112. Synthesis of *N*-Acetylallosamine-Derived Disaccharides

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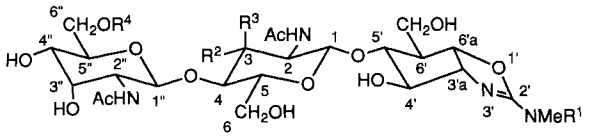
The protected disaccharide **44**, a precursor for the synthesis of allosamidin, was prepared from the glycosyl acceptor **8** and the donors **26**–**28**, best yields being obtained with the trichloroacetimidate **28** (*Scheme 6*). Glycosidation of **8** or of **32** by the triacetylated, less reactive donors **38**–**40** gave the disaccharides **46** and **45**, respectively, in lower yields (*Scheme 7*). Regioselective glycosidation of the diol **35** by the donors **38**–**40** gave **42**, the axial, intramolecularly H-bonded OH–C(3) group reacting exclusively (*Scheme 5*). The glycosyl acceptor **8** was prepared from **9** by reductive opening of the dioxolane ring (*Scheme 3*). The donors **26**–**28** were prepared from the same precursor **9** *via* the hemiacetal **25**. To obtain **9**, the known **10** was de-*N*-acetylated (→ **18**), treated with phthalic anhydride (→ **19**), and benzylated, leading to **9** and **23** (*Schemes 2* and *3*). Saponification of **23**, followed by acetylation also gave **9**. Depending upon the conditions, acetylation of **19** yielded a mixture of **20** and **21** or exclusively **20**. Deacetylation of **20** led to the hydroxyphthalamide **22**. De-*N*-acetylation of the 3-*O*-benzylated α-D-glycosides **11** and **15**, which were both obtained from **10**, was very sluggish and accompanied by partial reduction of the *O*-allyl to an *O*-propyl group (*Scheme 2*). The β-D-glycoside **30** behaved very similarly to **11** and **15**. Reductive ring opening of **31**, derived from **29**, yielded the 3-*O*-acetylated acceptor **32**, while the analogous reaction of the α-D-anomer **20** was accompanied by a rapid 3-*O* →4-*O* acyl migration (→**34**; *Scheme 4*). Reductive ring opening of **21** gave the diol **35**. The triacetylated donors **38**–**40** were obtained from **20** by debenzylidenation, acetylation (→ **36**), and deallylation (→ **37**), followed by either acetylation (→ **38**), treatment with Me_3SiSEt (→ **39**), or Cl_3CCN (→ **40**).

Introduction. – Chitin, a polymer of β-(1–4)-linked *N*-acetyl-D-glucosamine, is the second most abundant polysaccharide in nature. In insects, chitin is one of the main constituent of the cuticle. It plays a critical role at each stage of insect morphogenesis [1] [2], and may thus be a target for rationally designed growth regulators. The metabolism of chitin is controlled by the activity of synthetases, which transfer *N*-acetyl-D-glucosamine to the growing chitin chain, and exo- and endochitinases, which degrade the polymer to chitobiose. Allosamidin (**1**) is the first naturally occurring, strong inhibitor of insect endochitinases. It has been isolated from fermentation broths of *Streptomyces* sp. by *Sakuda et al.* (culture No. *1713*) [3] [4] and by *Somers et al.* (culture *A82516*) [5].



1 R^1 = Me, R^2 = R^4 = H, R^3 = OH
2 R^1 = R^2 = R^4 = H, R^3 = OH
3 R^1 = R^4 = Me, R^2 = H, R^3 = OH
4 R^1 = R^2 = H, R^3 = OH, R^4 = Me
5 R^1 = R^4 = Me, R^2 = OH, R^3 = H
6 R^1 = R^3 = H, R^2 = OH, R^4 = Me

Allosamidin (**1**) is a novel pseudotrisaccharide [6] [7], constituted of a disaccharide unit, derived from β-(1–4)-linked *N*-acetyl-D-allosamine, which is bound to allosamizoline [8][1]), a highly functionalized cyclopentane derivative. Several new allosamidin-type inhibitors of chitinase, termed demethylallosamidin (**2**) [12], methylallosamidin (**3**) [13], methyl *N*-demethylallosamidin (**4**), glucoallosamidin A (**5**), and glucoallosamidin B (**6**) have subsequently been isolated from the mycelium of *Streptomyces sp. SA-684* [14]. Chitinases from different sources are inhibited to a different extent [13–17] by these antibiotics. This emphasizes the interest in a flexible synthesis of allosamidin, giving access, in principle, to a range of analogues and, thereby, to potential insecticides.

