl), 1.02 (s, 9 H, 2×CH_3, CH_3-4 tMB), 0.95 (t, J = 7.3 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 82.1 (C-3), 81.5 (C-4), 77.5, 70.5 (C-2, C-5), 60.8 (C-6), 52.8 (CH_2-2 tMB), 49.9 (NCH_2 butyl), 32.6 (C_q-3 tMB), 32.2 (2×CH_3, CH_3-4 tMB), 29.6, 29.4 (2×CH_3 tMB), 21.9 (CH_2 butyl), 14.6 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3312, 2957, 1651, 1439, 1366, 1226, 1155, 1066 cm^{-1}. $[\alpha]_D^{20}$ = 20.9 (c = 0.2, MeOH). HRMS: calcd. for $[C_{18}H_{36}O_4N_2 + H]^+$ 345.2748 $[M + H]^+$; found 345.2748.

1,1,3,3-Tetramethylbutyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]-imino-2,5-dideoxy-L-*gulo*-hexonamide (71): Compound **71** (13 mg, 25 μmol, 42%) was synthesized in two steps from **59** (60 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.85 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.83 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, MeOD): δ = 3.97 (s, 1 H, 4-H), 3.89 (s, 1 H, 3-H), 3.81 (dd, J = 5.1, 11.5 Hz, 1 H, 6a-H), 3.68 (dd, J = 3.1, 11.5 Hz, 1 H, 6b-H), 3.39 (t, J = 6.3 Hz, 2 H, CH_2-5 pentyl), 3.30–3.23 (m, 2 H, 2-H, 5-H), 2.97 (s, 2 H, OCH_2-Ada), 2.93–2.84 (m, 1 H, NC*H*H pentyl), 2.61–2.53 (m, 1 H, NCH*H* pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.89 (d, J = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.81–1.65 (m, 7 H, CH*H*-2 tMB, 3×CH_2 Ada), 1.64–1.37 (m, 18 H, 3×CH_2 Ada, 2×CH_3 tMB, 3×CH_2 pentyl), 1.03 (s, 9, 2×CH_3, CH_3-4 tMBH) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 82.1 (C-3), 81.6 (C-4), 77.7 (C-2), 72.6 (CH_2-5 pentyl), 70.4 (C-5), 60.9 (C-6), 56.1 (NHC_q-1 tMB), 52.8 (CH_2-2 tMB), 50.1 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 32.6 (C_q-3 tMB), 32.2 (2×CH_3, CH_3-4 tMB), 30.9 (CH_2 pentyl), 29.9 (CH Ada), 29.7, 29.4 (2×CH_3 tMB), 25.5 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3342, 2903, 2850, 1651, 1440, 1227, 1064 cm^{-1}. $[\alpha]_D^{20}$ = 24.6 (c = 0.3, MeOH). HRMS: calcd. for $[C_{30}H_{54}O_5N_2 + H]^+$ 523.4105 $[M + H]^+$; found 523.4101.

1,1,3,3-Tetramethylbutyl 2,5-Dideoxy-2,5-imino-L-*ido*-hexonamide (72): Compound **72** (14 mg, 49 μmol, 78%) was synthesized from **60** (63 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.38 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH). ^{1}H NMR (400 MHz, MeOD): δ = 4.11 (dd, J = 2.4, 5.4 Hz, 1 H, 3-H), 3.90 (dd, J = 2.7 Hz, 1 H, 4-H), 3.81 (d, J = 5.4 Hz, 1 H, 2-H), 3.66 (dd, J = 4.1, 10.1 Hz, 1 H, 6a-H), 3.62 (dd, J = 4.3, 10.1 Hz, 1 H, 6b-H), 3.14 (dt, J = 2.9, 4.9 Hz, 1 H, 5-H), 1.83 (d, J = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.69 (d, J = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.41 (d, J = 6.0 Hz, 6 H, 2×CH_3 tMB), 1.03 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 172.9 [C(O)-1], 80.3 (C-4), 79.4 (C-3), 67.3 (C-5), 66.2 (C-2), 64.6 (C-6), 56.0 (NHC_q-1 tMB), 53.2 (CH_2-2 tMB), 32.6 (C_q-3 tMB), 32.1 (2×CH_3, CH_3-4 tMB), 29.6 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3328, 2955, 2481, 1667, 1559, 1454, 1367, 1226, 1042 cm^{-1}. $[\alpha]_D^{20}$ = –44.1 (c = 0.3, MeOH). HRMS: calcd. for $[C_{14}H_{28}O_4N_2 + H]^+$ 289.2122 $[M + H]^+$; found 289.2123.

1,1,3,3-Tetramethylbutyl 2,5-Butylimino-2,5-dideoxy-L-*ido*-hexonamide (73): Compound **73** (12 mg, 35 μmol, 55%) was synthesized in two steps from **60** (63 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.66 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.88 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.15–4.07 (m, 1 H, 3-H), 4.02 (dd, J = 2.6 Hz, 1 H, 4-H), 3.68 (s, 2 H, CH_2-6), 3.41 (s, 1 H, 2-H), 2.88–2.57 (m, 3 H, 5-H, NCH_2 butyl), 1.87 (d, J = 14.7 Hz, 1 H, C*H*H-2 tMB), 1.70 (d, J = 14.2 Hz, 1 H, CH*H*-2 tMB), 1.65–1.21 (m, 10 H, 2×CH_2 butyl, 2×CH_3 tMB), 1.06 (s, 9 H, 2×CH_3, CH_3-4 tMB), 0.97 (t, J = 7.3 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD, collapsed iminosugar signals): δ = 79.7 (C-4), 78.7 (C-3), 74.2 (C-2), 73.4 (C-5), 63.7 (C-6), 57.5 (NCH_2 butyl), 56.2 (C_q-3 tMB), 53.9 (CH_2-2 tMB), 32.6 (C_q-3 tMB), 32.3 (CH_2 butyl), 32.2 (2×CH_3, CH_3-4 tMB), 29.7, 29.1 (2×CH_3 tMB), 21.9 (CH_2 butyl), 14.4 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3290, 2957, 2420, 1651, 1458, 1366, 1227, 1072, 756 cm^{-1}. $[\alpha]_D^{20}$ = –30.7 (c = 0.3, MeOH). HRMS: calcd. for $[C_{18}H_{36}O_4N_2 + H]^+$ 345.2748 $[M + H]^+$; found 345.2748.

1,1,3,3-Tetramethylbutyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]-imino-2,5-dideoxy-L-*ido*-hexonamide (74): Compound **74** (28 mg, 54 μmol, 86%) was synthesized in two steps from **60** (63 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.25 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.83 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.72–3.44 (m, 6 H), 3.39 (t, J = 6.2 Hz, 2 H, CH_2-5 pentyl), 3.26–3.02 (m, 1 H), 2.97 (s, 2 H, OCH_2-Ada), 2.94–2.47 (m, 1 H), 2.20–1.31 (m, 23 H, CH_2-2 tMB, 3×CH Ada, 6×CH_2 Ada, 3×CH_2 pentyl), 1.04 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (101 MHz, MeOD, collapsed iminosugar signals): δ = 83.2 (OCH_2-Ada), 78.4 (CH), 72.3 (CH_2-5 pentyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 32.6 (C_q-3 tMB), 32.2 (2×CH_3, CH_3-4 tMB), 30.7 (CH_2 pentyl), 29.9 (CH Ada), 29.6 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3291, 2902, 2849, 2409, 1668, 1452, 1366, 1225, 1156, 1110, 755 cm^{-1}. $[\alpha]_D^{20}$ = –21.4 (c = 0.6, MeOH). HRMS: calcd. for $[C_{30}H_{54}O_5N_2 + H]^+$ 523.4105 $[M + H]^+$; found 523.4101.

Pentyl 2,5-Dideoxy-2,5-imino-L-*gulo*-hexonamide (75): Compound **75** (19 mg, 77 μmol, 51%) was synthesized from **61** (150 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.24 (MeOH/CH_2Cl_2, 1:5 + 2% NH_4OH). ^{1}H NMR (400 MHz, MeOD): δ = 4.24–4.11 (m, 1 H, 3-H), 4.06–3.94 (m, 1 H, 4-H), 3.91–3.81 (m, 1 H, 6a-H), 3.81–3.71 (m, 2 H, 2-H, 6b-H), 3.43–3.36 (m, 3 H, 5-H, NCH_2-1 pentyl), 1.68–1.55 (m, 2 H, CH_2-2 pentyl), 1.51–1.33 (m, 4 H, 2×CH_2 pentyl), 1.07–0.91 (m, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 172.3 [C(O)-1], 81.7 (C-3), 78.8 (C-4), 66.2, 66.1 (C-2, C-5), 61.9 (C-6), 40.7 (NCH_2-1 pentyl), 30.3, 30.2, 23.5 (3×CH_2 pentyl), 14.5 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3290, 2930, 1652, 1544, 1377, 1055 cm^{-1}. $[\alpha]_D^{20}$ = 1.1 (c = 0.4, MeOH). HRMS: calcd. for $[C_{11}H_{22}O_4N_2 + H]^+$ 247.1652 $[M + H]^+$; found 247.1653.

Pentyl 2,5-Butylimino-2,5-dideoxy-L-*gulo*-hexonamide (76): Compound **76** (13 mg, 43 μmol, 31%) was synthesized in two steps from **61** (140 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.69 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.77 (EtOAc/PE, 1:1). ^{1}H NMR (400 MHz, MeOD): δ = 4.01 (s, 1 H, 4-H), 3.94 (s, 1 H, 3-H), 3.85 (dd, J = 4.5, 11.8 Hz, 1 H, 6a-H), 3.75 (dd, J = 3.1, 11.8 Hz, 1 H, 6b-H), 3.61–3.51 (m, 1 H, 2-H), 3.41–3.33 (m, 1 H, 5-H), 3.23 (t, J = 7.0 Hz, 2 H, NCH_2-1 pentyl), 3.04–2.90 (m, 1 H, NC*H*H-1 butyl), 2.83–2.67 (m, 1 H, NCH*H*-1 butyl), 1.59–1.48 (m, 4 H, 2×CH_2-2 pentyl/butyl), 1.43–1.28 (m, 6 H, 3×CH_2 pentyl/butyl), 0.98–0.90 (m, 6 H, 2×CH_3 butyl/pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 81.9 (C-3), 80.7 (C-4), 75.5 (C-2), 71.3 (C-5), 60.3 (C-6), 50.4 (NCH_2 butyl),

40.4 (NCH_2-1 pentyl), 31.4, 30.3, 30.3, 23.5, 21.7 (5×CH_2 pentyl/butyl), 14.5, 14.4 (2×CH_3 pentyl/butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3294, 2959, 2930, 2871, 1652, 1461, 1378, 1066 cm^{-1}. $[\alpha]_D^{20}$ = 27.7 (*c* = 0.3, MeOH). HRMS: calcd. for $[C_{15}H_{30}O_4N_2 + H]^+$ 303.2278 $[M + H]^+$; found 303.2279.

Pentyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,5-dideoxy-L-*gulo*-hexonamide (77): Compound **77** (15 mg, 31 μmol, 22%) was synthesized in two steps from **61** (140 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.37 (MeOH/CH_2Cl_2, 1:9 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.80 (EtOAc/PE, 1:1). ^1H NMR (400 MHz, MeOD): δ = 3.96 (dd, *J* = 1.7 Hz, 1 H, 4-H), 3.89 (dd, *J* = 1.8 Hz, 1 H, 3-H), 3.80 (dd, *J* = 5.0, 11.4 Hz, 1 H, 6a-H), 3.69 (dd, *J* = 3.2, 11.4 Hz, 1 H, 6b-H), 3.40 (s, 1 H, 2-H), 3.38 (t, *J* = 4.9 Hz, 2 H, CH_2-5 pentyl), 3.28–3.12 [m, 3 H, 5-H, C(O)NCH_2-1 pentyl], 2.97 (s, 2 H, OCH_2-Ada), 2.90–2.78 (m, 1 H, NC*H*H-1 pentyl), 2.66–2.52 (m, 1 H, NCH*H*-1 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, *J* = 12.1, 32.1 Hz, 6 H, 3×CH_2 Ada), 1.64–1.26 (m, 18 H, 3×CH Ada, 6×CH_2 pentyl), 0.93 (t, *J* = 6.9 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 175.9 [C(O)-1], 83.2 (OCH_2-Ada), 82.4 (C-3), 81.6 (C-4), 76.4 (C-2), 72.7 (CH_2-5 pentyl), 70.8 (C-5), 61.0 (C-6), 50.0 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 40.2 [C(O)NCH_2-1 pentyl], 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 30.8, 30.4, 30.4, 29.7, 25.4, 23.6 (6×CH_2 pentyl), 14.5 (CH_3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3297, 2902, 2849, 1651, 1456, 1361, 1157, 1111 cm^{-1}. $[\alpha]_D^{20}$ = 11.4 (*c* = 0.3, MeOH). HRMS: calcd. for $[C_{27}H_{48}O_5N_2 + H]^+$ 481.3636 $[M + H]^+$; found 481.3632.

Pentyl 2,5-Dideoxy-2,5-imino-L-*ido*-hexonamide (78): Compound **78** (52 mg, 211 μmol, 78%) was synthesized from **62** (270 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.15 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 4.29 (dd, *J* = 2.1, 4.9 Hz, 1 H, 3-H), 4.25 (d, *J* = 4.9 Hz, 1 H, 2-H), 3.99 (dd, *J* = 2.4 Hz, 1 H, 4-H), 3.79 (d, *J* = 6.0 Hz, 2 H, CH_2-6), 3.41 (dt, *J* = 2.7, 6.0 Hz, 1 H, 5-H), 3.25 (t, *J* = 7.1 Hz, 2 H, NCH_2-1 pentyl), 1.61–1.49 (m, 2 H, CH_2-2 pentyl), 1.40–1.31 (m, 4 H, 2×CH_2 pentyl), 0.92 (t, *J* = 6.9 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 169.5 [C(O)-1], 79.0 (C-4), 78.4 (C-3), 68.5 (C-5), 65.3 (C-2), 62.0 (C-6), 40.7 (NCH_2-1 pentyl), 30.3, 30.2, 23.5 (3×CH_2 pentyl), 14.5 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3287, 2957, 2931, 2871, 1666, 1638, 1652, 1560, 1470, 1377, 1310, 1066, 1034 cm^{-1}. $[\alpha]_D^{20}$ = –54.5 (*c* = 1.0, MeOH). HRMS: calcd. for $[C_{11}H_{22}O_4N_2 + H]^+$ 247.1652 $[M + H]^+$; found 247.1654.

Pentyl 2,5-Butylimino-2,5-dideoxy-L-*ido*-hexonamide (79): Compound **79** (24 mg, 79 μmol, 49%) was synthesized in two steps from **62** (160 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.58 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.75 (EtOAc/PE, 1:1). ^1H NMR (400 MHz, MeOD): δ = 4.08 (dd, *J* = 3.2, 6.1 Hz, 1 H, 3-H), 3.96 (dd, *J* = 3.2 Hz, 1 H, 4-H), 3.67 (d, *J* = 4.0 Hz, 2 H, CH_2-6), 3.51 (d, *J* = 6.2 Hz, 1 H, 2-H), 3.35–3.25 (m, 1 H, NC*H*H-1 pentyl), 3.17 (dt, *J* = 6.9, 13.5 Hz, 1 H, NCH*H*-1 pentyl), 2.80 (dd, *J* = 3.7, 7.2 Hz, 1 H, 5-H), 2.70 (ddd, *J* = 5.9, 9.3, 12.5 Hz, 1 H, NC*H*H-1 butyl), 2.59 (ddd, *J* = 6.4, 9.3, 12.5 Hz, 1 H, NCH*H*-1 butyl), 1.59–1.26 (m, 10 H, 5×CH_2 pentyl/butyl), 0.96–0.89 (m, 6 H, 2×CH_3 butyl/pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 174.6 [C(O)-1], 79.3 (C-4), 78.4 (C-3), 73.3, 73.2 (C-2, C-5), 63.0 (C-6), 57.1 (NCH_2-1 butyl), 40.1 (NCH_2-1 pentyl), 31.9, 30.4, 23.6, 21.8 (5×CH_2 pentyl/butyl), 14.5 (2×CH_3 butyl/pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3274, 2959, 2931, 2871, 1637, 1464, 1376, 1118, 1069, 754 cm^{-1}. $[\alpha]_D^{20}$ = –39.3 (*c* = 0.3, MeOH). HRMS: calcd. for $[C_{15}H_{30}O_4N_2 + H]^+$ 303.2278 $[M + H]^+$; found 303.2279.

Pentyl 2,5-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,5-dideoxy-L-*ido*-hexon-amide (80): Compound **80** (40 mg, 83 μmol, 52%) was synthesized in two steps from **62** (160 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.69 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.80 (EtOAc/PE, 1:1). ^1H NMR (400 MHz, MeOD): δ = 4.08 (dd, *J* = 3.2, 6.1 Hz, 1 H, 3-H), 3.97 (dd, *J* = 3.1 Hz, 1 H, 4-H), 3.69–3.66 (m, 2 H, CH_2-6), 3.51 (d, *J* = 6.1 Hz, 1 H, 2-H), 3.38 (t, *J* = 6.3 Hz, 2 H, CH_2-5 pentyl), 3.35–3.26 [m, 1 H, C(O)NC*H*H-1 pentyl], 3.17 [dt, *J* = 6.9, 13.5 Hz, 1 H, C(O)NCH*H*-1 pentyl], 2.96 (s, 2 H, OCH_2-Ada), 2.80 (dd, *J* = 3.6, 7.1 Hz, 1 H, 5-H), 2.70 (ddd, *J* = 5.8, 9.1, 12.5 Hz, 1 H, NC*H*1 pentyl-H), 2.59 (ddd, *J* = 6.5, 9.1, 12.5 Hz, 1 H, NCH*H*-1 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, *J* = 11.9, 32.3 Hz, 6 H, 3×CH_2 Ada), 1.60–1.29 (m, 18 H, 3×CH_2 Ada, 6×CH_2 pentyl), 0.92 (t, *J* = 6.9 Hz, 3 H, CH_3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 174.6 [C(O)-1], 83.2 (OCH_2-Ada), 79.4 (C-4), 78.4 (C-3), 73.4 (C-2), 73.2 (C-5), 72.6 (CH_2-5 pentyl), 63.1 (C-6), 57.4 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 40.1 [C(O)NCH_2-1 pentyl], 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 30.7, 30.4, 30.4, 29.5, 25.3, 23.6 (6×CH_2 pentyl), 14.6 (CH_3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3343, 2903, 2850, 1637, 1457, 1374, 1157, 1072 cm^{-1}. $[\alpha]_D^{20}$ = –32.1 (*c* = 0.7, MeOH). HRMS: calcd. for $[C_{27}H_{48}O_5N_2 + H]^+$ 481.3636 $[M + H]^+$; found 481.3632.

2,3,4,6-Tetra-*O*-benzyl-1-*O*-*tert*-butyldiphenylsilyl-D-glucitol (82): *tert*-Butyl-diphenylsilyl chloride (21 mL, 80.7 mmol) was added over a 2 min period to an anhydrous solution of 2,3,4,6-tetra-*O*-benzyl-D-glucitol (**81**; 39.0 g, 71.9 mmol)[6c] and imidazole (10.8 g, 158.6 mmol) in DMF (75 mL). The reaction mixture was stirred for 20 h and subsequently concentrated. The residue was purified by silica gel column chromatography (EtOAc/PE, 20→25%) to provide **82** (55.7 g, 71.4 mmol, 99%) as a colorless oil. R_f = 0.85 (EtOAc/toluene, 1:1). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.66–7.61 (m, 4 H, H_{Ar} TBDPS), 7.42–7.07 (m, 26 H, H_{Ar} TBDPS/Bn), 4.64 (s, 2 H, CH_2 Bn), 4.63 (d, *J* = 11.6 Hz, 1 H, C*H*H Bn), 4.54–4.45 (m, 5 H, CH*H* Bn, 2×CH_2 Bn), 3.97 (dd, *J* = 4.5 Hz, 1 H, 3-H), 3.96–3.92 (m, 1 H, 5-H), 3.88 (dd, *J* = 4.9, 10.6 Hz, 1 H, 1a-H), 3.83 (dd, *J* = 4.9, 9.9 Hz, 1 H, 2-H), 3.78 (dd, *J* = 3.9, 6.5 Hz, 1 H, 4-H), 3.76 (dd, *J* = 4.9, 10.1 Hz, 1 H, 1b-H), 3.60 (dd, *J* = 2.5, 8.9 Hz, 1 H, 6b-H), 3.58 (dd, *J* = 4.2, 8.9 Hz, 1 H, 6b-H), 2.91 (d, *J* = 4.8 Hz, 1 H, OH-5), 1.04 (s, 9 H, *t*Bu-Si) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.6, 138.4, 138.3, 138.3 (4×C_q Bn), 135.8 (CH_{Ar} TBDPS), 133.5 (C_q Si-Ph), 129.9, 129.9, 128.6, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7 (CH_{Ar} Bn/TBDPS), 79.8 (C-2), 78.1 (C-3), 77.6 (C-4), 74.4, 73.6, 73.5, 73.2 (4×CH_2 Bn), 71.4 (C-6), 71.2 (C-5), 63.3 (C-1), 27.1 (CH_3 *t*Bu), 19.4 (C_q *t*Bu) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3030, 2929, 2862, 1490, 1454, 1358, 1208, 1080, 1027, 823, 735, 698 cm^{-1}. $[\alpha]_D^{20}$ = 16.2 (*c* = 2.1, $CHCl_3$). HRMS: calcd. for $[C_{50}H_{56}O_6Si + Na]^+$ 803.3744 $[M + Na]^+$; found 803.3739.

5-Azido-2,3,4,6-tetra-*O*-benzyl-*tert*-1-*O*-butyldiphenylsilyl-L-iditol (83): Diisopropyl azodicarboxylate (2.52 mL, 12.8 mmol) and diphenylphosphoryl azide (2.76 mL, 12.8 mmol) were successively added over 2 min to a cooled (0 °C), anhydrous solution of **82** (5.00 g, 6.4 mmol) and triphenylphosphane (3.36 g, 12.8 mmol) in THF (48 mL). The reaction mixture was stirred for 20 h and warmed to room temp. The mixture was concentrated and the re-

sulting residue was purified by silica gel column chromatography (EtOAc/PE, 0→10%) to afford **83** (3.70 g, 4.2 mmol, 66%) as a colorless oil. R_f = 0.60 (EtOAc/PE, 1:6). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (dd, J = 6.7, 19.6 Hz, 4 H, H_{Ar} TBDPS), 7.43–7.13 (m, 26 H, H_{Ar} TBDPS/Bn), 4.78–4.71 (m, 2 H, C*H*H Bn, C*H*H Bn), 4.64 (d, J = 11.3 Hz, 1 H, CH*H* Bn), 4.59 (d, J = 12.0 Hz, 1 H, C*H*H Bn), 4.52 (d, J = 11.5 Hz, 1 H, CH*H* Bn), 4.39–4.32 (m, 2 H, CH_2 Bn), 4.29 (d, J = 12.0 Hz, 1 H, CH*H* Bn), 4.04 (dd, J = 2.7, 7.6 Hz, 1 H, 3-H), 3.93 (dd, J = 6.3, 10.5 Hz, 1 H, 1a-H), 3.87 (dd, J = 5.6, 10.5 Hz, 1 H, 1b-H), 3.82 (dd, J = 3.0, 7.7 Hz, 1 H, 4-H), 3.61–3.56 (m, 1 H, 2-H), 3.53 (dd, J = 8.1, 9.2 Hz, 1 H, 6a-H), 3.34 (dd, J = 4.8, 9.5 Hz, 1 H, 6b-H), 3.30–3.23 (m, 1 H, 5-H), 1.08 (s, 9 H, *t*Bu-Si) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 138.8, 138.6, 138.4 (4×C_q Bn), 136.3, 136.2 (CH_{Ar} TBDPS), 133.9 (C_q Si-Ph), 130.5, 130.4, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2 (CH_{Ar} Bn/TBDPS), 79.6, 79.0, 78.6 (C-2, C-2, C-4), 75.8, 75.5, 73.8, 73.0 (4×CH_2 Bn), 70.4 (C-6), 63.0 (C-1), 61.9 (C-5), 27.5 (CH_3 *t*Bu), 19.8 (C_q *t*Bu) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3030, 2928, 2857, 2955, 2097, 1494, 1454, 1428, 1358, 1208, 1080, 1027, 734, 699 cm^{-1}. $[\alpha]_D^{20}$ = 21.3 (c = 8.2, $CHCl_3$). HRMS: calcd. for $[C_{50}H_{55}N_3O_5Si + Na]^+$ 828.3809 $[M + Na]^+$; found 828.3807.

5-Azido-2,3,4,6-tetra-*O*-benzyl-L-iditol (84): Tetrabutylammonium fluoride (1 M in THF, 12 mL, 12 mmol) was added to an anhydrous solution of **83** (7.25 g, 9.0 mmol) in THF (150 mL) and the resulting reaction mixture was stirred for 20 h. The mixture was concentrated, redissolved in Et_2O (100 mL) and washed with satd. aq. NaCl (100 mL). The organic phase was dried (Na_2SO_4), concentrated, and the resulting residue was purified by silica gel column chromatography (EtOAc/PE, 9→25%) to produce **84** (3.62 g, 6.38 mmol, 71%) as a colorless oil. R_f = 0.20 (EtOAc/PE, 1:4). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38–7.17 (m, 20 H, H_{Ar} Bn), 4.75 (d, J = 11.5 Hz, 1 H, C*H*H Bn), 4.67 (d, J = 11.1 Hz, 1 H, C*H*H Bn), 4.65–4.60 (m, 2 H, C*H*H Bn, CH*H* Bn), 4.55–4.52 (m, 2 H, C*H*H Bn, C*H*H Bn), 4.38 (d, J = 11.8 Hz, 1 H, C*H*H Bn), 4.35 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 3.91 (dd, J = 4.0, 7.3 Hz, 1 H, 3-H), 3.87 (dd, J = 2.8, 7.4 Hz, 1 H, 4-H), 3.78 (dd, J = 5.0, 11.5 Hz, 1 H, 1a-H), 3.71 (dd, J = 5.0, 11.6 Hz, 1 H, 1b-H), 3.60 (dd, J = 4.9, 9.2 Hz, 1 H, 2-H), 3.59–3.52 (m, 2 H, 5-H, 6a-H), 3.46 (dd, J = 4.5, 8.9 Hz, 1 H, 6b-H), 3.24–2.79 (m, 1 H, OH-1) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 137.8, 137.7, 137.5 (4×C_q Bn), 128.2, 128.1, 128.1, 128.1, 127.9, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3 (CH_{Ar} Bn), 78.9 (C-3), 78.1 (C-2), 78.0 (C-4), 74.6, 74.5, 72.9, 72.1 (4×CH_2 Bn), 69.3 (C-6), 61.0 (C-1), 60.8 (C-5) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3469, 3032, 2866, 2097, 1496, 1454, 1353, 1263, 1210, 1061, 1027, 734, 698 cm^{-1}. $[\alpha]_D^{20}$ = 17.8 (c = 13.2, $CHCl_3$). HRMS: calcd. for $[C_{34}H_{37}N_3O_5 + Na]^+$ 590.2631 $[M + Na]^+$; found 590.2620.

5-Azido-2,3,4,6-tetra-*O*-benzyl-L-idose (85): Azido alcohol **84** (2.22 g, 3.9 mmol) was subjected to a Dess–Martin mediated oxidation (General Procedure A) to produce **85** (1.97 g, 3.5 mmol, 89%) as a colorless oil. R_f = 0.55 (EtOAc/PE, 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.66 (s, 1 H, 1-H), 7.36–7.21 (m, 18 H, H_{Ar} Bn), 7.21–7.13 (m, 2 H, H_{Ar} Bn), 4.81 (d, J = 11.9 Hz, 1 H, C*H*H Bn), 4.63 (d, J = 11.1 Hz, 1 H, C*H*H Bn), 4.56–4.50 (m, 3 H, CH*H* Bn, CH_2 Bn), 4.47 (d, J = 11.9 Hz, 1 H, CH*H* Bn), 4.41 (d, J = 12.2 Hz, 1 H, C*H*H Bn), 4.38 (d, J = 12.2 Hz, 1 H, CH*H* Bn), 3.96 (dd, J = 4.8, 4.8 Hz, 1 H, 3-H), 3.92 (d, J = 4.6 Hz, 1 H, 2-H), 3.86 (dd, J = 5.0, 5.0 Hz, 1 H, 4-H), 3.58–3.51 (m, 1 H, 5-H), 3.51–3.43 (m, 2 H, CH_2-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.8 (CH-1), 137.8, 137.6, 137.2, 137.0 (4×C_q Bn), 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8 (CH_{Ar} Bn), 80.9 (C-2), 79.3 (C-3), 77.4 (C-4), 74.5, 74.1, 73.3, 73.2 (4×CH_2 Bn), 69.5 (C-6), 61.6 (C-1) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3032, 2864, 2097, 1729, 1496, 1454, 1352, 1264, 1210, 1092, 1027, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = 23.7 (c = 10.7, $CHCl_3$). HRMS: calcd. for $[C_{34}H_{35}N_3O_5 + Na]^+$ 588.2474 $[M + Na]^+$; found 588.2468.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-L-*glycero*-D-*gulo*-heptonamide (86): Subjecting azido aldehyde **85** (1.16 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced a separable 1.25:1 mixture of **87** (314 mg, 0.36 mmol) and **86** (248 mg, 0.28 mmol) in a combined yield of 55%. R_f = 0.27 (EtOAc/toluene, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$, 2.5:1 mixture of rotamers; major rotamer/collapsed iminosugar signals): δ = 7.37–7.16 (m, 20 H, H_{Ar} Bn), 6.18 [s, 1 H, C(O)NH], 5.83–5.74 (m, 1 H, =CH pentenyl), 5.03–4.91 (m, 2 H, =CH_2 pentenyl), 4.81–3.60 (m, 15 H, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 3.30 (t, J = 6.6 Hz, 2 H, CH_2-5 pentyl), 3.27–3.09 (m, 2 H, NCH_2-1 pentyl), 2.92 (s, 2 H, OCH_2-Ada), 2.71–2.40 (m, 2 H, CH_2 pentenyl), 2.40–2.23 (m, 2 H, CH_2 pentenyl), 1.95 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 11.8, 30.7 Hz, 6 H, 3×CH_2 Ada), 1.56–1.13 (m, 12 H, 3×CH_2 Ada, 3×CH_2 pentyl) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, major rotamer/collapsed iminosugar signals): δ = 174.1 [NC(O) pentenyl], 169.0 [NHC(O)-1], 138.3, 138.0, 138.0, 137.8, 137.6 (C_q Bn, =CH pentenyl), 128.6–127.7 (CH_{Ar} Bn), 115.0 (=CH_2 pentenyl), 82.0 (OCH_2-Ada), 78.1, 73.4, 71.9, 71.5 (CH_2-5 pentyl), 59.0, 54.8 (C-2, C-6), 39.9 (NCH_2-1 pentyl), 39.8 (CH_2 Ada), 37.3 (CH_2 Ada), 34.2 (C_q Ada), 29.4, 29.3, 29.0, 28.4 (CH Ada), 23.6 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3328, 2902, 2849, 1635, 1543, 1453, 1361, 1092, 910, 732, 696 cm^{-1}. $[\alpha]_D^{20}$ = –11.7 (c = 4.7, $CHCl_3$). HRMS: calcd. for $[C_{56}H_{70}N_2O_7 + H]^+$ 883.5256 $[M + H]^+$; found 883.5265.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-L-*glycero*-D-*ido*-heptonamide (87): R_f = 0.46 (EtOAc/toluene, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$, 3.5:1 mixture of rotamers; major rotamer): δ = 7.41–7.18 (m, 20 H, H_{Ar} Bn), 6.69 [t, J = 5.7 Hz, 1 H, C(O)NH], 5.80–5.68 (m, 1 H, =CH pentenyl), 5.13 (d, J = 6.7 Hz, 1 H, 2-H), 5.00–4.91 (m, 2 H, =CH_2 pentenyl), 4.89–4.59 (m, 7 H, 3×CH_2 Bn, 4-H), 4.45 (d, J = 11.9 Hz, 1 H, C*H*H Bn), 4.38 (d, J = 11.9 Hz, 1 H, CH*H* Bn), 4.26–4.19 (m, 1 H, 6-H), 4.07 (dd, J = 10.1 Hz, 1 H, 7a-H), 3.81 (dd, J = 4.3, 9.9 Hz, 1 H, 7b-H), 3.54 (dd, J = 6.5, 9.4 Hz, 1 H, 5-H), 3.48 (dd, J = 6.7, 9.3 Hz, 1 H, 3-H), 3.28 (t, J = 6.6 Hz, 2 H, CH_2-5 pentyl), 3.26–3.13 (m, 1 H, NC*H*H-1 pentyl), 2.97–2.84 (m, 3 H, OCH_2-Ada, NCH*H*-1 pentyl), 2.66–2.17 (m, 4 H, 2×CH_2 pentenyl), 1.94 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 11.7, 32.0 Hz, 6 H, 3×CH_2 Ada), 1.51 (d, J = 2.4 Hz, 6 H, 3×CH_2 Ada), 1.48–1.15 (m, 6 H, 3×CH_2 pentyl) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, major rotamer): δ = 175.1 [NC(O) pentenyl], 169.1 [NHC(O)-1], 139.0, 138.5, 138.3, 138.1 (4×C_q Bn), 137.4 (=CH pentenyl), 128.8, 128.7, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.1 (CH_{Ar} Bn), 115.4 (=CH_2 pentenyl), 82.1 (OCH_2-Ada), 79.3 (C-5), 78.8 (C-4), 78.5 (C-3), 75.7, 74.0, 74.0, 73.1 (4×CH_2 Bn), 71.5 (CH_2-5 pentyl), 67.0 (C-7), 55.8 (C-6), 53.4 (C-2), 39.9 (CH_2 Ada), 39.5 (NCH_2-1 pentyl), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 33.0 (CH_2 pentenyl), 29.4, 29.4, 29.3 (CH_2 pentenyl, 2×CH_2 pentyl), 28.5 (CH Ada), 23.7 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3361, 2902, 2849, 1727, 1681, 1638, 1530, 1497, 1453, 1364, 1092, 1027, 911, 733, 697 cm^{-1}. $[\alpha]_D^{20}$ = –45.4 (c = 1.7, $CHCl_3$). HRMS: calcd. for $[C_{56}H_{70}N_2O_7 + H]^+$ 883.5256 $[M + H]^+$; found 883.5265.

1,1,3,3-Tetramethylbutyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-en-imido)-L-*glycero*-D-*gulo*-heptonamide (88): Subjecting azido aldehyde **85** (1.16 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced a separable 0.94:1 mixture of **89** (260 mg, 0.34 mmol) and **88** (278 mg, 0.37 mmol) in a combined

yield of 61%. R_f = 0.59 (EtOAc/toluene, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$, complex mixture of rotamers; major signals): δ = 7.38–7.17 (m, 20 H, H_{Ar} Bn), 5.89–5.75 (m, 1 H, =CH pentenyl), 5.67 [s, 1 H, C(O)NH], 5.12–3.65 (m, 17 H, =CH_2 pentenyl, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 2.76–2.30 (m, 4 H, 2×CH_2 pentenyl), 1.66–1.10 (m, 8 H, CH_2-2 tMB, 2×CH_3 tMB), 0.94–0.82 (m, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ (major signals) = 174.3 [NC(O) pentenyl], 168.1 [NHC(O)-1], 138.2, 137.7 (C_q Bn), 136.7 (=CH pentenyl), 128.7–127.1 (CH_{Ar} Bn), 115.7 (=CH_2 pentenyl), 71.8, 65.4, 53.0, 33.4, 31.7 (CH_3-4, 2×CH_3 tMB), 29.3 (CH_2 pentenyl), 28.6, 28.3 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3347, 2953, 2869, 1725, 1682, 1636, 1537, 1454, 1365, 1276, 1209, 1073, 1027, 911, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = –16.8 (c = 3.2, $CHCl_3$). HRMS: calcd. for $[C_{48}H_{60}N_2O_6 + H]^+$ 761.4524 $[M + H]^+$; found 461.4531.