Both, *Griffith* and *Danishefsky* [10] and we [18] have reported syntheses of allosamidin (**1**), and we now describe the details of the preparation and reactivity of several allosamine-derived glycosyl donors and acceptors and the synthesis of the disaccharide moiety of **1**.

N-Acetylallosamine had not been found in nature before the isolation of allosamidin [6]. Its chemistry has not been extensively studied [19], although *Jeanloz et al.* [20] have reported an efficient synthesis of *N*-acetylallosamine based on the intramolecular substitution of a 3-mesyloxy by the 2-acetamido group.

The synthesis of the β-(1–4)-linked, *N*-acetylallosamine-derived disaccharide and of allosamidin itself requires the formation of two equatorial 1,2-*trans*-configurated glycosidic bonds. In a dependable way, 1,2-*trans*-glycosides are synthesized from glycosyl donors possessing a participating C(2) substituent. The analogy to *N*-acetyl-D-glucosamine [21] suggests a poor reactivity of OH–C(4) for *N*-acetylallosamine derivatives. A high reactivity of the glycosyl donors is thus required, as it is realized in 2-deoxy-2-phthalimido derivatives. The phthalimido group is compatible with a large range of protecting groups, leaving groups, and promotors, and the 'phthalimido procedure' is characterized by high yields and by a high degree of diastereoselectivity [22–26]. It has been used with very good results for the synthesis of chitobiose derivatives [27] and appeared to be appropriate to our needs, although the transformation of the phthalimido into the *N*-Ac group is not without problems [28].

Allosamidin may be derived from the partially protected allosamizoline derivative **7** [9] (see *Scheme 1*) by regioselective glycosidation with a disaccharide donor **A**. This donor may be prepared by glycosidation of the acceptor **8** with a 2-phthalimido glycosyl donor **B**. The potential leaving group X of the donors **A** and **B** may correspond, *e.g.*, to bromide, chloride, an acyloxy, a thioalkyl, or the trichloroacetamido group. The glycosyl donor **B** and the glycosyl acceptor **8** should both be prepared from the same precursor, the 3-*O*-benzyl-2-phthalimido derivative **9**. The α-D-glycoside was preferred, as it is easily available by a *Fischer*-type glycosidation [29] [21], while the preparation of the β-D-anomer requires a *Koenigs-Knorr*-type glycosidation [30] [21] which is less convenient on a large scale.

In this context, we planned to also investigate the influence of *O*-acyl groups on the reactivity of *N*-phthaloylallosamine-derived donors and acceptors and to prepare analogues of **B**, possessing AcO groups at C(3), C(4), and C(6), and analogues of **8**, unprotected at O–C(3) or possessing an AcO group at C(3).