1,1,3,3-Tetramethylbutyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-en-imido)-L-*glycero*-D-*ido*-heptonamide (89): R_f = 0.67 (EtOAc/toluene, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$, 3.5:1 mixture of rotamers; major rotamer): δ = 7.35–7.22 (m, 20 H, H_{Ar} Bn), 6.66 [s, 1 H, C(O)NH], 5.86–5.70 (m, 1 H, =CH pentenyl), 5.19 (d, J = 6.8 Hz, 1 H, 2-H), 5.01–4.35 (m, 11 H, =CH_2 pentenyl, 4×CH_2 Bn, 4-H), 4.23–4.16 (m, 1 H, 6-H), 4.05 (dd, J = 9.8 Hz, 1 H, 7a-H), 3.85 (dd, J = 3.7, 9.9 Hz, 1 H, 7b-H), 3.49 (dd, J = 6.5, 9.7 Hz, 1 H, 5-H), 3.44 (dd, J = 6.7, 9.6 Hz, 1 H, 3-H), 2.46–2.18 (m, 4 H, 2×CH_2 pentenyl), 1.73 (d, J = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.49 (d, J = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.37 (s, 3 H, CH_3 tMB), 1.27 (s, 3 H, CH_3 tMB), 0.93 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.7 [NC(O) pentenyl], 167.9 [NHC(O)-1], 139.0, 138.6, 138.3, 138.1 (4×C_q Bn), 137.4 (=CH pentenyl), 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 127.6, 127.4 (CH_{Ar} Bn), 115.3 (=CH_2 pentenyl), 79.4 (C-5), 78.8, 78.7 (C-3, C-4), 75.8, 74.1, 73.9, 73.0 (4×CH_2 Bn), 67.1 (C-7), 56.6 (C-6), 55.2 (NHC$_q$-1 tMB), 54.0 (C-2), 52.7 (CH_2-2 tMB), 33.3 (C_q-3 tMB), 32.8 (CH_2 pentenyl), 31.6 (CH_3-4, 2×CH_3 tMB), 29.3 (CH_2 pentenyl), 28.8, 28.5 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2952, 1726, 1683, 1638, 1532, 1454, 1365, 1227, 1091, 1027, 911, 734, 696 cm^{-1}. $[\alpha]_D^{20}$ = –51.0 (c = 3.0, $CHCl_3$). HRMS: calcd. for $[C_{48}H_{60}N_2O_6 + H]^+$ 761.4524 $[M + H]^+$; found 461.4531.

Pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-L-*glycero*-D-*gulo*-heptonamide (90): Subjecting azido aldehyde **85** (1.16 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced a separable 1.6:1 mixture of **91** (297 mg, 0.41 mmol) and **90** (182 mg, 0.25 mmol) in a combined yield of 57%. R_f = 0.27 (EtOAc/toluene, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$, complex mixture of rotamers; major signals): δ = 7.38–7.19 (m, 20 H, H_{Ar} Bn), 5.82–5.74 (m, 1 H, =CH pentenyl), 5.02–4.92 (m, 2 H, =CH_2 pentenyl), 4.81–3.61 (m, 15 H, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 3.23–3.12 (m, 2 H, NCH$_2$-1 pentyl), 2.68–2.22 (m, 4 H, 2×CH_2 pentenyl), 1.73–0.97 (m, 6 H, 3×CH_2 pentyl), 0.85 (t, J = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) major signals δ = 174.2 [NC(O) pentenyl], 169.1 [NHC(O)-1], 138.4, 138.2, 138.2, 137.8 (4×C_q Bn), 138.0 (=CH pentenyl), 128.8–127.7 (CH_{Ar} Bn), 115.0 (=CH_2 pentenyl), 80.8, 78.7, 78.2, 73.6, 72.0, 70.1, 69.1, 64.5, 59.1, 54.9, 40.1 (NCH$_2$-1 pentyl), 33.3 (CH_2 pentenyl), 29.3, 29.2, 22.5 (CH_2 pentyl/pentenyl), 14.2 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3325, 2929, 2862, 1726, 1636, 1543, 1454, 1417, 1363, 1279, 1072, 1027, 911, 724, 967 cm^{-1}. $[\alpha]_D^{20}$ = –12.4 (c = 0.9, $CHCl_3$). HRMS: calcd. for $[C_{45}H_{54}N_2O_6 + H]^+$ 719.4055 $[M + H]^+$; found 719.4058.

Pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-L-*glycero*-D-*ido*-heptonamide (91): R_f = 0.45 (EtOAc/toluene, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$, major rotamer; 3.5:1 mixture of rotamers): δ = 7.39–7.14 (m, 20 H, H_{Ar} Bn), 6.67 [t, J = 5.7 Hz, 1 H, C(O)NH], 5.79–5.68 (m, 1 H, =CH pentenyl), 5.13 (d, J = 6.7 Hz, 1 H, 2-H), 5.03–4.50 (m, 9 H, =CH_2 pentenyl, 3×CH_2 Bn, 4-H), 4.45 (d, J = 11.8 Hz, 1 H, C*H*H Bn), 4.38 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.27–4.19 (m, 1 H, 6-H), 4.07 (dd, J = 10.1 Hz, 1 H, 7a-H), 3.82 (dd, J = 4.3, 9.9 Hz, 1 H, 7b-H), 3.54 (dd, J = 6.5, 9.5 Hz, 1 H, 5-H), 3.48 (dd, J = 6.7, 9.4 Hz, 1 H, 3-H), 3.26–3.16 (m, 1 H, NC*H*H-1), 2.97–2.85 (m, 1 H, NCH*H*-1), 2.67–2.21 (m, 4 H, 2×CH_2 pentenyl), 1.40–1.27 (m, 2 H, CH_2 pentyl), 1.27–1.12 (m, 4 H, 2×CH_2 pentyl), 0.82 (t, J = 7.1 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, major rotamer): δ = 175.0 [NC(O) pentenyl], 169.1 [NHC(O)-1], 139.0, 138.5, 138.3, 138.1 (4×C_q Bn), 137.4 (=CH pentenyl), 128.7, 128.6, 128.4, 128.3, 128.3, 127.9, 127.9, 127.8, 127.4, 127.1 (CH_{Ar} Bn), 115.3 (=CH_2 pentenyl), 79.3 (C-4), 78.8 (C-5), 78.5 (C-3), 75.7, 74.0, 74.0, 73.0 (4×CH_2 Bn), 67.0 (C-7), 55.8 (C-6), 53.4 (C-2), 39.5 (NCH$_2$-1 pentyl), 33.0 (CH_2 pentenyl), 29.2, 29.2, 29.2, 22.4 (CH_2 pentenyl, 3×CH_2 pentyl), 14.1 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3364, 2930, 2862, 1681, 1531, 1454, 1365, 1208, 1091, 1027, 911, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = –58.1 (c = 2.0, $CHCl_3$). HRMS: calcd. for $[C_{45}H_{54}N_2O_6 + H]^+$ 719.4055 $[M + H]^+$; found 719.4059.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-L-*glycero*-D-*gulo*-heptonamide (92): Compound **92** (108 mg, 0.14 mmol, 50%) was synthesized from **86** (0.27 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.17 (EtOAc/toluene, 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.20 (m, 20 H, H_{Ar} Bn), 6.86 [t, J = 5.7 Hz, 1 H, C(O)NH], 4.72–4.45 (m, 8 H, 4×CH_2 Bn), 4.01 (dd, J = 5.7 Hz, 1 H, 3-H), 3.77 (dd, J = 6.1 Hz, 1 H, 4-H), 3.63–3.52 (m, 3 H, CH_2-7, 5-H), 3.50 (d, J = 5.6 Hz, 1 H, 2-H), 3.39 (dt, J = 4.2, 8.3 Hz, 1 H, 6-H), 3.30 (t, J = 6.5 Hz, 2 H, CH_2-5 pentyl), 3.29–3.20 (m, 1 H, NC*H*H-1 pentyl), 3.19–3.08 (m, 1 H, NCH*H*-1 pentyl), 2.91 (s, 2 H, OCH$_2$-Ada), 2.47 (s, 1 H, NH), 1.94 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 12.1, 24.3 Hz, 6 H, 3×CH_2 Ada), 1.55–1.36 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.36–1.24 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6 [C(O)-1], 138.5, 138.4, 138.3, 138.3 (4×C_q Bn), 128.6, 128.5, 128.4, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6 (CH_{Ar} Bn), 82.0 (OCH$_2$-Ada), 77.3 (C-4), 76.9 (C-5), 76.7 (C-3), 73.7, 73.6, 73.5, 72.3 (4×CH_2 Bn), 71.5 (CH_2-5 pentyl), 68.9 (C-7), 58.1 (C-2), 52.2 (C-6), 39.9 (CH_2 Ada), 39.5 (NCH$_2$-1 pentyl), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 29.5, 29.4 (2×CH_2 pentyl), 28.4 (CH Ada), 23.7 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3313, 2901, 2849, 1667, 1524, 1497, 1453, 1363, 1207, 1092, 1027, 908, 730, 696 cm^{-1}. $[\alpha]_D^{20}$ = –8.4 (c = 2.1, $CHCl_3$). HRMS: calcd. for $[C_{51}H_{64}N_2O_6 + H]^+$ 801.4837 $[M + H]^+$; found 801.4840.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-L-*glycero*-D-*ido*-heptonamide (93): Compound **93** (130 mg, 0.16 mmol, 65%) was synthesized from **87** (0.25 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.20 (EtOAc/toluene, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.12 (m, 20 H, H_{Ar} Bn), 7.05 [t, J = 5.9 Hz, 1 H, C(O)NH], 4.62 (d, J = 11.7 Hz, 1 H, C*H*H Bn), 4.55–4.25 (m, 7 H, CH*H* Bn, 3×CH_2 Bn), 4.18–4.13 (m, 1 H, 3-H), 3.67 (dd, J = 2.6 Hz, 1 H, 4-H), 3.60 (d, J = 1.9 Hz, 1 H, 2-H), 3.53 (dd, J = 6.7, 9.2 Hz, 1 H, 7a-H), 3.45 (dd, J = 7.5, 9.2 Hz, 1 H, 7b-H), 3.43–3.40 (m, 1 H, 5-H), 3.33 (t, J = 6.5 Hz, 2 H, CH_2-5 pentyl), 3.30–3.23 (m, 2 H, NCH$_2$-1 pentyl), 3.20 (dt, J = 2.3, 7.2 Hz, 1 H, 6-H), 2.93 (s, 2 H, OCH$_2$-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.90 (s, 1 H, NH), 1.67 (dd, J = 12.2, 24.6 Hz, 6 H, 3×CH_2 Ada), 1.58–1.46 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.40–1.28 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3 [C(O)-1], 138.8, 138.4, 138.4, 138.0 (4×C_q Bn), 128.6, 128.5, 128.4, 128.4,

128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7 (CH_{Ar} Bn), 82.1 (OCH_2-Ada), 73.7, 73.4 (2×CH_2 Bn), 73.3 (C-3), 73.1 (C-5), 72.3, 72.2 (2×CH_2 Bn), 71.7 (C-4), 71.5 (CH_2-5 pentyl), 70.6 (C-7), 60.1 (C-2), 56.0 (C-6), 39.9 (CH_2 Ada), 39.3 (NCH_2-1 pentyl), 37.4 (CH_2 Ada), 34.3 (C_q Ada), 29.7, 29.4 (2×CH_2 pentyl), 28.5 (CH Ada), 23.8 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2902, 2849, 1726, 1670, 1454, 1363, 1288, 1208, 1093, 1028, 909, 735, 698 cm^{-1}. $[\alpha]_D^{20}$ = 0.4 (*c* = 0.9, $CHCl_3$). HRMS: calcd. for $[C_{51}H_{64}N_2O_6 + H]^+$ 801.4837 $[M + H]^+$; found 801.4839.

1,1,3,3-Tetramethylbutyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-L-*glycero*-D-*gulo*-heptonamide (94): Compound **94** (94 mg, 0.14 mmol, 40%) was synthesized from **88** (0.35 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.37 (EtOAc/toluene, 1:3). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.19 (m, 20 H, H_{Ar} Bn), 6.99 [s, 1 H, C(O)NH], 4.71–4.43 (m, 8 H, 4×CH_2 Bn), 4.11 (dd, *J* = 4.9 Hz, 1 H, 3-H), 3.78 (dd, *J* = 5.4 Hz, 1 H, 4-H), 3.61–3.48 (m, 3 H, 5-H, CH_2-7), 3.44 (d, *J* = 4.7 Hz, 1 H, 2-H), 3.41–3.33 (m, 1 H, 6-H), 2.38 (s, 1 H, NH), 1.76 (d, *J* = 14.8 Hz, 1 H, C*H*2-H tMB), 1.61 (d, *J* = 14.8 Hz, 1 H, CH2-H tMB), 1.32 (d, *J* = 11.7 Hz, 6 H, 2×CH_3 tMB), 0.94 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2 [C(O)-1], 138.4, 138.4, 138.3, 138.3 (4×C_q Bn), 128.4, 128.4, 128.3, 128.3, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6 (CH_{Ar} Bn), 75.9, 75.8 (C-4, C-5), 75.2 (C-3), 73.4, 73.1, 73.0, 72.0 (4×CH_2 Bn), 69.4 (C-7), 58.7 (C-2), 54.6 (NHC_q-1 tMB), 52.0 (CH_2-2 tMB), 51.6 (C-6), 31.6 (C_q-3 tMB), 31.5 (CH_3-4, 2×CH_3 tMB), 28.8, 28.7 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3329, 2867, 1671, 1517, 1454, 1366, 1208, 1093, 1027, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = –4.6 (*c* = 1.0, $CHCl_3$). HRMS: calcd. for $[C_{43}H_{54}N_2O_5 + H]^+$ 679.4105 $[M + H]^+$; found 679.4102.

1,1,3,3-Tetramethylbutyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-L-*glycero*-D-*ido*-heptonamide (95): Compound **95** (120 mg, 0.18 mmol, 55%) was synthesized from **89** (0.32 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.59 (EtOAc/toluene, 1:3). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.13 (m, 20 H, H_{Ar} Bn), 7.05 [s, 1 H, C(O)NH], 4.62 (d, *J* = 11.5 Hz, 1 H, C*H*H Bn), 4.56–4.28 (m, 7 H, CH*H* Bn, 3×CH_2 Bn), 4.20–4.17 (m, 1 H, 3-H), 3.68 (dd, *J* = 2.7 Hz, 1 H, 4-H), 3.54–3.48 (m, 2 H, CH_2-7), 3.47 (d, *J* = 2.0 Hz, 1 H, 2-H), 3.44 (s, 1 H, 5-H), 3.19 (dt, *J* = 2.1, 7.3 Hz, 1 H, 6-H), 1.90 (s, 1 H, NH), 1.79 (d, *J* = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.65 (d, *J* = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.40 (d, *J* = 11.9 Hz, 6 H, 2×CH_3 tMB), 0.96 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1 [C(O)-1], 138.9, 138.6, 138.5, 138.1 (4×C_q Bn), 128.6, 128.6, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6 (CH_{Ar} Bn), 73.6, 73.4 (2×CH_2 Bn), 73.1, 73.0 (C-3, C-5), 72.3, 72.2 (2×CH_2 Bn), 71.9 (C-4), 70.5 (C-7), 60.5 (C-2), 56.2 (C-6), 54.7 (NHC_q-1 tMB), 52.3 (CH_2-2 tMB), 31.8 (C_q-3 tMB), 31.7 (CH_3-4, 2×CH_3 tMB), 29.1, 29.0 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3371, 2868, 1678, 1518, 1454, 1365, 1208, 1071, 1028, 911, 724, 698 cm^{-1}. $[\alpha]_D^{20}$ = 4.7 (*c* = 0.4, $CHCl_3$). HRMS: calcd. for $[C_{43}H_{54}N_2O_5 + H]^+$ 679.4105 $[M + H]^+$; found 679.4102.

Pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-L-*glycero*-D-*gulo*-hepton-amide (96): Compound **96** (98 mg, 0.15 mmol, 59%) was synthesized from **90** (0.26 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.17 (EtOAc/toluene, 1:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.18 (m, 20 H, H_{Ar} Bn), 6.84 [t, *J* = 5.6 Hz, 1 H, C(O)NH], 4.73–4.45 (m, 8 H, 4×CH_2 Bn), 4.02 (dd, *J* = 5.7 Hz, 1 H, 3-H), 3.78 (dd, *J* = 6.1 Hz, 1 H, 4-H), 3.60 (dd, *J* = 8.4, 9.6 Hz, 1 H, 7a-H), 3.57–3.52 (m, 2 H, 5-H, 7b-H), 3.50 (d, *J* = 5.7 Hz, 1 H, 2-H), 3.40 (dt, *J* = 4.2, 8.4 Hz, 1 H, 6-H), 3.32–3.21 (m, 1 H, NC*H*H-1 pentyl), 3.20–3.06 (m, 1 H, NCH*H*-1 pentyl), 2.35 (s, 1 H, NH), 1.48–1.32 (m, 2 H, CH_2-2 pentyl), 1.32–1.13 (m, 4 H, 2×CH_2 pentyl), 0.84 (t, *J* = 6.9 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6 [C(O)-1], 138.5, 138.5, 138.4, 138.3 (4×C_q Bn), 128.5, 128.5, 128.4, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6 (CH_{Ar} Bn), 77.3 (C-4), 76.9 (C-5), 76.7 (C-3), 73.6, 73.6, 73.5, 72.3 (4×CH_2 Bn), 68.9 (C-7), 58.1 (C-2), 52.2 (C-3), 39.5 (NCH_2-1 penty), 29.3, 29.2, 22.5 (3×CH_2 pentyl), 14.1 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3306, 2928, 2861, 1725, 1653, 1527, 1497, 1454, 1365, 1208, 1069, 1027, 908, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = –9.9 (*c* = 1.5, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{48}N_2O_5 + H]^+$ 637.3636 $[M + H]^+$; found 637.3633.

Pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-L-*glycero*-D-*ido*-hepton-amide (97): Compound **97** (181 mg, 0.28 mmol, 77%) was synthesized from **91** (0.37 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.20 (EtOAc/toluene, 1:3). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.12 (m, 20 H, H_{Ar} Bn), 7.04 [t, *J* = 5.9 Hz, 1 H, C(O)NH], 4.62 (d, *J* = 11.7 Hz, 1 H, C*H*H Bn), 4.54–4.27 (m, 7 H, CH*H* Bn, 3×CH_2 Bn), 4.18–4.16 (m, 1 H, 3-H), 3.67 (dd, *J* = 2.7 Hz, 1 H, 4-H), 3.60 (d, *J* = 2.0 Hz, 1 H, 2-H), 3.53 (dd, *J* = 6.7, 9.3 Hz, 1 H, 7a-H), 3.45 (dd, *J* = 7.2, 9.3 Hz, 1 H, 7b-H), 3.43–3.40 (m, 1 H, 5-H), 3.31–3.17 (m, 3 H, NCH_2-1 pentyl, 6-H), 2.01 (s, 1 H, NH), 1.53–1.44 (m, 2 H, CH_2-2 pentyl), 1.35–1.22 (m, 4 H, 2×CH_2 pentyl), 0.87 (t, *J* = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3 [C(O)-1], 138.8, 138.4, 138.4, 138.0 (4×C_q Bn), 128.6, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7 (CH_{Ar} Bn), 73.7, 73.4 (2×CH_2 Bn), 73.3 (C-3), 73.1 (C-5), 72.3, 72.2 (2×CH_2 Bn), 71.7 (C-4), 70.6 (C-7), 60.2 (C-2), 56.0 (C-6), 39.3 (NCH_2-1 penty), 29.6, 29.3, 22.6 (3×CH_2 pentyl), 14.2 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3387, 2927, 2862, 1725, 1668, 1521, 1497, 1454, 1364, 1288, 1208, 1070, 908, 735, 698 cm^{-1}. $[\alpha]_D^{20}$ = 2.1 (*c* = 0.6, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{48}N_2O_5 + H]^+$ 637.3636 $[M + H]^+$; found 637.3633.

5-(Adamantan-1-yl-methoxy)pentyl 2,6-Dideoxy-2,6-imino-L-*glycero*-D-*gulo*-heptonamide (98): Compound **98** (7 mg, 16 μmol, 41%) was synthesized from **92** (39 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). ^1H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.01–3.35 (m, 9 H, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7, CH_2-5 pentyl), 3.28–3.22 (m, 2 H, NCH_2-1 pentyl), 2.96 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.72 (d, *J* = 21.1 Hz, 6 H, 3×CH_2 Ada), 1.63–1.49 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.49–1.35 (m, 2 H, CH_2-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 171.8 [C(O)-1], 83.2 (OCH_2-Ada), 74.3, 73.3, 71.9 (C-3, C-4, C-5), 72.6 (CH_2-3 pentyl), 59.2 (C-7), 59.1, 57.7 (C-2, C-6), 41.0 (CH_2 Ada), 40.7 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5, 30.3 (2×CH_2 pentyl), 29.9 (CH Ada), 24.8 (CH_2-3 pentyl) ppm. $[\alpha]_D^{20}$ = –3.0 (*c* = 1.0, MeOH). IR (thin film): $\tilde{\nu}_{max}$ = 3312, 2901, 2848, 1652, 1455, 1099 cm^{-1}. HRMS: calcd. for $[C_{23}H_{40}N_2O_6 + H]^+$ 441.2959 $[M + H]^+$; found 441.2957.

5-(Adamantan-1-yl-methoxy)pentyl 2,6-Butylimino-2,6-dideoxy-L-*glycero*-D-*gulo*-heptonamide (99): Compound **99** (17 mg, 34 μmol, 83%) was synthesized in two steps from **92** (41 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.36 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.62 (EtOAc/toluene, 1:2). ^1H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.16–3.47 (m, 6 H, 2-H, 3-H, 4-H, 5-H, CH_2-7), 3.39 (t, *J* = 6.4 Hz, 3 H, 6-H, CH_2-5 pentyl), 3.30–3.17 (m, 2 H, NCH_2-1 pentyl), 3.10–2.86 (m, 3 H, OCH_2-Ada, NC*H*H butyl), 2.81–2.57 (m, 1 H, NCH*H* butyl), 1.95 (s, 3 H, 3×CH Ada), 1.80–1.26 (m,

22 H, 6×CH_2 Ada, 3×CH_2 pentyl, 2×CH_2 butyl), 0.94 (t, J = 7.3 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.3 (OCH_2-Ada), 75.3, 73.1 (C-3, C-4, C-5), 72.6 (CH_2-5 pentyl), 68.1, 62.9 (C-2, C-5), 56.2 (C-7), 52.2 (NCH_2 butyl), 41.0 (CH_2 Ada), 40.7 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5, 30.2 (CH_2 pentyl/butyl), 29.9 (CH Ada), 24.9 (CH_2-3 pentyl), 21.4 (CH_2 butyl), 14.3 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3316, 2903, 2849, 1652, 1458, 1074 cm^{-1}. $[\alpha]_D^{20}$ = –1.0 (c = 0.2, MeOH). HRMS: calcd. for $[C_{27}H_{48}N_2O_6 + H]^+$ 497.3585 $[M + H]^+$; found 497.3581.

5-(Adamantan-1-yl-methoxy)pentyl 2,6-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,6-dideoxy-L-*glycero*-D-*gulo*-heptonamide (100): Compound **100** (22 mg, 33 μmol, 79%) was synthesized in two steps from **92** (42 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (*N*-alkylated penultimate) = 0.66 (EtOAc/toluene, 1:2). ^{1}H NMR (400 MHz, MeOD): δ = 3.96–3.82 (m, 2 H, CH_2-7), 3.77–3.69 (m, 1 H, 5-H), 3.67–3.53 (m, 1 H, 3-H), 3.53–3.43 (m, 1 H, 4-H), 3.43–3.34 (m, 5 H, 2×CH_2-5 pentyl, 2-H), 3.33–3.12 [m, 3 H, 5-H, C(O)-NCH_2-1 pentyl], 3.00–2.95 (m, 3 H, 2×OCH_2-Ada), 2.86–2.73 (m, 1 H, NC*H*H pentyl), 2.61–2.49 (m, 1 H, NCH*H* pentyl), 1.95 (s, 6 H, 6×CH Ada), 1.82–1.26 (m, 24 H, 6×CH_2 Ada, 6×CH_2 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.3, 83.2 (2×OCH_2-Ada), 75.9 (C-4), 73.6 (C-3), 72.7, 72.6 (2×CH_2-5 pentyl), 71.8 (C-5), 68.0 (C-2), 62.5 (C-6), 56.9 (C-7), 51.7 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 40.6 [C(O)NCH_2-1 pentyl], 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.7, 30.6, 30.3 (CH_2 pentyl), 29.9 (CH Ada), 25.1, 25.0 (2×CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3366, 2901, 2848, 1652, 1455, 130, 1157, 1110 cm^{-1}. $[\alpha]_D^{20}$ = –2.3 (c = 0.4, MeOH). HRMS: calcd. for $[C_{39}H_{66}N_2O_7 + H]^+$ 675.4943 $[M + H]^+$; found 675.4941.

5-(Adamantan-1-yl-methoxy)pentyl 2,6-Dideoxy-2,6-imino-L-*glycero*-D-*ido*-heptonamide (101): Compound **101** (14 mg, 32 μmol, 71%) was synthesized from **93** (45 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). ^{1}H NMR (400 MHz, MeOD): δ = 4.10 (s, 1 H, 3-H), 3.97 (dd, J = 3.1 Hz, 1 H, 4-H), 3.90 (s, 1 H, 2-H), 3.86–3.73 (m, 3 H, 5-H, CH_2-7), 3.39 (t, J = 6.4, 2 Hz, CH_2-5 pentyl), 3.34–3.23 (m, 3 H, 6-H, NCH_2-1 pentyl), 2.97 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 11.7, 32.5 Hz, 6 H, 3×CH_2 Ada), 1.63–1.52 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.47–1.37 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 171.3 [C(O)-1], 83.2 (OCH_2-Ada), 72.6 (CH_2-5 pentyl), 71.3 (C-3), 69.7, 69.7 (C-4, C-5), 62.2 (C-7), 59.9 (C-2), 57.6 (C-6), 41.0 (CH_2 Ada), 40.6 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.5, 30.3 (2×CH_2 pentyl), 29.9 (CH Ada), 24.8 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3304, 2902, 2848, 1652, 1453, 1056 cm^{-1}. $[\alpha]_D^{20}$ = –11.3 (c = 0.3, MeOH). HRMS: calcd. for $[C_{23}H_{40}N_2O_6 + H]^+$ 441.2959 $[M + H]^+$; found 441.2957.

5-(Adamantan-1-yl-methoxy)pentyl 2,6-Butylimino-2,6-dideoxy-L-*glycero*-D-*ido*-heptonamide (102): Compound **102** (6 mg, 12 μmol, 41%) was synthesized from **93** (29 μmol) through reductive amination with the appropriate aldehyde (General Procedure G). ^{1}H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 3.99–3.60 (m, 6 H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 3.53 (d, J = 3.4 Hz, 1 H, 2-H), 3.39 (t, J = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.34–3.15 (m, 4 H, 5-H, NCH_2-1 pentyl), 2.97 (s, 2 H, OCH_2-Ada), 2.84–2.64 (m, 2 H, NCH_2 butyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 12.0, 31.0 Hz, 6 H, 3×CH_2 Ada), 1.62–1.23 (m, 16 H, 3×CH_2 Ada, 3×CH_2 pentyl, 2×CH_2 butyl), 0.94 (t, J = 7.3 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 81.7 (OCH_2-Ada), 71.8, 71.7, 70.0 (C-3, C-4, C-5), 71.1 (CH_2-5 pentyl), 63.8 (C-2), 60.3 (C-7), 59.5 (C-6), 52.7 (NCH_2 butyl), 39.5 (CH_2 Ada), 38.8 (NCH_2-1 pentyl), 36.9 (CH_2 Ada), 35.3 (C_q Ada), 28.4 (CH Ada), 29.0, 28.7, 23.5, 20.1 (3×CH_2 pentyl, 2×CH_2 butyl), 12.9 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3315, 2904, 2850, 1651, 1590, 1456, 1065 cm^{-1}. $[\alpha]_D^{20}$ = –6.7 (c = 0.1, MeOH). HRMS: calcd. for $[C_{27}H_{48}N_2O_6 + H]^+$ 497.3585 $[M + H]^+$; found 497.3580.

1,1,3,3-Tetramethylbutyl 2,6-Dideoxy-2,6-imino-L-*glycero*-D-*gulo*-heptonamide (103): Compound **103** (17 mg, 53 μmol, 88%) was synthesized from **94** (60 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.30 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH). ^{1}H NMR (400 MHz, MeOD): δ = 3.95–3.55 (m, 7 H, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 1.88 (s, 1 H, C*H*H-2 tMB), 1.72 (s, 1 H, CH*H*-2 tMB), 1.41 (s, 6 H, 2×CH_3 tMB), 1.02 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 166.5 [C(O)-1], 72.2, 70.9, 69.0 (C-3, C-4, C-5), 57.3 (C-2), 57.0 (C-7), 56.0 (C-6), 55.3 (NHC_q-1 tMB), 51.2 (CH_2-2 tMB), 31.0 (C_q-3 tMB), 30.5 (2×CH_3, CH_3-4 tMB), 28.0, 27.7 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3319, 2953, 2438, 1667, 1444, 1366, 1226, 1062 cm^{-1}. $[\alpha]_D^{20}$ = –13.6 (c = 0.8, MeOH). HRMS: calcd. for $[C_{15}H_{30}N_2O_5 + H]^+$ 319.2222 $[M + H]^+$; found 319.2229.

1,1,3,3-Tetramethylbutyl 2,6-Butylimino-2,6-dideoxy-L-*glycero*-D-*gulo*-hepton-amide (104): Compound **104** (11 mg, 29 μmol, 59%) was synthesized in two steps from **94** (49 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.47 ($MeOH/CH_2Cl_2$, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.74 (EtOAc/toluene, 1:3). ^{1}H NMR (400 MHz, MeOD): δ = 3.87 (dd, J = 4.1, 11.8 Hz, 1 H, 7a-H), 3.79 (dd, J = 6.8, 11.7 Hz, 1 H, 7b-H), 3.70 (dd, J = 5.6, 9.7 Hz, 1 H, 5-H), 3.59 (dd, J = 9.2 Hz, 1 H, 3-H), 3.40 (dd, J = 9.1 Hz, 1 H, 4-H), 3.23–3.17 (m, 1 H, 6-H), 3.16 (d, J = 9.5 Hz, 1 H, 2-H), 2.71 (ddd, J = 5.5, 9.6, 12.6 Hz, 1 H, NC*H*H-1 pentyl), 2.54 (ddd, J = 5.6, 9.7, 12.6 Hz, 1 H, NCH*H*-1 pentyl), 1.92 (d, J = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.68 (d, J = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.61–1.38 (m, 8 H, 2×CH_3 tMB, CH_2 butyl), 1.36–1.24 (m, 2 H, CH_2 butyl), 1.03 (s, 9 H, 2×CH_3, CH_3-4 tMB), 0.92 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 173.1 [C(O)-1], 76.1 (C-4), 73.6 (C-3), 71.8 (C-5), 67.8 (C-2), 62.2 (C-6), 57.4 (C-7), 56.5 (NHC_q-1 tMB), 52.9 (CH_2-2 tMB), 51.1 (NCH_2 butyl), 32.6 (C_q-3 tMB), 32.2 (2×CH_3, CH_3-4 tMB), 32.0 (CH_2 butyl), 29.6, 29.2 (2×CH_3 tMB), 21.6 (CH_2 butyl), 14.6 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3374, 2957, 2497, 1728, 1652, 1434, 1366, 1276, 1228, 1122, 1072 cm^{-1}. $[\alpha]_D^{20}$ = –7.8 (c = 0.2, MeOH). HRMS: calcd. for $[C_{19}H_{38}N_2O_5 + H]^+$ 375.2853 $[M + H]^+$; found 375.2854.

1,1,3,3-Tetramethylbutyl 2,6-[5-(Adamantan-1-yl-methoxy)pentyl]-imino-2,6-dideoxy-L-*glycero*-D-*gulo*-heptonamide (105): Compound **105** (20 mg, 36 μmol, 69%) was synthesized in two steps from **94** (52 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (*N*-alkylated penultimate) = 0.77 (EtOAc/toluene, 1:3). ^{1}H NMR (400 MHz, MeOD): δ = 3.98–3.80 (m, 2 H, CH_2-7), 3.80–3.65 (m, 1 H, 4-H), 3.65–3.50 (m, 1 H, 3-H), 3.50–3.21 (m, 5 H, CH_2-5 pentyl, 2-H, 4-H, 6-H), 3.03–2.91 (m, 2 H, OCH_2-Ada), 2.89–2.74 (m, 1 H, NC*H*H-1 pentyl), 2.73–2.53 (m, 1 H, NCH*H*-1 pentyl), 2.03–1.17 (m, 27 H, 3×CH Ada, CH_2-2 tMB, 6×CH_2 Ada, 3×CH_2 pentyl, 2×CH_3 tMB), 1.03 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 81.6 (OCH_2-Ada), 74.3 (C-4), 71.9 (C-3), 71.0 (CH_2-5 pentyl), 70.0 (C-5), 66.5 (C-2), 60.8 (C-6), 55.5 (NHC_q-1 tMB), 55.1 (C-7), 51.4 (CH_2-2 tMB), 50.1 (NCH_2-1 pentyl), 39.5

(CH_2 Ada), 36.9 (CH_2 Ada), 33.7 (C_q Ada), 31.0, 30.7, 29.2, 28.4 (CH Ada), 28.0, 27.7 (2×CH_3 tMB), 23.6 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3342, 2902, 2849, 1652, 1449, 1366, 1227, 1157, 1111 cm^{-1}. $[\alpha]_D^{20}$ = –3.1 (*c* = 0.4, MeOH). HRMS: calcd. for $[C_{31}H_{56}N_2O_6 + H]^+$ 553.4211 $[M + H]^+$; found 553.4208.

1,1,3,3-Tetramethylbutyl 2,6-Dideoxy-2,6-imino-L-*glycero*-D-*ido*-heptonamide (106): Compound **106** (12 mg, 37 μmol, 81%) was synthesized from **95** (46 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.41 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 4.13 (s, 1 H, CH), 3.97 (s, 1 H, CH), 3.87 (s, 1 H, CH), 3.82 (s, 3 H, CH_2-7, CH), 3.33 (s, 1 H, 6-H), 1.81 (s, 2 H, CH_2-2 tMB), 1.42 (s, 6 H, 2×CH_3 tMB), 1.02 (d, *J* = 4.6 Hz, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 71.1, 69.6, 69.5 (C-3, C-4, C-5), 61.8 (C-7), 60.1 (C-2), 57.7 (C-5), 56.7 (NHC_q-1 tMB), 52.4 (CH_2-2 tMB), 32.6 (C_q-3 tMB), 32.0 (2×CH_3, CH_3-4 tMB), 29.8, 29.5 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3311, 2955, 2409, 1667, 1752, 1453, 1391, 1366, 1225, 1056 cm^{-1}. $[\alpha]_D^{20}$ = –4.5 (*c* = 0.6, MeOH). HRMS: calcd. for $[C_{15}H_{30}N_2O_5 + H]^+$ 319.2222 $[M + H]^+$; found 319.2229.

1,1,3,3-Tetramethylbutyl 2,6-Butylimino-2,6-dideoxy-L-*glycero*-D-*ido*-heptonamide (107): Compound **107** (7 mg, 19 μmol, 49%) was synthesized from **95** (39 μmol) through reductive amination with the appropriate aldehyde (General Procedure G). ^1H NMR (400 MHz, MeOD): δ = 3.88–3.78 (m, 2 H, 7a-H, CH), 3.77–3.70 (m, 2 H, 2×CH), 3.66 (dd, *J* = 6.6, 11.3 Hz, 1 H, 7b-H), 3.40 (d, *J* = 3.3 Hz, 1 H, 2-H), 2.97 (dd, *J* = 5.9, 9.8 Hz, 1 H, 6-H), 2.88–2.65 (m, 2 H, NCH_2-1 butyl), 1.86 (d, *J* = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.72 (d, *J* = 14.8 Hz, 1 H, CH*H*-2 tMB), 1.59–1.46 (m, 2 H, CH_2 butyl), 1.42 (d, *J* = 1.7 Hz, 6 H, 2×CH_3 tMB), 1.37–1.26 (m, 2 H, CH_2 butyl), 1.03 (s, 9 H, 2×CH_3, CH_3-4 tMB), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 73.2, 73.1, 71.8 (C-3, C-4, C-5), 65.0 (C-2), 61.9 (C-6), 61.4 (C-7), 56.4 (NHC_q-1 tMB), 54.9 (NCH_2 butyl), 53.0 (CH_2-2 tMB), 32.6 (C_q-3 tMB), 32.1 (2×CH_3, CH_3-4 tMB), 29.3 (CH_2 butyl), 29.1, 29.1 (CH_2-2 tMB), 21.6 (CH_2 butyl), 14.5 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3339, 2955, 1638, 1434, 1366, 1227, 1048 cm^{-1}. $[\alpha]_D^{20}$ = –1.4 (*c* = 0.1, MeOH). HRMS: calcd. for $[C_{19}H_{38}N_2O_5 + H]^+$ 375.2853 $[M + H]^+$; found 375.2856.

1,1,3,3-Tetramethylbutyl 2,6-[5-(Adamantan-1-yl-methoxy)pentyl]-imino-2,6-dideoxy-L-*glycero*-D-*ido*-heptonamide (108): Compound **108** (5 mg, 9 μmol, 21%) was synthesized from **95** (43 μmol) through reductive amination with the appropriate aldehyde (General Procedure G). ^1H NMR (400 MHz, MeOD): δ = 3.85 (dd, *J* = 5.7, 11.4 Hz, 1 H, 7a-H), 3.82–3.79 (m, 1 H, 5-H), 3.77–3.71 (m, 2 H, 3-H, 4-H), 3.68 (dd, *J* = 6.4, 11.4 Hz, 1 H, 7b-H), 3.42 (d, *J* = 3.3 Hz, 1 H, 2-H), 3.39 (t, *J* = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.02–2.95 (m, 3 H, 6-H, OCH_2-Ada), 2.90–2.64 (m, 2 H, NCH_2-1 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.87 (d, *J* = 14.8 Hz, 1 H, C*H*H-2 tMB), 1.81–1.64 (m, 7 H, 3×CH_2 Ada, CH*H*-2 tMB), 1.63–1.50 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.42 (d, *J* = 1.9 Hz, 6 H, 2×CH_3 tMB), 1.39–1.25 (m, 2 H, CH_2-3 pentyl), 1.03 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 81.7 (OCH_2-Ada), 71.1 (CH_2-5 pentyl), 71.5, 71.5, 70.1 (C-3, C-4, C-5), 63.5 (C-2), 60.3 (C-6), 60.0 (C-7), 54.9 (NHC_q-1 tMB), 53.5 (NCH_2-1 pentyl), 51.4 (CH_2-2 tMB), 39.5 (CH_2 Ada), 36.9 (CH_2 Ada), 33.8 (CH Ada), 31.0 (C_q-3 tMB), 30.6 (2×CH_3, CH_3-4 tMB), 29.2 (CH_2 pentyl), 28.4 (CH Ada), 27.8, 27.6 (2×CH_3 tMB), 25.1 (CH_2 pentyl), 23.6 (CH_2 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3367, 2903, 2849, 1638, 1451, 1227, 1056 cm^{-1}. $[\alpha]_D^{20}$ = –2.0 (*c* = 0.1, MeOH). HRMS: calcd. for $[C_{31}H_{56}N_2O_6 + H]^+$ 553.4211 $[M + H]^+$; found 553.4207.

Pentyl 2,6-Dideoxy-2,6-imino-L-*glycero*-D-*gulo*-heptonamide (109): Compound **109** (13 mg, 46 μmol, 92%) was synthesized from **96** (50 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.85 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 3.89 (dd, *J* = 4.5, 11.7 Hz, 1 H, 7a-H), 3.86–3.75 (m, 3 H, 2-H, 5-H, 7b-H), 3.73 (t, *J* = 7.3 Hz, 1 H, CH), 3.67 (t, *J* = 7.3 Hz, 1 H, CH), 3.57 (dt, *J* = 4.7, 9.0 Hz, 1 H, 6-H), 3.24 (dt, *J* = 2.7, 7.0 Hz, 2 H, NCH_2-1 pentyl), 1.61–1.47 (m, 2 H, CH_2-2 pentyl), 1.46–1.23 (m, 4 H, 2×CH_2 pentyl), 0.92 (t, *J* = 6.8 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 170.0 [C(O)-1], 73.7, 72.7, 70.9 (C-3, C-4, C-5), 58.9 (C-2), 58.8 (C-7), 57.7 (C-6), 40.9 (NCH_2-1 pentyl), 30.3, 30.1, 23.6 (3×CH_2 pentyl), 14.5 (CH_3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3312, 2931, 1652, 1460, 1062 cm^{-1}. $[\alpha]_D^{20}$ = –7.5 (*c* = 0.8, MeOH). HRMS: calcd. for $[C_{12}H_{24}N_2O_5 + H]^+$ 277.1758 $[M + H]^+$; found 277.1759.

Pentyl 2,6-Butylimino-2,6-dideoxy-L-*glycero*-D-*gulo*-heptonamide (110): Compound **110** (10 mg, 30 μmol, 64%) was synthesized in two steps from **96** (47 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.37 (MeOH/CH_2Cl_2, 1:4 + 2% NH_4OH); R_f (*N*-alkylated penultimate) = 0.59 (EtOAc/toluene, 1:2). ^1H NMR (400 MHz, MeOD): δ = 3.88 (dd, *J* = 4.2, 11.8 Hz, 1 H, 7a-H), 3.82 (dd, *J* = 6.4, 11.8 Hz, 1 H, 7b-H), 3.76–3.69 (m, 1 H, 5-H), 3.63–3.57 (m, 1 H, 3-H), 3.41 (dd, *J* = 8.9, 9.9 Hz, 1 H, 4-H), 3.29–3.14 (m, 4 H, 2-H, 6-H, NCH_2-1 pentyl), 2.70 (ddd, *J* = 5.4, 9.6, 12.5 Hz, 1 H, NC*H*H butyl), 2.47 (ddd, *J* = 5.7, 9.7, 12.5 Hz, 1 H, NCH*H* butyl), 1.62–1.23 (m, 10 H, 3×CH_2 pentyl, 2×CH_2 butyl), 0.96–0.88 (m, 6 H, 2×CH_3 pentyl/butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 174.2 [C(O)-1], 76.1 (C-4), 73.8 (C-3), 72.1 (C-5), 67.9 (C-2), 62.3 (C-6), 57.1 (C-7), 51.1 (NCH_2 butyl), 40.6 (NCH_2-1 pentyl), 31.6, 30.5, 30.2, 23.6, 21.6 (3×CH_2 pentyl, 2×CH_2 butyl), 14.5, 14.5 (2×CH_3 butyl/pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3329, 2958, 2931, 2871, 1730, 1637, 1462, 1378, 1278, 1122, 1073 cm^{-1}. $[\alpha]_D^{20}$ = –7.8 (*c* = 0.2, MeOH). HRMS: calcd. for $[C_{16}H_{32}N_2O_5 + H]^+$ 333.2384 $[M + H]^+$; found 333.2385.

Pentyl 2,6-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,6-dideoxy-L-*glycero*-D-*gulo*-heptonamide (111): Compound **111** (13 mg, 25 μmol, 51%) was synthesized in two steps from **96** (49 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (*N*-alkylated penultimate) = 0.62 (EtOAc/toluene, 1:2). ^1H NMR (400 MHz, MeOD): δ = 3.89 (dd, *J* = 2.8, 11.6 Hz, 1 H, 7a-H), 3.84 (dd, *J* = 6.1, 11.7 Hz, 1 H, 7b-H), 3.72 (dd, *J* = 5.6, 9.8 Hz, 1 H, 5-H), 3.60 (dd, *J* = 9.2 Hz, 1 H, 3-H), 3.46–3.39 (m, 1 H, 4-H), 3.36 (t, *J* = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.30–3.09 [m, 4 H, 2-H, 6-H, C(O)NCH_2-1 pentyl], 2.96 (s, 2 H, OCH_2-Ada), 2.83–2.68 (m, 1 H, NC*H*H pentyl), 2.56–2.43 (m, 1 H, NCH*H* pentyl), 1.94 (s, 3 H, 3×CH Ada), 1.72 (dd, *J* = 12.2, 33.0 Hz, 6 H, 3×CH_2 Ada), 1.64–1.26 (m, 18 H, 3×CH_2 Ada, 6×CH_2 pentyl), 0.92 (t, *J* = 6.2 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 81.7 (OCH_2-Ada), 74.5 (C-4), 72.2 (C-3), 71.1 (CH_2-5 pentyl), 70.4 (C-5), 66.4 (C-2), 60.9 (C-6), 55.5 (C-7), 49.9 (NCH_2-1 pentyl), 39.5 (CH_2 Ada), 39.1 [C(O)NCH_2-1 pentyl], 36.9 (CH_2 Ada), 33.8 (C_q Ada), 28.4 (CH Ada), 29.2, 28.9, 28.7, 27.5, 23.5, 22.1 (6×CH_2 pentyl), 13.0 (CH_3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3342, 2903, 2849, 1651, 1458, 1157, 1051 cm^{-1}. $[\alpha]_D^{20}$ = –1.1 (*c* = 0.2, MeOH). HRMS: calcd. for $[C_{28}H_{50}N_2O_6 + H]^+$ 511.3742 $[M + H]^+$; found 511.3738.

Pentyl 2,6-Dideoxy-2,6-imino-L-*glycero*-D-*ido*-heptonamide (112): Compound **112** (13 mg, 46 μmol, 79%) was synthesized from **97**

(58 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.29 ($MeOH/CH_2Cl_2$, 1:4 + 2% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 4.13–4.10 (m, 1 H, 3-H), 3.98 (m, 1 H, 4-H), 3.92 (d, J = 2.1 Hz, 1 H, 2-H), 3.86–3.80 (m, 1 H, 7a-H), 3.80–3.75 (m, 2 H, 7b-H, 5-H), 3.36–3.32 (m, 1 H, 6-H), 3.24 (dt, J = 0.9, 7.0 Hz, 2 H, $NHCH_2$-1 pentyl), 1.60–1.50 (m, 2 H, CH_2-2 pentyl), 1.39–1.29 (m, 4 H, 2×CH_2 pentyl), 0.92 (t, J = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 169.1 [C(O)-1], 69.8 (C-3), 68.1, 67.9 (C-4, C-5), 60.4 (C-7), 58.3 (C-2), 56.2 (C-6), 39.1 (NCH_2-1 pentyl), 28.8, 28.7, 22.0 (3×CH_2 pentyl), 12.9 (CH_3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3259, 2929, 1652, 1460, 1058 cm^{-1}. $[\alpha]_D^{20}$ = –9.8 (c = 0.8, MeOH). HRMS: calcd. for $[C_{12}H_{24}N_2O_5 + H]^+$ 277.1758 $[M + H]^+$; found 277.1758.

Pentyl 2,6-Butylimino-2,6-dideoxy-L-*glycero*-D-*ido*-heptonamide (113): Compound **113** (5 mg, 15 μmol, 33%) was synthesized from **97** (45 μmol) through reductive amination with the appropriate aldehyde (General Procedure G). ^1H NMR (400 MHz, MeOD): δ = 3.98 (dd, J = 3.9, 8.0 Hz, 1 H, 7a-H), 3.91–3.52 (m, 5 H, 2-H, 3-H, 4-H, 5-H, 7b-H), 3.29–3.10 (m, 2 H, NCH_2-1 pentyl), 3.10–2.94 (m, 1 H, 6-H), 2.94–2.64 (m, 2 H, NCH_2 butyl), 1.76–1.25 (m, 10 H, 3×CH_2 pentyl, 2×CH_2 butyl), 0.97–0.88 (m, 6 H, 2×CH_3 pentyl/butyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 71.7, 71.6, 71.1 (C-3, C-4, C-5), 63.7 (C-2), 60.2 (C-7), 59.8 (C-6), 52.6 (NCH_2 butyl), 38.8 (NCH_2-1 pentyl), 36.4 (CH_2 butyl), 28.9, 28.7 (2×CH_2 pentyl), 22.0 (CH_2 pentyl), 20.0 (CH_2 butyl), 12.9, 12.7 (2×CH_3 pentyl/butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3344, 2959, 2931, 2872, 1638, 1461, 1061 cm^{-1}. $[\alpha]_D^{20}$ = –2.0 (c = 0.1, MeOH). HRMS: calcd. for $[C_{16}H_{32}N_2O_5 + H]^+$ 333.2384 $[M + H]^+$; found 333.2385.

Pentyl 2,6-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,6-dideoxy-L-*glycero*-D-*ido*-heptonamide (114): Compound **114** (6 mg, 12 μmol, 24%) was synthesized from **97** (50 μmol) through reductive amination with the appropriate aldehyde (General Procedure G). ^1H NMR (400 MHz, MeOD): δ = 3.90–3.81 (m, 2 H, 5-H, 7a-H), 3.80–3.68 (m, 3 H, 3-H, 4-H, 7b-H), 3.53 (d, J = 3.5 Hz, 1 H, 2-H), 3.38 (t, J = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.30–3.12 [m, 2 H, $C(O)NCH_2$-1 pentyl], 3.00–2.93 (m, 3 H, 6-H, OCH_2-Ada), 2.85–2.63 (m, 2 H, NCH_2-1 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 11.8, 31.6 Hz, 6 H, 3×CH_2 Ada), 1.65–1.49 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl/butyl), 1.42–1.26 (m, 6 H, 3×CH_2 pentyl/butyl), 0.93 (t, J = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 83.2 (OCH_2-Ada), 72.7 (CH_2-5 pentyl), 73.3, 73.3, 71.5 (C-3, C-4, C-5), 65.4 (C-2), 61.9 (C-7), 61.1 (C-6), 54.5 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 40.4 [$C(O)NCH_2$-1 pentyl], 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 30.7, 30.5, 30.2, 25.9, 25.2, 23.6 (6×CH_2 pentyl), 14.5 (CH_3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3327, 2903, 2850, 1649, 1638, 1455, 1362, 1157, 1096, 1057 cm^{-1}. $[\alpha]_D^{20}$ = –1.7 (c = 0.1, MeOH). HRMS: calcd. for $[C_{28}H_{50}N_2O_6 + H]^+$ 511.3742 $[M + H]^+$; found 511.3737.

2,3,4,6-Tetra-*O*-benzyl-1-*O*-*tert*-butyldiphenylsilyl-5-*O*-*para*-nitrobenzoyl-L-iditol (115): Diisopropyl azodicarboxylate (7.54 mL, 38.4 mmol) was added over a 2 min period to a cooled (0 °C), anhydrous solution of **82** (15.02 g, 19.2 mmol), *p*-nitrobenzoic acid (6.42 g, 38.4 mmol) and triphenylphosphane (10.07 g, 38.4 mmol) in THF (77 mL). The reaction mixture was stirred for 20 h and allowed to warm to room temp. The reaction mixture was diluted with EtOAc (200 mL) and successively washed with satd. aq. $NaHCO_3$ (3× 100 mL) and satd. aq. NaCl (100 mL). The organic phase was dried (Na_2SO_4) and concentrated, and the residue was used crude in the next reaction. A portion of the residue was purified for characterization by silica gel column chromatography (EtOAc/PE, 2→5%) to provide **115** as a colorless oil. R_f = 0.60 (EtOAc/PE, 1:6). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.64–7.55 (m, 6 H, H_{Ar} TBDPS/*p*-NO_2Bz), 7.45–7.07 (m, 28 H, H_{Ar} Bn/TBDPS/*p*-NO_2Bz), 5.49 (dd, J = 5.3, 9.5 Hz, 1 H, 5-H), 4.84–4.27 (m, 8 H, 4×CH_2 Bn), 4.19–3.48 (m, 7 H, CH_2-1, 2-H, 3-H, 4-H, CH_2-6), 0.90 (s, 9 H, *t*Bu-Si) ppm. MS (ESI): calcd. for $[C_{57}H_{59}NO_9Si + H]^+$ 930.4 $[M + H]^+$; found 930.4.

2,5-Anhydro-1-*O*-*tert*-butyldiphenylsilyl-3,4,6-tri-*O*-benzyl-L-iditol (116): Byproduct **116**[16] was formed during the Mitsunobu raction of **82** and could be separated from **117** (the saponification product of **115**) by silica gel column chromatography (EtOAc/PE, 5→15%) to provide **116** (5.94 g, 8.83 mmol, 46%) as a colorless oil. R_f = 0.65 (EtOAc/PE, 1:6). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.63 (m, 4 H, H_{Ar} TBDPS), 7.42–7.16 (m, 21 H, H_{Ar} TBDPS/Bn), 4.59 (d, J = 12.0 Hz, 1 H, C*H*H Bn), 4.56–4.44 (m, 5 H, CH*H* Bn, 2×CH_2 Bn), 4.37–4.30 (m, 2 H, 2-H, 5-H), 4.09 (dd, J = 1.5, 4.0 Hz, 1 H, 3-H), 4.04 (dd, J = 1.4, 4.0 Hz, 1 H, 4-H), 3.98 (dd, J = 7.9, 9.9 Hz, 1 H, 1a-H), 3.87 (dd, J = 5.2, 10.0 Hz, 1 H, 1b-H), 3.71 (dd, J = 5.8, 9.9 Hz, 1 H, 6a-H), 3.66 (dd, J = 6.5, 9.8 Hz, 1 H, 6b-H), 1.06 (s, 9 H, *t*Bu-Si) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 138.2, 138.1 (3×C_q Bn), 135.7, 135.7 (CH_{Ar} TBDPS), 133.7, 133.5 (2×C_q Si-Ph), 129.7, 129.7, 128.5, 128.5, 128.4, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6 (CH_{Ar} Bn/TBDPS), 81.9 (C-4), 81.3 (C-3), 80.5 (C-2), 79.2 (C-5), 73.5, 72.6, 72.4 (3×CH_2 Bn), 68.8 (C-6), 61.7 (C-1), 27.0 (CH_3 *t*Bu), 19.3 (C_q *t*Bu) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3032, 2931, 2858, 1494, 1454, 1428, 1358, 1208, 1080, 1027, 823, 735, 699, 611, 504 cm^{-1}. $[\alpha]_D^{20}$ = 9.4 (c = 10.6, $CHCl_3$). HRMS: calcd. for $[C_{43}H_{48}O_5Si + Na]^+$ 695.3169 $[M + Na]^+$; found 695.3161.