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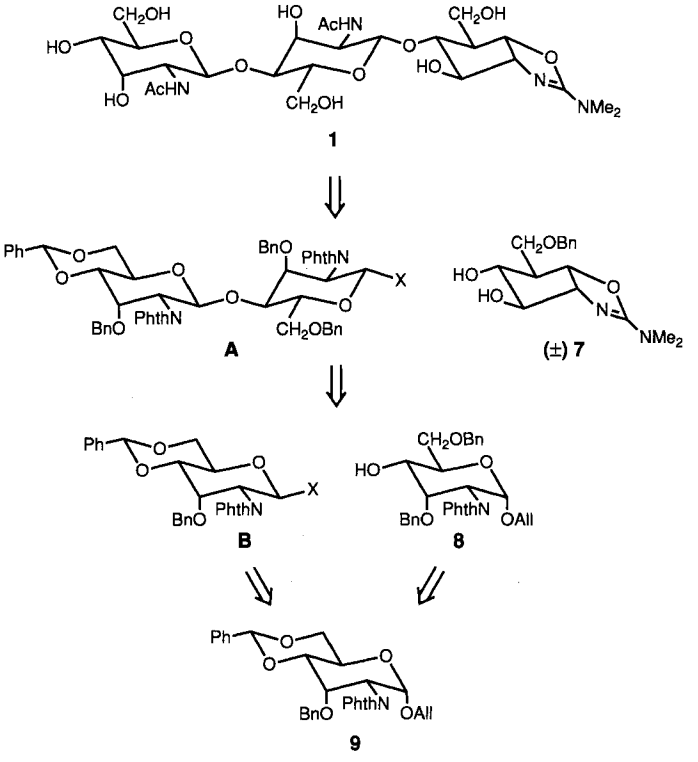
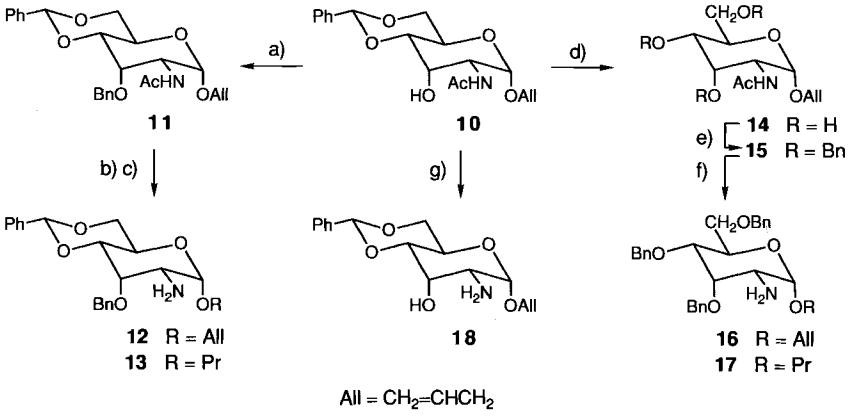
[1]) For the synthesis of allosamizoline, see *Trost* and *van Vranken* [9], *Griffith* and *Danishefsky* [10], and *Tatsuta* and coworkers [11].

Scheme 1



Results and Discussion. – 1. *Glycosyl Acceptors and Donors Derived from 3-O-Benzyl-allosamine.* We intended to prepare **9** *via* the amine **12** (*Scheme 2*), and **12** by deacetylation of **11**, which had been obtained in high yield by *O*-benzylation of **10** [31]. The acetamide **11** proved very resistant to hydrolysis and was recovered in high yield after being heated under reflux with 1M aq. NaOH or after treatment with 10M NaOH in DMSO and thiophenol at 100° [32] or at 140°. Heating **11** with $NH_2NH_2 \cdot H_2O$ [33] at 140° for 5 days gave an inseparable 1.1:1 mixture of **12** and **13** (81%). The reduction of the allyloxy group, presumably by diimide [34], was not significantly decreased by shortening the reaction time to 3 days. Under these conditions, however, hydrazinolysis was incomplete, and 30% of **11** were recovered. The dependence of the hydrolysis of amides upon steric hindrance is well known [32], and the conformational bias of the *trans*-trioxadecalin system may contribute to the difficulty of hydrolysis **11**. Hydrazinolysis of the pyranoside **15**, obtained from **10** by hydrolysis to **14** and benzylation, indeed proceeded faster than the one of **11**. Nonetheless, partial reduction of **15** yielded **16** and **17** (1:1), again as an inseparable mixture. Before investigating the influence of the anomeric configuration (see below), we submitted the hydroxyamide **10** to 1M aq. NaOH under reflux. As described for the analogous methyl glycoside [35], this procedure yielded **18** almost quantitatively, evidencing the participation of the vicinal *cis*-OH group.