2,3,4,6-Tetra-*O*-benzyl-1-*O*-*tert*-butyldiphenylsilyl-L-iditol (117): The crude residue containing **115** and **116** from the previous reaction was dissolved in a mixture of H_2O/EtOH/THF (100 mL, 1:2:2, v/v/v). Lithium hydroxide (2.85 g, 119 mmol) was added to the solution and the resulting yellow reaction mixture was stirred for 2 h, after which TLC analysis showed complete consumption of the starting material. The pH of reaction mixture was adjusted to pH ca. 7 with 1 M aq. HCl. The mixture was concentrated to ca. 1/4 of its initial volume, diluted with Et_2O (100 mL) and washed successively with satd. aq. $NaHCO_3$ (3× 100 mL) and satd. aq. NaCl (100 mL). The organic phase was dried (Na_2SO_4) and concentrated. The resulting residue was purified by silica gel column chromatography (EtOAc/PE, 5→15%) to provide **117** (5.68 g, 7.28 mmol, 38%) over the two steps as a colorless oil. R_f = 0.35 (EtOAc/PE, 1:61:6). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.67–7.63 (m, 4 H, H_{Ar} TBDPS), 7.47–7.16 (m, 26 H, H_{Ar} TBDPS/Bn), 4.77–4.70 (m, 2 H, C*H*H Bn, C*H*H Bn), 4.67–4.58 (m, 2 H, C*H*H Bn, CH*H* Bn), 4.49 (d, J = 11.2 Hz, 1 H, CH*H* Bn), 4.43 (d, J = 11.9 Hz, 1 H, C*H*H Bn), 4.41 (d, J = 8.9 Hz, 1 H, CH*H* Bn), 4.38 (d, J = 11.9 Hz, 1 H, CH*H* Bn), 4.02 (dd, J = 3.1, 7.7 Hz, 1 H, 3-H), 3.87 (dd, J = 4.5, 9.1 Hz, 1 H, 1a-H), 3.85 (dd, J = 4.5, 9.1 Hz, 1 H, 1b-H), 3.80 (dd, J = 2.3, 7.7 Hz, 1 H, 4-H), 3.75–3.69 (m, 2 H, 2-H, 5-H), 3.42 (dd, J = 6.8, 9.2 Hz, 1 H, 6a-H), 3.26 (dd, J = 5.7, 9.2 Hz, 1 H, 6b-H), 2.51 (d, J = 6.5 Hz, 1 H, OH-5), 1.04 (s, 9 H, *t*Bu-Si) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.5, 138.5, 138.4, 138.3 (4×C_q Bn), 135.9, 135.8 (CH_{Ar} TBDPS), 133.5 (C_q Si-Ph), 130.0, 129.9, 128.6, 128.5, 128.4, 128.0, 127.9, 127.9, 127.9, 127.8 (CH_{Ar} Bn/TBDPS), 79.0 (C-3), 78.9 (C-2), 78.7 (C-4), 75.1, 75.0, 73.4, 73.1 (4×CH_2 Bn), 71.6 (C-6), 69.9 (C-5), 63.2 (C-1), 27.1 (CH_3 *t*Bu), 19.3 (C_q *t*Bu) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3031, 2929, 2861, 1495, 1454, 1358, 1208, 1080, 1027, 823, 734, 699 cm^{-1}. $[\alpha]_D^{20}$ = 13.0 (c = 0.3, $CHCl_3$). HRMS: calcd. for $[C_{50}H_{56}O_6Si + Na]^+$ 803.3744 $[M + Na]^+$; found 803.3736.

5-Azido-2,3,4,6-tetra-*O*-benzyl-1-*O*-*tert*-butyldiphenylsilyl-D-glucitol (118): Diisopropyl azodicarboxylate (2.87 mL, 14.6 mmol) and

diphenylphosphoryl azide (3.15 mL, 14.6 mmol) were successively added over 2 min periods to a cooled (0 °C) anhydrous solution of **117** (5.68, 7.3 mmol) and triphenylphosphane (3.83 g, 14.6 mmol) in THF (55 mL). The reaction mixture was stirred for 20 h and allowed to warm to room temp. The mixture was concentrated and the resulting residue was purified by silica gel column chromatography (EtOAc/PE, 0→10%) to afford **118** (3.70 g, 4.60 mmol, 63%) as a colorless oil. R_f = 0.6 (EtOAc/PE, 1:6). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.63 (m, 4 H, H_{Ar} TBDPS), 7.42–7.11 (m, 26 H, H_{Ar} TBDPS/Bn), 4.69–4.64 (m, 3 H, C*H*H Bn, CH_2 Bn), 4.58 (d, J = 11.2 Hz, 1 H, C*H*H Bn), 4.54 (d, J = 11.2 Hz, 1 H, CH*H* Bn), 4.48–4.43 (m, 3 H, CH*H* Bn, CH_2 Bn), 3.93–3.61 (m, 8 H, CH_2-1, 2-H, 3-H, 4-H, 5-H, CH_2-6), 1.06 (s, 9 H, *t*Bu-Si) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 138.3, 138.2, 138.0 (4×C_q Bn), 135.8 (CH_{Ar} TBDPS), 133.4 (C_q Si-Ph), 129.9, 129.9, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7 (CH_{Ar} Bn/TBDPS), 79.5, 78.9, 78.7 (C-2, C-2, C-4), 75.1, 74.5, 73.4, 72.9 (4×CH_2 Bn), 69.8 (C-6), 63.1 (C-1), 61.9 (C-5), 27.0 (CH_3 *t*Bu), 19.3 (C_q *t*Bu) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3031, 2926, 2864, 2097, 1495, 1454, 1354, 1209, 1076, 1027, 734, 699 cm^{-1}. $[\alpha]_D^{20}$ = –4.1 (c = 0.7, $CHCl_3$). HRMS: calcd. for $[C_{50}H_{55}N_3O_5Si + Na]^+$ 828.3809 [M + Na]$^+$; found 828.3805.

5-Azido-2,3,4,6-tetra-*O*-benzyl-D-glucitol (119): Tetrabutylammonium fluoride (1 M in THF, 4.2 mL, 4.2 mmol) was added to an anhydrous solution of **118** (2.26 g, 2.8 mmol) in THF (47 mL) and the resulting reaction mixture was stirred for 20 h. The mixture was concentrated, redissolved in Et_2O (100 mL), and washed with satd. aq. NaCl (100 mL). The organic phase was dried (Na_2SO_4) and concentrated and the resulting residue was purified by silica gel column chromatography (EtOAc/PE, 9→25%) to produce **119** (1.17 g, 2.07 mmol, 74%) as a colorless oil. R_f = 0.20 (EtOAc/PE, 1:4). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42–7.15 (m, 20 H, H_{Ar} Bn), 4.70 (d, J = 11.2 Hz, 1 H, C*H*H Bn), 4.68–4.61 (m, 3 H, CH*H* Bn, C*H*H Bn), 4.58 (d, J = 11.8 Hz, 1 H, CH*H* Bn), 4.47 (s, 2 H, CH_2 Bn), 3.86–3.83 (m, 1 H, 4-H), 3.82–3.78 (m, 3 H, 1a-H, 3-H, 5-H), 3.76–3.66 (m, 3 H, 1b-H, 2-H, 6a-H), 3.59 (dd, J = 4.9, 11.7 Hz, 1 H, 6b-H), 3.09–2.72 (m, 1 H, OH-1) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 138.0, 138.0, 137.8, 137.6 (4×C_q Bn), 128.3, 128.3, 128.2, 128.2, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5 (CH_{Ar} Bn), 79.1 (C-4), 78.8 (C-3), 78.3 (C-2), 74.8, 74.0, 73.1, 72.6 (4×CH_2 Bn), 69.4 (C-6), 61.4 (C-5), 61.3 (C-1) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3031, 2865, 2095, 1495, 1454, 1353, 1353, 1264, 1209, 1094, 1027, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = –3.1 (c = 11.5, $CHCl_3$). HRMS: calcd. for $[C_{34}H_{37}N_3O_5 + Na]^+$ 590.2631 [M + Na]$^+$; found 590.2621.

5-Azido-2,3,4,6-tetra-*O*-benzyl-D-glucose (120): Azido alcohol **119** (1.80 g, 3.2 mmol) was subjected to a Dess–Martin mediated oxidation (General Procedure A) to produce **120** (1.71 g, 3.0 mmol, 96%) as a colorless oil. R_f = 0.60 (EtOAc/PE, 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1 H, 1-H), 7.40–7.20 (m, 18 H, H_{Ar} Bn), 7.20–7.14 (m, 2 H, H_{Ar} Bn), 4.85 (d, J = 12.0 Hz, 1 H, C*H*H Bn), 4.64 (d, J = 11.5 Hz, 1 H, C*H*H Bn), 4.59 (d, J = 11.5 Hz, 1 H, CH*H* Bn), 4.56–4.47 (m, 4 H, CH_2 Bn, CH*H* Bn, C*H*H Bn), 4.37 (d, J = 10.9 Hz, 1 H, CH*H* Bn), 4.02 (dd, J = 2.9, 5.8 Hz, 1 H, 3-H), 3.89 (d, J = 5.9 Hz, 1 H, 2-H), 3.86–3.78 (m, 2 H, 4-H, 6a-H), 3.75–3.67 (m, 2 H, 5-H, 6b-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2 (CH-1), 137.7, 137.5, 137.4, 137.3 (4×C_q Bn), 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.0, 128.0, 127.9 (CH_{Ar} Bn), 80.0 (C-2), 79.9 (C-3), 76.7 (C-4), 74.3, 74.0, 73.6, 73.3 (4×CH_2 Bn), 69.5 (C-6), 60.8 (C-5) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3064, 3032, 2865, 2096, 1727, 1496, 1454, 1328, 1265, 1211, 1072, 1027, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = 3.8 (c = 10.2, $CHCl_3$). HRMS: calcd. for $[C_{34}H_{35}N_3O_5 + Na]^+$ 588.2474 [M + Na]$^+$; found 588.2466.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-D-*glycero*-D-*ido*-heptonamide (121): Subjecting azido aldehyde **120** (1.01 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced **121** (655 mg, 0.74 mmol, 73%). R_f = 0.50 (EtOAc/toluene, 1:2). ^{1}H NMR (500 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 7.44–7.16 [m, 21 H, H_{Ar} Bn, C(O)NH], 5.85–5.74 (m, 1 H, =CH pentenyl), 4.97 (dd, J = 13.5, 34.2 Hz, 2 H, =CH_2 pentenyl), 4.86–3.43 (m, 15 H, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 3.25 (t, J = 6.6 Hz, 2 H, CH_2-5 pentyl), 3.02–2.87 (m, 4 H, NCH_2-1 pentyl, OCH_2-Ada), 2.50–2.21 (m, 4 H, 2×CH_2 pentenyl), 1.95 (s, 3 H, 3×CH Ada), 1.67 (dd, J = 11.9, 32.0 Hz, 6 H, 3×CH_2 Ada), 1.52 (d, J = 1.9 Hz, 6 H, 3×CH_2 Ada), 1.43–1.34 (m, 2 H, CH_2 pentyl), 1.20–1.07 (m, 4 H, 2×CH_2 pentyl) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 174.5 (NC=O pentenyl), 168.2 [NHC(O)-1], 138.3, 137.8, 137.6, 137.2 (4×C_q Bn), 137.4 (=CH pentenyl), 128.5, 128.5, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7 (CH_{Ar} Bn), 115.3 (=CH_2 pentenyl), 82.0 (OCH_2-Ada), 73.4, 73.2, 72.0, 71.5 (CH_2-5 pentyl), 70.9, 68.8 (C-7), 39.8 (CH_2 Ada), 39.4 (NCH_2-1 pentyl), 37.4 (CH_2 Ada), 34.2 (C_q Ada), 33.2, 29.2, 29.2, 29.1 (2×CH_2 pentenyl, 2×CH_2 pentyl), 28.4 (CH Ada), 23.5 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3352, 2902, 2849, 1667, 1541, 1454, 1365, 1209, 1090, 909, 731, 697 cm^{-1}. $[\alpha]_D^{20}$ = 11.1 (c = 3.8, $CHCl_3$). HRMS: calcd. for $[C_{56}H_{70}N_2O_7 + H]^+$ 883.5256 [M + H]$^+$; found 883.5263.

1,1,3,3-Tetramethylbutyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-D-*glycero*-D-*ido*-heptonamide (122): Subjecting azido aldehyde **120** (1.01 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced **122** (625 mg, 0.82 mmol, 81%). R_f = 0.48 (EtOAc/toluene, 1:3). ^{1}H NMR (400 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 7.44–7.22 (m, 20 H, H_{Ar} Bn), 7.08 [s, 1 H, C(O)NH], 5.95–5.80 (m, 1 H, =CH pentenyl), 5.04 (dd, J = 13.1, 25.0 Hz, 2 H, =CH_2 pentenyl), 4.86–3.53 (m, 15 H, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 2.50–2.26 (m, 4 H, 2×CH_2 pentenyl), 1.88–1.52 (m, 2 H, CH_2-2 tMB), 1.23 (s, 6 H, 2×CH_3 tMB), 0.92 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 174.7 (NC=O pentenyl), 167.0 [NHC(O)-1], 138.4, 137.7, 137.6, 137.4 (4×C_q Bn), 137.4 (=CH pentenyl), 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9 (CH_{Ar} Bn), 115.2 (=CH_2 pentenyl), 75.1, 73.7, 73.2, 71.5, 70.6, 68.8, 65.2, 55.3 (NHC_q-1 tMB), 51.3 (CH_2-2 tMB), 33.3 (CH_2 pentenyl), 31.5 (CH_3-4, 2×CH_3 tMB), 29.2 (CH_2 pentenyl), 29.4, 28.5 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3363, 2950, 1667, 1531, 1454, 1366, 1208, 1073, 1027, 911, 734, 697 cm^{-1}. $[\alpha]_D^{20}$ = 6.6 (c = 2.8, $CHCl_3$). HRMS:; calcd. for $[C_{48}H_{60}N_2O_6 + H]^+$ 761.4524 [M + H]$^+$; found 461.4529.

Pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-D-*glycero*-D-*ido*-heptonamide (123): Subjecting azido aldehyde **120** (1.01 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced **123** (556 mg, 0.77 mmol, 77%). R_f = 0.45 (EtOAc/toluene, 1:2). ^{1}H NMR (400 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 7.45–7.16 [m, 21 H, H_{Ar} Bn, C(O)NH], 5.90–5.71 (m, 1 H, =CH pentenyl), 4.97 (dd, J = 13.6, 28.1 Hz, 2 H, =CH_2 pentenyl), 4.87–3.29 (m, 15 H, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 3.08–2.87 (m, 2 H, NCH_2-1 pentyl), 2.56–2.20 (m, 4 H, 2×CH_2 pentenyl), 1.24–0.97 (m, 6 H, 3×CH_2 pentyl), 0.79 (t, J = 7.1 Hz, 3 H, CH_3 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 174.5 (NC=O pentenyl), 168.2 [NHC(O)-1], 138.3, 137.7, 137.6, 137.1 (4×C_q Bn), 137.4 (=CH pentenyl), 128.5, 128.4, 128.4, 128.2, 128.0, 128.0, 127.9, 127.7, 127.6 (CH_{Ar} Bn), 115.3 (=CH_2 pentenyl), 77.7, 76.0, 73.4, 73.2, 71.9, 70.9, 68.8 (C-7), 39.4 (NCH_2-1 pentyl), 33.1 [NC(O)*C*H_2 pentenyl], 29.1, 29.0, 28.9, 22.3 (CH_2 pentenyl, 3×CH_2 pentyl),

14.1 (CH_3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3351, 2929, 1667, 1540, 1454, 1367, 1208, 1071, 1027, 910, 732, 696 cm^{-1}. $[\alpha]_D^{20}$ = 16.0 (c = 3.5, $CHCl_3$). HRMS: calcd. for $[C_{45}H_{54}N_2O_6 + H]^+$ 719.4055 $[M + H]^+$; found 719.4060.

5-(Adamantan-1-yl-methoxy)pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonamide (124): Compound **124** (585 mg, 0.73 mmol, 99%) was synthesized from **121** (0.74 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.22 (EtOAc/toluene, 1:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 [t, J = 5.0 Hz, 1 H, C(O)NH], 7.55 (s, 1 H, NH), 7.41–7.00 (m, 20 H, H_{Ar} Bn), 4.94 (d, J = 10.9 Hz, 1 H, C*H*H Bn), 4.90 (d, J = 11.2 Hz, 1 H, C*H*H Bn), 4.80 (d, J = 10.9 Hz, 1 H, CH*H* Bn), 4.76–4.67 (m, 3 H, 2-H, CH*H* Bn, C*H*H Bn), 4.58–4.43 (m, 3 H, 3-H, CH_2 Bn), 4.36 (d, J = 11.0 Hz, 1 H, CH*H* Bn), 3.80–3.64 (m, 4 H), 3.59–3.48 (m, 1 H, 6-H), 3.28 (t, J = 6.5 Hz, 2 H, CH_2-5 pentyl), 3.20 (dt, J = 6.8, 20.8 Hz, 2 H, NCH_2-1 pentyl), 2.91 (s, 2 H, OCH_2-Ada), 1.93 (s, 3 H, 3×CH Ada), 1.65 (dd, J = 12.0, 27.5 Hz, 6 H, 3×CH_2 Ada), 1.53–1.39 (m, 11 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.31–1.22 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7 [C(O)-1], 137.7, 137.2, 136.8, 136.6 (4×C_q Bn), 128.6, 128.4, 128.4, 128.4, 128.3, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8 (CH_{Ar} Bn), 81.8 (OCH_2-Ada), 80.9, 76.9, 76.7 (C-3, C-4, C-5), 75.1, 74.6, 73.1 (CH_2 Bn), 71.2 (CH_2-5 pentyl), 66.6 (C-7), 55.8 (C-6), 54.5 (C-2), 39.8 (NCH_2-1 pentyl), 39.6 (CH_2 Ada), 37.1 (CH_2 Ada), 34.0 (C_q Ada), 29.1, 28.8, 28.2 (CH Ada), 23.5 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 2901, 2848, 1679, 1545, 1497, 1453, 1362, 1210, 1155, 1067, 1027, 909, 730, 697 cm^{-1}. $[\alpha]_D^{20}$ = 28.1 (c = 9.1, $CHCl_3$). HRMS: calcd. for $[C_{51}H_{64}N_2O_6 + H]^+$ 801.4837 $[M + H]^+$; found 801.4839.

1,1,3,3-Tetramethylbutyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonamide (125): Compound **125** (468 mg, 0.69 mmol, 90%) was synthesized from **122** (0.77 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.34 (EtOAc/toluene, 1:3). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 [s, 1 H, C(O)NH], 7.43–7.01 (m, 20 H, H_{Ar} Bn), 4.96–4.89 (m, 2 H, 2×C*H*H Bn), 4.86 (d, J = 10.5 Hz, 1 H, CH*H* Bn), 4.80 (d, J = 11.3 Hz, 1 H, CH*H* Bn), 4.76 (d, J = 10.8 Hz, 1 H, C*H*H Bn), 4.58 (d, J = 12.4 Hz, 1 H, C*H*H Bn), 4.53 (d, J = 12.4 Hz, 1 H, CH*H* Bn), 4.47–4.38 (m, 3 H, CH*H* Bn, 2-H, 3-H), 3.75–3.70 (m, 3 H, 5-H, CH_2-7), 3.63 (dd, J = 8.8 Hz, 1 H, 4-H), 3.38 (dt, J = 5.5, 10.8 Hz, 1 H, 6-H), 1.70 (d, J = 14.9 Hz, 1 H, C*H*H-2 tMB), 1.47 (d, J = 14.9 Hz, 1 H, CH*H*-2 tMB), 1.27 (d, J = 10.0 Hz, 6 H, 2×CH_3 tMB), 0.87 (s, 9 H, 2×CH_3, CH_3-4 tMB) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8 [NHC(O)-1], 137.9, 137.2, 136.9, 136.6 (4×C_q Bn), 128.8, 128.7, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8 (4×C_q Bn), 81.9 (C-4), 77.7 (C-3), 77.5 (C-5), 75.5, 75.4, 75.2, 73.3 (4×CH_2 Bn), 67.2 (C-7), 56.1 (C-6), 56.0 (NHC_q-1 tMB), 55.1 (C-2), 51.8 (CH_2-2 tMB), 31.5 (CH_3-4, 2×CH_3 tMB), 29.4, 28.5 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3327, 3032, 2951, 1680, 1637, 1543, 1454, 1366, 1223, 1153, 1067, 1027, 910, 731, 697 cm^{-1}. $[\alpha]_D^{20}$ = 33.7 (c = 4.3, $CHCl_3$). HRMS: calcd. for $[C_{43}H_{54}N_2O_5 + H]^+$ 679.4105 $[M + H]^+$; found 679.4105.

Pentyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6–2,6-imino-D-*glycero*-D-*ido*-heptonamide (126): Compound **126** (459 mg, 0.72 mmol, 95%) was synthesized from **123** (0.76 mmol) by deprotection of the pent-4-enamide (General Procedure D). R_f = 0.22 (EtOAc/toluene, 1:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 [t, J = 5.5 Hz, 1 H, C(O)NH], 7.33–7.12 (m, 20 H, H_{Ar} Bn), 4.84 (d, J = 11.1 Hz, 1 H, C*H*H Bn), 4.77–4.72 (m, 3 H, 2×C*H*H Bn, CH*H* Bn), 4.68 (d, J = 11.3 Hz, 1 H, CH*H* Bn), 4.58 (d, J = 12.1 Hz, 1 H, C*H*H Bn), 4.47–4.41 (m, 2 H, CH*H* Bn, CH*H* Bn), 4.02 (dd, J = 5.0, 8.8 Hz, 1 H, 3-H), 3.70 (dd, J = 7.6, 8.9 Hz, 1 H, 4-H), 3.66 (d, J = 5.0 Hz, 1 H, 2-H), 3.62 (dd, J = 2.7, 9.7 Hz, 1 H, 7a-H), 3.51 (dd, J = 6.1, 9.7 Hz, 1 H, 7b-H), 3.41 (dd, J = 7.7, 9.7 Hz, 1 H, 5-H), 3.33–3.12 (m, 2 H, CH_2-1 pentyl), 3.06–2.98 (m, 1 H, 6-H), 2.85 (s, 1 H, NH), 1.47–1.38 (m, 2 H, CH_2-2 pentyl), 1.32–1.17 (m, 4 H, 2×CH_2 pentyl), 0.85 (t, J = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8 [NHC(O)-1], 138.4, 138.3, 138.1, 137.4 (4×C_q Bn), 128.6, 128.4, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6 (4×CH_2 Bn), 82.8 (C-4), 79.7 (C-3), 79.6 (C-5), 74.9, 74.5, 74.0, 72.9 (4×CH_2 Bn), 69.9 (C-7), 56.2 (C-2), 55.0 (C-6), 39.2 (CH_2-1 pentyl), 29.2 (CH_2-2 pentyl), 29.1, 22.3 (2×CH_2 pentyl), 14.0 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3344, 2929, 2861, 1667, 1532, 1497, 1454, 1362, 1209, 1066, 1027, 909, 733, 696 cm^{-1}. $[\alpha]_D^{20}$ = 35.4 (c = 4.9, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{48}N_2O_5 + H]^+$ 637.3636 $[M + H]^+$; found 637.3632.

5-(Adamantan-1-yl-methoxy)pentyl 2,6-Dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonamide (127): Compound **127** (23 mg, 52 μmol, 36%) was synthesized from **124** (144 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.14 ($MeOH/CH_2Cl_2$, 1:6.6 + 2% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 8.06–8.03 {m, 1 H, [C(O)N]}, 3.86 (dd, J = 3.1, 11.2 Hz, 1 H, 7a-H), 3.79 (d, J = 5.7 Hz, 1 H, 2-H), 3.72 (dd, J = 5.7, 9.5 Hz, 1 H, 3-H), 3.63 (dd, J = 6.4, 11.2 Hz, 1 H, 7b-H), 3.51 (dd, J = 8.7, 9.5 Hz, 1 H, 4-H), 3.39 (t, J = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.29–3.19 (m, 3 H, 5-H, NCH_2-1 pentyl), 2.97 (s, 2 H, OCH_2-Ada), 2.92 (ddd, J = 3.1, 6.4, 9.6 Hz, 1 H, 6-H), 1.94 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 11.8, 31.8 Hz, 6 H, 3×CH_2 Ada), 1.63–1.51 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.46–1.36 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 172.4 [C(O)-1], 83.2 (OCH_2-Ada), 76.2 (C-4), 73.0 (C-3), 72.6 (CH_2-5 pentyl), 72.6 (C-5), 62.3 (C-7), 59.3 (C-6), 58.3 (C-2), 41.0 (CH_2 Ada), 40.3 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.4, 30.4 (2×CH_2 pentyl), 29.9 (CH Ada), 24.9 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3304, 2902, 2848, 1643, 1454, 1052 cm^{-1}. $[\alpha]_D^{20}$ = 18.7 (c = 0.5, MeOH). HRMS: calcd. for $[C_{23}H_{40}N_2O_6 + H]^+$ 441.2959 $[M + H]^+$; found 441.2956.

5-(Adamantan-1-yl-methoxy)pentyl 2,6-Butylimino-2,6-dideoxy-D-*glycero*-D-*ido*-heptonamide (128): Compound **128** (66 mg, 133 μmol, 92%) was synthesized in two steps from **124** (144 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (N-alkylated penultimate) = 0.64 (EtOAc/toluene, 1:2). ^1H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.18–2.92 (m, 15 H, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7, 2×NCH_2, OCH_2-Ada, CH_2-5 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.82–1.51 (m, 18 H, 6×CH_2 Ada, 3×CH_2 pentyl/butyl), 1.51–1.25 (m, 4 H, 2×CH_2 pentyl/butyl), 1.06–0.93 (m, 3 H, CH_3 butyl) ppm. ^{13}C NMR (100 MHz, MeOD, collapsed iminosugar signals): δ = 83.2 (OCH_2-Ada), 74.8, 74.8, 72.7 (CH_2-5 pentyl), 70.1, 70.0, 64.1, 41.0 (CH_2 Ada), 40.6 (NCH_2-1 pentyl), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 29.9 (CH Ada), 30.4, 30.2, 24.9, 21.3 (CH_2 pentyl/butyl), 14.2 (CH_3 butyl) ppm. $[\alpha]_D^{20}$ = 8.6 (c = 0.7, MeOH). IR (thin film): $\tilde{\nu}_{max}$ = 3344, 2901, 2848, 1668, 1652, 1456, 1360, 1093, 1027 cm^{-1}. HRMS: calcd. for $[C_{27}H_{48}N_2O_6 + H]^+$ 497.3585 $[M + H]^+$; found 497.3581.

5-(Adamantan-1-yl-methoxy)pentyl 2,6-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,6-dideoxy-D-*glycero*-D-*ido*-heptonamide (129): Compound **129** (59 mg, 87 μmol, 60%) was synthesized in two steps from **124** (145 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (N-alkylated penultimate) = 0.69 (EtOAc/toluene, 1:2). ^1H NMR

(400 MHz, MeOD, collapsed iminosugar signals): δ = 3.94–3.33 (m, 11 H, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7, 2×CH_2-5 pentyl), 3.29–3.08 [m, 2 H, C(O)NCH_2-1 penty], 2.98–2.91 (s, 5 H, 2×OCH_2-Ada, NC*H*H-1 pentyl), 2.88–2.78 (m, 1 H, NCH*H*-1 pentyl), 1.94 (s, 6 H, 6×CH Ada), 1.81–1.47 (m, 20 H, 6×CH_2 Ada, 4×CH_2 pentyl), 1.46–1.31 (m, 4 H, 2× CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD, collapsed iminosugar signals): δ = 83.2, 83.2 (2×OCH_2-Ada), 76.0 (C-4), 72.7, 72.6 (2×CH_2-5 pentyl), 71.4 (C-3), 71.1 (C-5), 64.5 (C-2), 63.9 (C-6), 59.1 (C-7), 50.9 (NCH_2-1 pentyl), 41.0 (2×CH_2 Ada), 40.3 [C(O)NCH_2-1 pentyl], 38.5 (2×CH_2 Ada), 35.3 (2×C_q Ada), 30.7, 30.5, 30.4 (CH_2), 29.9 (2×CH Ada), 28.3 (CH_2), 25.1, 24.9 (2×CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3367, 2901, 2848, 1638, 1455, 1109 cm^{-1}. $[\alpha]_D^{20}$ = 12.8 (*c* = 0.5, MeOH). HRMS: calcd. for $[C_{39}H_{66}N_2O_7 + H]^+$ 675.4943 $[M + H]^+$; found 675.4942.

1,1,3,3-Tetramethylbutyl 2,6-Dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonamide (130): Compound **130** (20 mg, 63 μmol, 67%) was synthesized from **125** (94 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.21 (MeOH/CH_2Cl_2, 1:6.6 + 2% NH_4OH). ^{1}H NMR (400 MHz, MeOD): δ = 3.88 (dd, *J* = 3.2, 11.3 Hz, 1 H, 7a-H), 3.79 (dd, *J* = 5.7, 9.4 Hz, 1 H, 3-H), 3.75 (d, *J* = 5.7 Hz, 1 H, 2-H), 3.67 (dd, *J* = 6.4, 11.3 Hz, 1 H, 7b-H), 3.47 (dd, *J* = 8.7, 9.4 Hz, 1 H, 4-H), 3.27 (d, *J* = 8.7 Hz, 1 H, 5-H), 2.94–2.86 (m, 1 H, 6-H), 1.86 (d, *J* = 14.9 Hz, 1 H, C*HH*-2 tMB), 1.70 (d, *J* = 14.9 Hz, 1 H, CH*H*-2 tMB), 1.43 (d, *J* = 11.8 Hz, 6 H, 2×CH_3 tMB), 1.03 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 169.9 [C(O)-1], 76.1 (C-4), 72.3 (C-3), 72.0 (C-5), 61.7 (C-7), 59.4 (C-6), 58.5 (C-1), 56.6 (NHC_q-1 tMB), 53.0 (CH_2-2 tMB), 32.6 (C_q-3 tMB), 32.1 (CH_3-4, 2×CH_3 tMB), 29.6, 29.5 (2×CH_3 tMB) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3304, 2955, 2362, 1726, 1651, 1559, 1419, 1366, 1272, 1227, 1119, 1073, 1040 cm^{-1}. $[\alpha]_D^{20}$ = 47.7 (*c* = 0.3, MeOH). HRMS: calcd. for $[C_{15}H_{30}N_2O_5 + H]^+$ 319.2222 $[M + H]^+$; found 319.2229.

1,1,3,3-Tetramethylbutyl 2,6-Butylimino-2,6-dideoxy-D-*glycero*-D-*ido*-heptonamide (131): Compound **131** (30 mg, 80 μmol, 82%) was synthesized in two steps from **125** (97 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (*N*-alkylated penultimate) = 0.70 (EtOAc/toluene, 1:3). ^{1}H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.01–3.39 (m, 7 H, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 3.06–3.02 (s, 2 H, NCH_2 butyl), 1.84–1.73 (m, 2 H, CH_2-2 tMB), 1.71–1.24 (m, 8 H, 2×CH_3 tMB, 2×CH_2 butyl), 1.03 (s, 9 H, CH_3-4, 2×CH_3 tMB), 0.98 (t, *J* = 7.4 Hz, 3 H, CH_3 butyl) ppm. ^{13}C NMR (101 MHz, MeOD, collapsed iminosugar signals): δ = 70.4, 64.8, 63.2, 56.9 (NHC_q-1 tMB), 54.0, 53.7, 52.9 (CH_2-2 tMB), 33.7 (CH_2 butyl), 32.5 (C_q-3 tMB), 32.1 (CH_3-4, 2×CH_3 tMB), 29.4, 29.3 (2×CH_3 tMB), 21.4 (CH_2 butyl), 14.3 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3327, 2959, 1668, 1652, 1458, 1366, 1227, 1051 cm^{-1}. $[\alpha]_D^{20}$ = 22.2 (*c* = 0.4, MeOH). HRMS: calcd. for $[C_{19}H_{38}N_2O_5 + H]^+$ 375.2853 $[M + H]^+$; found 375.2854.

1,1,3,3-Tetramethylbutyl 2,6-[5-(Adamantan-1-yl-methoxy)pentyl]-imino-2,6-dideoxy-D-*glycero*-D-*ido*-heptonamide (132): Compound **132** (33 mg, 60 μmol, 54%) was synthesized in two steps from **125** (111 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (*N*-alkylated penultimate) = 0.74 (EtOAc/toluene, 1:3). ^{1}H NMR (400 MHz, MeOD): δ = 3.89 (dd, *J* = 3.5, 11.8 Hz, 1 H, 7a-H), 3.78 (dd, *J* = 6.4, 11.8 Hz, 1 H, 7b-H), 3.68 (dd, *J* = 6.0, 9.6 Hz, 1 H, 3-H), 3.62 (d, *J* = 5.9 Hz, 1 H, 2-H), 3.58–3.51 (m, 1 H, 4-H), 3.39 (t, *J* = 6.3 Hz, 2 H, CH_2-5 pentyl), 3.37–3.32 (m, 1 H, 5-H), 3.06–2.98 (m, 1 H, 6-H), 2.97 (s, 2 H, OCH_2-Ada), 2.91–2.81 (m, 1 H, NC*H*H-1 pentyl), 2.76–2.65 (m, 1 H, NCH*H*-1 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.85 (d, *J* = 14.8 Hz, 1 H, C*HH*-2 tMB), 1.80–1.64 (m, 7 H, 3×CH_2 Ada, CH*H*-2 tMB), 1.64–1.51 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.47–1.34 (m, 8 H, CH_2-3 pentyl, 2×CH_3 tMB), 1.03 (s, 9 H, CH_3-4, 2×CH_3 tMB) ppm. ^{13}C NMR (101 MHz, MeOD): δ = 83.3 (OCH_2-Ada), 77.7 (C-4), 72.7 (CH_2-5 pentyl), 71.6, 71.4 (C-3, C-5), 63.6 (C-6), 63.1 (C-2), 60.0 (C-7), 56.3 (NHC_q-1 tMB), 53.0 (CH_2-2 tMB), 48.9 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 33.6 (C_q-3 tMB), 32.6 (CH_2 pentyl), 32.2 (CH_3-4, 2×CH_3 tMB), 30.8 (CH_2 pentyl), 29.9 (CH Ada), 29.5, 29.2 (2×CH_3 tMB), 25.2 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3377, 2902, 2849, 1651, 1424, 1366, 1227, 1157, 1098 cm^{-1}. $[\alpha]_D^{20}$ = 24.8 (*c* = 0.4, MeOH). HRMS: calcd. for $[C_{31}H_{56}N_2O_6 + H]^+$ 553.4211 $[M + H]^+$; found 553.4208.

Pentyl 2,6-Dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonamide (133): Compound **133** (20 mg, 72 μmol, 77%) was synthesized from **126** (93 μmol) by deprotection of the benzyl ethers (appropriate method in General Procedure F). R_f = 0.13 (MeOH/CH_2Cl_2, 1:6.6 + 2% NH_4OH). ^{1}H NMR (400 MHz, MeOD): δ = 3.90 (d, *J* = 5.7 Hz, 1 H, 2-H), 3.87 (dd, *J* = 3.2, 11.4 Hz, 1 H, 7a-H), 3.78 (dd, *J* = 5.7, 9.4 Hz, 1 H, 3-H), 3.74–3.70 (dd, *J* = 6.1, 11.4 Hz, 1 H, 7b-H), 3.52 (dd, *J* = 8.5, 9.4 Hz, 1 H, 4-H), 3.35–3.30 (m, 1 H, 5-H), 3.30–3.17 (m, 2 H, NCH_2-1 pentyl), 3.09 (ddd, *J* = 3.2, 6.1, 9.6 Hz, 1 H, 6-H), 1.59–1.50 (m, 2 H, CH_2-2 pentyl), 1.40–1.27 (m, 4 H, 2×CH_2 pentyl), 0.92 (t, *J* = 7.0 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 169.4 [C(O)-1], 74.3 (C-4), 70.6 (C-3), 70.2 (C-5), 59.9 (C-7), 57.9 (C-6), 56.5 (C-2), 38.9 (NCH_2-1 pentyl), 28.8, 28.7, 22.0 (3×CH_2 pentyl), 12.9 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3289, 2957, 2929, 1729, 1651, 1558, 1454, 1274, 1074, 1037 cm^{-1}. $[\alpha]_D^{20}$ = 35.9 (*c* = 0.4, MeOH). HRMS: calcd. for $[C_{12}H_{24}N_2O_5 + H]^+$ 277.1758 $[M + H]^+$; found 277.1759.