Scheme 2



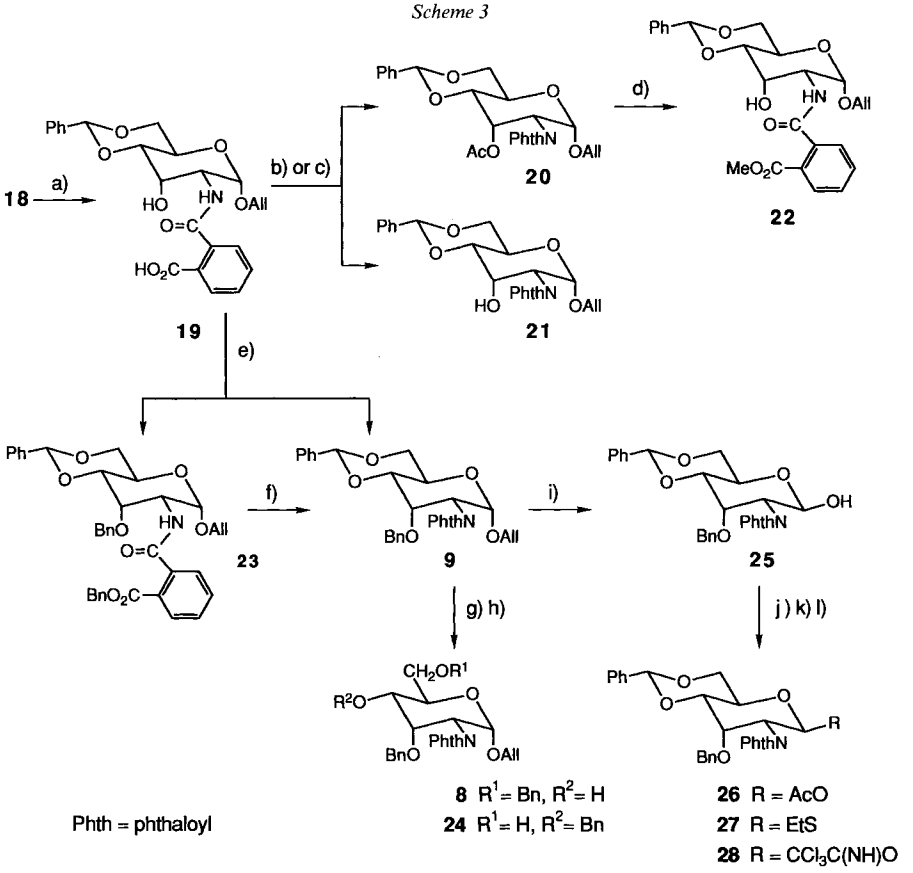
a) BaO, $Ba(OH)_2 \cdot 8\ H_2O$, BnBr, DMF, 4 h, r.t., 92%. b) $NH_2NH_2 \cdot H_2O$, Autoclave, 5 days, 140°, **12**:42%, **13**:39%. c) $NH_2NH_2 \cdot H_2O$, Autoclave, 3 days, 140°, **12**:39%, **13**:26%. d) CH_2Cl_2/80% aq. AcOH 2:1, 50°, 4 h, 95%. e) BaO, $Ba(OH)_2 \cdot 8\ H_2O$, BnBr, DMF, 16 h, r.t., 91%. f) $NH_2NH_2 \cdot H_2O$, Autoclave, 3 days, 140°, **16**:38%, **17**:38%. g) 1M NaOH, 110°, 6 days, 98%.

Treatment of **18** with phthalic anhydride in the presence of Et_3N gave the phthalamide **19** (*Scheme 3*). Acetylation (Ac_2O, pyridine) of **19** yielded the acetylated phthalimide **20** and the hydroxyphthalimide **21**. Apparently, **20** is formed by 3-*O*-acetylation before the pyrroline-dione ring is closed, as **21** proved resistant to a variety of acetylation conditions. Acetylation of **19** in the presence of 4-(dimethylamino)pyridine (4-$(Me_2N)C_5H_4N$) [36], however, yielded only **20** (98%). Selective deacetylation of **20** failed, only leading to **22**, and so did the *O*-benzylation of **21**, but treatment of **19** with $PhCH_2Br$/NaH gave mainly the desired 3-*O*-benzylphthalimide **9** (52%) and the 3-*O*-benzylphthalamide **23** (44%). Hydrolysis of the benzyloxycarbonyl group of **23**, followed by treatment of the crude with Ac_2O yielded 75% of **9**, which is thus available from **19** in an overall yield of 71%.