Pentyl 2,6-Butylimino-2,6-dideoxy-D-*glycero*-D-*ido*-heptonamide (134): Compound **134** (23 mg, 69 μmol, 71%) was synthesized in two steps from **126** (97 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (*N*-alkylated penultimate) = 0.64 (EtOAc/toluene, 1:2). ^{1}H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.18–3.44 (m, 7 H, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 3.30–2.87 (m, 4 H, 2×NCH_2 pentyl/butyl), 1.84–1.28 (m, 10 H, 5×CH_2 pentyl/butyl), 0.98 (t, *J* = 7.4 Hz, 3 H, CH_3 butyl), 0.92 (t, *J* = 6.2 Hz, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD, collapsed iminosugar signals): δ = 73.3, 68.6, 63.7, 62.6, 39.1, 39.0, 28.8, 28.5, 22.0, 19.8, 12.9 (CH_3-5 pentyl), 12.7 (CH_3 butyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3323, 2960, 1652, 1460, 1030 cm^{-1}. $[\alpha]_D^{20}$ = 13.0 (*c* = 0.2, MeOH). HRMS: calcd. for $[C_{16}H_{32}N_2O_5 + H]^+$ 333.2384 $[M + H]^+$; found 333.2385.

Pentyl 2,6-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,6-dideoxy-D-*glycero*-D-*ido*-heptonamide (135): Compound **135** (40 mg, 78 μmol, 71%) was synthesized in two steps from **126** (110 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f (*N*-alkylated penultimate) = 0.69 (EtOAc/toluene, 1:2). ^{1}H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.31–2.99 (m, 13 H, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7, CH_2-5 pentyl, 2×NCH_2), 2.97 (s, 2 H, OCH_2 Ada), 1.94 (s, 3 H, 3×CH Ada), 1.87–1.28 (m, 18 H, 3×CH_2 Ada, 6×CH_2 pentyl), 0.97–0.85 (m, 3 H, CH_3-5 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD, collapsed iminosugar signals): δ = 83.2 (OCH_2 Ada), 74.7, 72.2 (CH_2-5 pentyl), 69.9, 65.5, 64.0, 41.0 (CH_2 Ada), 40.6 [C(O)NCH_2-1 pentyl], 38.5 (CH_2 Ada), 35.3 (C_q Ada),

29.9 (CH Ada), 30.4, 30.4, 30.1, 26.6, 24.8, 23.6 (6×CH_2 pentyl), 14.5 (CH_3-5 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3328, 2903, 2849, 1668, 1652, 1455, 1093, 1028 cm^{-1}. $[\alpha]_D^{20}$ = 6.8 (*c* = 0.8, MeOH). HRMS: calcd. for $[C_{28}H_{50}N_2O_6 + H]^+$ 511.3742 $[M + H]^+$; found 511.3738.

1-Cyclohexenyl Isocyanide (137): Phorphoryl chloride (1.15 mL, 12.35 mmol) was added dropwise to a cooled (–30 °C), anhydrous solution of known[18] *N*-(1-cyclohexenyl)formamide (**136**; 1.03 g, 8.23 mmol) and Et_3N (5.70 mL, 41.1 mmol) in CH_2Cl_2 (41 mL). The reaction mixture was stirred for 1 h at –30 °C, after which TLC analysis indicated complete consumption of **136**. The dark-brown reaction mixture was quenched by addition of satd. aq. $NaHCO_3$ (5 mL), diluted with Et_2O (100 mL), and washed successively with satd. aq. $NaHCO_3$ (2× 100 mL) and brine (50 mL). The organic phase was dried (Na_2SO_4) and concentrated. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/hexane, 20→100%) to afford **137** (574 mg, 5.35 mmol, 65%) as a colorless oil. Isocyanide **137** was preferably used immediately, but was stable when stored at –20 °C under argon. R_f = 0.85 (**137**), 0.40 (**136**) (EtOAc/PE, 1:1); $KMnO_4$ staining. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.17–5.88 (m, 1 H, =CH-2), 2.26–2.19 (m, 2 H, CH_2 3 or 6), 2.15–2.07 (m, 2 H, CH_2 3 or 6), 1.73–1.65 (m, 2 H, CH_2 4 or 5), 1.61–1.52 (m, 2 H, CH_2 4 or 5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1 (t, J_{CN} = 5.7 Hz, NC), 129.1 (=CH-2), 124.9 (t, J_{CN} = 11.7 Hz, N-C1), 28.6, 24.3 (t, *J* = 1.6 Hz), 21.9, 21.0 ppm.

1-Cyclohexenyl 3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-D-*glycero*-D-*ido*-heptonamide (138): Subjecting azido aldehyde **120** (0.89 mmol) to the tandem SAWU-3CR (General procedure B in MeOH) produced **138** (520 mg, 0.71 mmol, 80%). R_f = 0.50 (EtOAc/toluene, 1:3). ^1H NMR (400 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 8.20 [s, 1 H, C(O)NH], 7.43–7.10 (m, 20 H, H_{Ar} Bn), 5.94–5.72 (m, 2 H, =CH-2 cyclohexenyl, =CH pentenyl), 5.13–4.89 (m, 2 H, =CH_2 pentenyl), 4.87–3.30 (m, 15 H, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 2.52–2.21 (m, 4 H, 2×CH_2 pentenyl), 2.09–1.42 (m, 8 H, 4×CH_2 cyclohexenyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 176.4, 174.6 (2×C=O), 138.2, 137.7, 137.3, 137.1 (4×C_q Bn), 137.4 (=CH pentenyl), 132.3 (C_q-1 cyclohexenyl), 128.7, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6 (CH_{Ar} Bn), 115.3 (=CH_2 pentenyl), 113.3 (=CH-2 cyclohexenyl), 77.7, 75.6, 73.5, 73.2, 71.9, 70.9, 68.7 (C-7), 33.3, 33.1, 29.1, 28.8, 27.6, 24.0, 22.5, 21.9 ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3330, 2927, 1653, 1543, 1497, 1453, 1368, 1209, 1072, 911, 732, 696 cm^{-1}. $[\alpha]_D^{20}$ = 25.4 (*c* = 4.4, $CHCl_3$). HRMS: calcd. for $[C_{46}H_{52}N_2O_6 + H]^+$ 729.3898 $[M + H]^+$; found 729.3902.

3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-D-*glycero*-D-*ido*-heptonic Acid (139): Compound **139** (245 mg, 0.38 mmol, 82%) was synthesized from **138** (0.46 mmol) by isomerization and hydrolysis of the 1-cyclohexenecarboxamide moiety (General Procedure C). R_f = 0.36 (EtOAc/toluene, 1:1 + 5% AcOH). ^1H NMR (400 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 9.83–8.15 (m, 1 H, COOH), 7.43–7.13 (m, 20 H, H_{Ar} Bn), 5.79 (ddd, *J* = 6.2, 10.3, 16.7 Hz, 1 H, =CH pentenyl), 4.97 (dd, *J* = 13.7, 23.2 Hz, 2 H, =CH_2 pentenyl), 4.89–3.16 (m, 15 H, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7), 2.50–2.30 (m, 4 H, 2×CH_2 pentenyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 174.2 (NC=O pentenyl), 169.5 [NHC(O)-1], 137.6, 136.5 (C_q Bn), 137.1 (=CH pentenyl), 128.6, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.7 (CH_{Ar} Bn), 115.5 (=CH_2 pentenyl), 73.2, 56.1, 32.6 [C(O)N*C*H_2 pentenyl], 29.0 (CH_2 pentenyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3031, 2868, 1739, 1652, 1496, 1454, 1367, 1203, 1074, 1027, 912, 736, 698 cm^{-1}. $[\alpha]_D^{20}$ = 11.6 (*c* = 2.8, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{43}NO_7 + H]^+$ 650.3112 $[M + H]^+$; found 650.3114.

3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-(pent-4-enimido)-D-*glycero*-D-*ido*-heptonamide (140): Ethyl chloroformate (25 µL, 0.25 mmol) was added to a cooled (0 °C) solution of **139** (100 mg, 0.15 mmol) and Et_3N (36 µL, 0.26 mmol) in THF (1.5 mL). After stirring for 1 h at 0 °C, aqueous ammonia (0.2 mL, 25%) was added and the reaction was stirred for 1 h at 0 °C. The mixture was diluted with H_2O (20 mL) and extracted with Et_2O (3× 30 mL), and the combined organic layers were dried and concentrated. The residue was purified with silica gel column chromatography (EtOAc/toluene, 0→50%) to afford **140** (64 mg, 0.10 mmol, 64%) as a colorless oil. R_f = 0.52 (EtOAc/toluene, 1:1 + 5% AcOH). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.18 (m, 20 H, H_{Ar} Bn), 6.86 [s, 1 H, C(O)NH], 5.80 (ddt, *J* = 6.5, 10.2, 16.8 Hz, 1 H, =CH pentenyl), 5.06–4.93 (m, 3 H, =CH_2 pentenyl, 2-H), 4.87–4.39 (m, 8 H, 4×CH_2 Bn), 4.36 (dd, *J* = 7.5, 9.8 Hz, 1 H, 3-H), 4.22 (t, *J* = 7.5 Hz, 1 H, 6-H), 3.67 (dd, *J* = 6.8, 9.8 Hz, 1 H, 4-H), 3.64–3.54 (m, 2 H, 5-H, C*H*H-7), 3.46 (dd, *J* = 6.7, 9.7 Hz, 1 H, CH*H*-7), 2.59–2.51 [m, 2 H, C(O)N*C*H_2 pentenyl], 2.42–2.33 (m, 2 H, CH_2 pentenyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2 (NC=O pentenyl), 172.4 [NHC(O)-1], 138.4, 138.4, 137.8, 137.8 (4×C_q Bn), 137.3 (=CH pentenyl), 128.7, 128.6, 128.5, 128.5, 128.1, 128.1, 128.0, 127.8 (CH_{Ar} Bn), 115.5 (=CH_2 pentenyl), 81.9 (C-4), 80.3 (C-5), 75.5 (C-3), 74.8, 74.5, 73.4, 72.4 (4×CH_2 Bn), 70.1 (C-7), 59.5 (C-6), 58.3 (C-2), 32.7 [C(O)N*C*H_2 pentenyl], 29.2 (CH_2 pentenyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3033, 2867, 1695, 1639, 1496, 1454, 1365, 1070, 1028, 914, 735, 698 cm^{-1}. $[\alpha]_D^{20}$ = 47.0 (*c* = 1.3, $CHCl_3$). HRMS: calcd. for $[C_{40}H_{44}N_2O_6 + H]^+$ 649.3272 $[M + H]^+$; found 649.3272.

3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonic Acid (141): Compound **141** (58 mg, 73 µmol, 35%) was synthesized from **139** (0.21 mmol) by deprotection of the pent-4-enamide (General Procedure D). ^1H NMR (400 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 7.56–6.91 (m, 20 H, H_{Ar} Bn), 4.82–3.48 (m, 15 H, 4×CH_2 Bn, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, collapsed iminosugar signals): δ = 138.0, 137.9, 137.8, 137.5 (4×C_q Bn), 128.7, 128.6, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9 (CH_{Ar} Bn), 73.8, 73.3 (CH_2 Bn), 55.9 (C-2), 54.1 (C-6) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3031, 2864, 1635, 1453, 1360, 1323, 1091, 1072, 1026, 910, 733, 697 cm^{-1}. $[\alpha]_D^{20}$ = 26.0 (*c* = 0.9, $CHCl_3$). HRMS: calcd. for $[C_{35}H_{37}NO_6 + H]^+$ 568.2694 $[M + H]^+$; found 568.2690.

3,4,5,7-Tetra-*O*-benzyl-2,6-dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonamide (142): Compound **142** (45 mg, 79 µmol, 79%) was synthesized from **140** (100 µmol) by deprotection of the pent-4-enamide (General Procedure D). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.13 (m, 20 H, H_{Ar} Bn), 6.12 [d, *J* = 1.6 Hz, 1 H, C(O)N*H*H], 5.78 [d, *J* = 1.9 Hz, 1 H, C(O)NH*H*], 4.89 (s, 2 H, CH_2 Bn), 4.86 (d, *J* = 10.6 Hz, 1 H, C*H*H Bn), 4.81 (d, *J* = 10.9 Hz, 1 H, C*H*H Bn), 4.63 (d, *J* = 10.6 Hz, 1 H, CH*H* Bn), 4.55–4.47 (m, 2 H, C*H*H Bn, CH*H* Bn), 4.43 (d, *J* = 11.9 Hz, 1 H, CH*H* Bn), 3.64 (dd, *J* = 2.6, 9.0 Hz, 1 H, 7a-H), 3.62–3.54 (m, 3 H, 3-H, 4-H, 7b-H), 3.50–3.44 (m, 1 H, 5-H), 3.20 (d, *J* = 9.1 Hz, 1 H, 2-H), 2.77 (ddd, *J* = 2.6, 5.2, 9.6 Hz, 1 H, 6-H), 2.27 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1 [NHC(O)-1], 138.5, 138.2, 137.9, 137.8 (4×C_q Bn), 129.1, 128.7, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7 (CH_{Ar} Bn), 87.6, 82.2 (C-3, C-4), 80.0 (C-5), 75.7, 75.3, 75.2, 73.4 (4×CH_2 Bn), 69.5 (C-7), 61.9 (C-2), 58.3 (C-6) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3398, 3031, 2909, 2864, 1668, 1453, 1359, 1149, 1087, 1054, 1027, 735, 696 cm^{-1}. $[\alpha]_D^{20}$ = 29.1 (*c* = 0.9, $CHCl_3$). HRMS: calcd. for $[C_{35}H_{38}N_2O_5 + H]^+$ 567.2853 $[M + H]^+$; found 567.2850.

2,6-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,6-dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonamide (143): Compound **143** (12 mg,

27 μmol, 39%) was synthesized in two steps from **142** (70 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.31 ($MeOH/CH_2Cl_2$, 1:6.5 + 2% NH_4OH). ^1H NMR (400 MHz, MeOD): δ = 3.88 (dd, J = 3.4, 11.8 Hz, 1 H, 7a-H), 3.79 (dd, J = 5.2, 11.8 Hz, 1 H, 7b-H), 3.73 (d, J = 5.7 Hz, 1 H, 2-H), 3.71–3.60 (m, 2 H, 3-H, 4-H), 3.39 (t, J = 6.4 Hz, 2 H, CH_2-5 pentyl), 3.35–3.31 (m, 1 H, 5-H), 3.15–3.08 (m, 1 H, 6-H), 2.97 (s, 2 H, OCH_2-Ada), 2.79–2.74 (m, 2 H, NCH_2-1 pentyl), 1.95 (s, 3 H, 3×CH Ada), 1.72 (dd, J = 11.6, 31.4 Hz, 6 H, 3×CH_2 Ada), 1.64–1.52 (m, 10 H, 3×CH_2 Ada, 2×CH_2 pentyl), 1.44–1.33 (m, 2 H, CH_2-3 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 178.1 [C(O)-1], 83.2 (OCH_2-Ada), 76.8 (C-4), 72.7 (CH_2-5 pentyl), 72.2 (C-5), 71.6 (C-3), 63.8 (C-2), 63.1 (C-6), 60.6 (C-7), 49.9 (NCH_2-1 pentyl), 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.7 (CH_2 pentyl), 29.9 (CH Ada), 29.4 (CH_2 pentyl), 25.2 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3326, 2902, 2848, 1650, 1451, 1158, 1096 cm^{-1}. $[\alpha]_D^{20}$ = 17.5 (c = 0.2, MeOH). HRMS: calcd. for $[C_{23}H_{40}N_2O_6 + H]^+$ 441.2959 $[M + H]^+$; found 441.2956.

2,6-[5-(Adamantan-1-yl-methoxy)pentyl]imino-2,6-dideoxy-2,6-imino-D-*glycero*-D-*ido*-heptonic Acid (144): Compound **144** (6 mg, 14 μmol, 30%) was synthesized in two steps from **141** (45 μmol) through reductive amination with the appropriate aldehyde (General Procedure E) and subsequent benzyl ether deprotection (appropriate method in General Procedure F). R_f = 0.10 ($MeOH/CH_2Cl_2$, 1:3). ^1H NMR (400 MHz, MeOD, collapsed iminosugar signals): δ = 4.12–3.32 (m, 11 H, 2-H, 3-H, 4-H, 5-H, 6-H, CH_2-7, CH_2-5 pentyl, NCH_2), 2.97 (s, 2 H, OCH_2-Ada), 1.95 (s, 3 H), 1.82–1.36 (m, 18 H, 6×CH_2 Ada, 3×CH_2 pentyl) ppm. ^{13}C NMR (100 MHz, MeOD, collapsed iminosugar signals): δ = 83.3 (OCH_2-Ada), 72.3 (CH_2-5 pentyl), 70.1, 69.6, 41.0 (CH_2 Ada), 38.5 (CH_2 Ada), 35.3 (C_q Ada), 30.3, 29.9 (CH Ada), 24.7 (CH_2-3 pentyl) ppm. IR (thin film): $\tilde{\nu}_{max}$ = 3311, 2902, 2848, 1651, 1456, 1398, 1053 cm^{-1}. $[\alpha]_D^{20}$ = 2.3 (c = 0.1, MeOH). HRMS: calcd. for $[C_{23}H_{39}NO_7 + H]^+$ 442.2799 $[M + H]^+$; found 442.2801.

Supporting Information (see footnote on the first page of this article): Copies of NMR spectra ($^1H/^{13}C$) for all new compounds.

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