The mixture **12**/**13** shows an NH absorption at 3380 cm^{-1}. In the ^{1}H-NMR spectrum of **12**/**13**, NH_2 resonates at 1.52 ppm, and H–C(2) exhibits the high-field shift (**12**: 2.9 ppm; **13**: 2.7 ppm) of 2-amino-2-deoxypyranosides. The NMR spectra of **12** show the typical pattern of an allyl group (^{1}H-NMR: *dddd* at 5.94, *dq* at 5.34, and 5.17 ppm; ^{13}C-NMR: *d* at 134.3 and *t* 116.6 ppm), and those of **13** the characteristic pattern of a propyl group (^{1}H-NMR: *m* (2 H) at 1.65 and *t* (3 H) at 0.98 ppm; ^{13}C-NMR: *t* at 23 and *q* at 10.8 ppm). The amino-alcohol **18** absorbs at 3400 cm^{-1}. In its ^{1}H-NMR spectra, OH and NH_2 appear as a *m* at 1.96 ppm; H–C(2) resonates at 3 ppm. The OH absorption at 3460–3440 cm^{-1} in the IR spectrum of **21** is typical for a strongly H-bonded OH group. The phthalimido C=O absorb at 1715 cm^{-1}. In the ^{1}H-NMR spectrum, the signals of the phthalimido group appear as 2 *m* at 7.92–7.89 and at 7.80–7.78 ppm. OH resonates at 6.13 ppm, the low field indicating a strong H-bond. The NH group of the phthalamide **23** absorbs at 3430 cm^{-1}, while the 2 C=O absorb at 1720 and 1660 cm^{-1}. The aromatic H-atom *ortho* to the benzyloxycarbonyl group resonates at 7.96 ppm. NH appears at 6.36 ppm as a large *d*, and the benzylic H of the ester function give rise to an *AB* system at 5.27–5.23 ppm. In the ^{1}H-NMR of **9**, the H–C(1) and H–C(3) signals are shifted to lower fields as compared to, *e.g.*, **23**, appearing at 5.55 and 4.86 ppm, respectively. This deshielding of H–C(3) ($\Delta\delta$ = 0.72 ppm) and H–C(1) ($\Delta\delta$ = 0.87 ppm) must be due to the anisotropy of the phthalimido group, suggesting that the plane of the phthalimido group is almost parallel to the mean plane of the pyranose ring, with dihedral angles H–C(2)–N–C(O) of *ca.* +90 and −90°.

Regioselective, reductive opening of the 2-phenyldioxane ring [37] [38] of **9** should lead to the glycosyl acceptor **8**. *Garegg*'s procedure ($BH_3 \cdot Et_3N$, $AlCl_3$, THF) [39] worked

Scheme 3



a) Phthalic anhydride, Et_3N, MeOH, 30 min, r.t., 95%. b) Pyr., Ac_2O, 18 h, r.t., **20**:54%; **21**:44%. c) Pyr., Ac_2O, DMAP, 18 h, r.t., **20**:98%. d) MeONa, MeOH, 5 h, r.t., 88%. e) BnBr, NaH, DMF, 24 h, r.t., **9**:52%, **23**:44%. f) 1. 1M NaOH, dioxane, 5 h, r.t., 2. Pyr., Ac_2O, 48 h, r.t., 75%. g) 1. $NaBH_3CN$, THF, 2 h, 0°, 2. HCl soln. in Et_2O, **8**:59%, **24**:30%. h) Me_3NBH_3, $AlCl_3$, THF, 14 h, r.t., **8**:84%, **24**:5%; i) 1. (cycloocta-1,5-diene)-bis(methyldiphenylphosphine)iridium hexafluorophosphate, H_2, THF, 3 h, r.t., 2. HgO, $HgCl_2$, acetone/H_2O 9:1, 1 h, r.t., 76%. j) Pyr., Ac_2O, 12 h, r.t., **26**:97%. k) 1. as in j), 2. Me_3SiSEt, TMSOTf, CH_2Cl_2, 12 h, r.t., **27**:51% from **25**. l) CCl_3CN, K_2CO_3, CH_2Cl_2, 6 h, r.t., 77%.

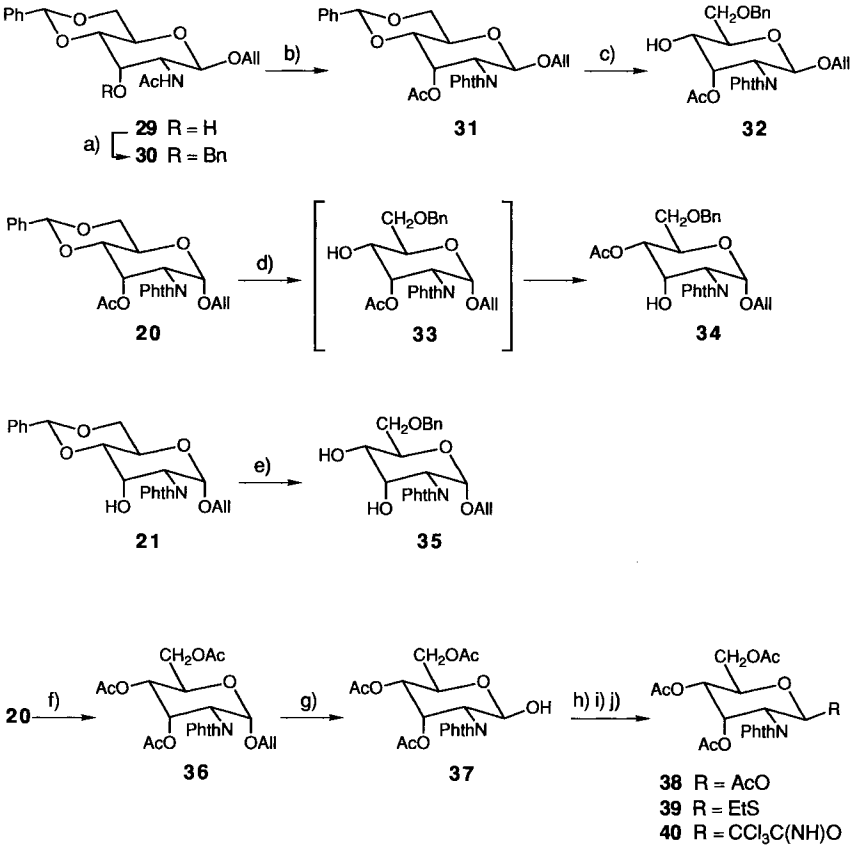
well, and we obtained 84% of **8**, accompanied by only 5% of the regioisomer **24**, while reductive opening with $NaBH_3CN$/HCl [40] yielded only 59% of **8** and 30% of **24** (*Scheme 3*). To obtain the required glycosyl donors, we deprotected **9** by catalytic isomerisation of the allyloxy group, followed by HgO/$HgCl_2$-promoted hydrolysis of the resulting vinyl ethers. A higher yield of the vinyl ethers was realized with [Ir(cycloocta-1,5-diene)$(PMePh_2)_2$]PF_6 [41] rather than with [Rh$(PPh_3)_3$]Cl [42], confirming earlier reports [43]. The equilibrium between the anomeric hemiacetals of 2-deoxy-2-phthalimidohexopyranoses is known to be in favor of the β-D-anomer [44] [45], and only the β-D-anomer **25** was observed. Considering how little is known about glycosidations with allosamine derivatives – a corresponding 3-*O*-acetyl-5,6-*O*-isopropylidenefuranose-derived oxazoline [46] and the 3-*O*-benzyl-4,6-*O*-benzylidenepyranose-derived sulfonyl-

aziridine [47] are the only reported glycosyl donors – we prepared the acetate **26**, the thioglycoside **27** and the trichloroacetimidate **28**. The β-D-acetate **26** was obtained almost quantitatively and treated with Me_3SiSEt and trimethylsilyl triflate (Me_3SiOTf) [48] to form the β-D-thioglycoside **27** (51%). Reaction of **25** with Cl_3CCN and K_2CO_3 [49] gave the crystalline β-D-imidate **28** (77%). Attempts to isolate the corresponding glycosyl bromide and chloride failed; they could be observed by TLC, but were not stable enough to be purified.

The OH group of **8** absorbs at 3690 and 3540 cm^{-1}. The ^{1}H-NMR spectrum of **8** indicates at distorted chair conformation, as shown by $J(4,5) = 7.6$ Hz, presumably due to the 1,3-diaxial interaction of the allyloxy and benzyloxy groups. OH–C(4) resonates at 3.57 ppm as a *d*. The antiperiplanar orientation of O*H*–C(4) and *H*–C(4) is indicated by the large coupling constant ($J = 10.7$ Hz). The IR spectrum of **24** shows OH bands at 3640 and 3570 cm^{-1}. The chemical shift of H–C(1) (5.55 ppm) and of H–C(3) (5.01 ppm) of **24** is in agreement with a similar conformation of the phthalimido group as it was deduced for **9**. OH–C(6) appears at 1.77 ppm as a *dd* ($J = 5.4$ and 7.35 Hz). In the ^{1}H-NMR spectrum of **25**, H–C(1) is strongly deshielded ($\Delta\delta = 0.86$ ppm, as compared to **9**) and resonates at 6.41 ppm as a *dd* ($J(1,2) = 8.75$ Hz, $J(1,OH) = 6.0$ Hz). An upfield shift is observed for H–C(3), which resonates at 4.23 ppm (in **9** at 4.86 ppm, $\Delta\delta = 0.63$ ppm), indicating that only H–C(1) is deshielded by the phthalimido group. A similar difference for the chemical shifts of H–C(1) and H–C(3) is observed for **26–28**, suggesting that in the β-D-series of these allopyranosides, the plane of the phthalimido group is almost perpendicular to the mean plane of the pyranose ring (dihedral angles H–C(2)–N–C(O) of *ca.* 0 and 180°). The imino group of **28** is characterized by IR bands at 3340 (NH) and at 1680 cm^{-1} (C=N); in the ^{1}H-NMR spectrum, NH resonates at 8.78 ppm, and H–C(1) appears as a *d* ($J(1,2) = 9.1$ Hz) at 7.36 ppm. In the ^{13}C-NMR spectrum, the C=NH signal is a *s* at 159.9 ppm, and C(1) resonates at 93 ppm. H–C(1) of **27** appears at 6.17 ppm as a *d* ($J(1,2) = 10.9$ Hz). The signals of the *S*-ethyl group are at 2.75 and 1.27 ppm in the ^{1}H-NMR spectrum, and at 24.5 and 14.8 ppm in the ^{13}C-NMR spectrum.

2. *Glycosyl Acceptors and Donors Derived from 3-O-Acetylallosamine: Partially Protected Acceptors.* One expects the 2-acetamido group in β-D-anomers to be less hindered then in α-D-anomers, but the benzyl ether **30** (*Scheme 4*) obtained from **29** [31] in a similar way as **11** from **10**, was about as resistant to hydrolysis as **11**. Similarly as for **11**, hydrazinolysis of **30** gave a 1:1 mixture of allyl and propyl glycosides. The preparation of **31** from **29** was, however, straightforward. Similarly to **10**, **29** was deacetylated with 1M NaOH. Treatment of the resulting amino-alcohol with phthalic anhydride, followed by Ac_2O/pyridine, gave **31** in high yields, even in the absence of 4-$(Me_2N)C_5H_4N$. The dioxane ring of **31** was reductively opened with $NaBH_3CN$/HCl in Et_2O, and the glycosyl acceptor **32** was obtained in good yields. It was not possible to obtain the analogous α-D-configurated glycosyl acceptor **33**. Although the same regioselectivity of the reductive ring opening was observed when **20** was subjected to similar reaction conditions, a concomitant migration of the Ac group led to **34**. This migration occurred very readily, even at 0°, and may be explained by the steric hindrance which destabilizes **33** relative to **34**, and by a strong H-bond between O*H*–C(3) and the allyloxy or the phthalimido group, which stabilizes the product **34**. The glycosyl acceptor **35**, requiring a subsequent regioselective glycosidation, was prepared by reductive ring opening of **21** (75%). To examine if glycosidation at OH–C(4) of *N*-phthaloylated allosamine derivatives is possible with more easily available, but less reactive glycosyl donors, we prepared **38–40**. Hydrolysis of **20**, followed by acetylation gave **36** in high yields. As detailed for the preparation of **25**, de-*O*-allylation of **36** proceeded well to yield **37** as a single anomer. The imidate **40** decomposed slightly during chromatography. Formation of the acetate **38** was straightforward, and the acetate was readily transformed into the thioglycoside **39**.

Scheme 4



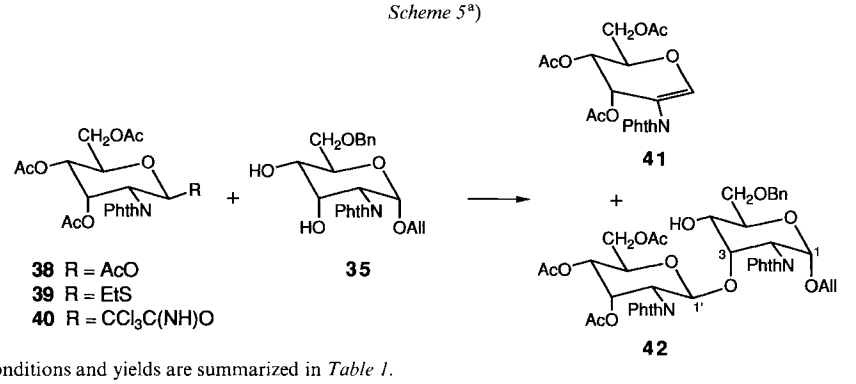
a) BaO, $Ba(OH)_2 \cdot 8H_2O$, BnBr, DMF, 4 h, r.t., 95%. b) 1. 1M NaOH, 110°, 6 days, 2. Phthalic anhydride, NEt_3, MeOH, 30 min, r.t., 3. Pyr., Ac_2O, 18 h, r.t., 95% from **29**. c) 1. $NaBH_3CN$, THF, 2 h, 0°, 2. HCl soln. in Et_2O, 83%. d) As c), 63%. e) As c), 76%. f) 1. CH_2Cl_2/80% aq. AcOH 2:1, 50°, 5 h, 2. Pyr., Ac_2O, 12 h, r.t., 96%. g) 1. (cycloocta-1,5-diene)bis(methyldiphenylphosphine)iridium hexafluorophosphate, H_2, THF, 3 h, r.t., 2. HgO, $HgCl_2$, acetone/H_2O 9:1, 1 h, r.t., 78%. h) Pyr., Ac_2O, 12 h, r.t., **38**: 98%. i) 1. As in h), 2. Me_3SiSEt, TMSOTf, 4 Å, CH_2Cl_2, 12 h, r.t., **39**: 75% from **37**. j) CCl_3CN, K_2CO_3, CH_2Cl_2, 6 h, r.t., **40**: 74%.

The OH group of **32** absorbs at 3590 and 3485 cm^{-1}. In the ^{1}H-NMR spectrum, H–C(3) resonates at 5.55 ppm, while the H–C(4), H–C(5), and OH–C(4) signals occur at 4.02–3.96 ppm. A weak, broad band at 3410 cm^{-1} in the IR spectrum of **34** is typical for a chelated OH group. The OH signal is shifted to low field (6.06 ppm). H–C(4) resonates at 5.1 ppm, while H–C(3) appears together with H–C(5) at 4.61–4.57 ppm. The diol **35** shows OH absorptions at 3450 and 3380 cm^{-1}. OH–C(3) resonates at 6.09 ppm, and OH–C(4) appears as a large *d* (J = 10.8 Hz) at 2.81 ppm, while the H–C(3) and H–C(4) signals resonate at 4.36 and 3.85 ppm, respectively. In the ^{1}H-NMR spectrum of **36**, H–C(3) resonates at 5.86 ppm, while H–C(4) and H–C(1) appear at 5.07 and 5.01 ppm, respectively. The coupling constants point to a $^4C_1$ conformation (J(4,5) = 10.4 Hz; J(3,4) = 2.8 Hz), less distorted then the one of **8** and similar to the one deduced for **9**. The OH group of **37** absorbs at 3550 and 3480 cm^{-1}. In the ^{1}H-NMR spectrum of **37**, H–C(1) resonates at 6.23 ppm as a *dd* (J(1,2) = 8.6 Hz, J(1,O*H*–C(1)) = 6.4 Hz). An upfield shift is observed for H–C(3) (5.61 ppm, as compared to 5.86 ppm for **36**), indicating a change of the torsion angle for the C(2)–N bond in the direction of the one observed for **25**. The imino group of **40** is characterized by IR bands at 3340 (NH) and at 1680 cm^{-1} (C=N). NH resonates at 8.68 ppm, and

H–C(1) appears as a *d* ($J(1,2) = 9.0$ Hz) at 7.11 ppm similarly to the one of **38** (*d* at 7.06 ppm, $J(1,2) = 9.1$ Hz). In the ^{13}C-NMR spectrum, the C=NH signal is a *s* at 160.2 ppm and the one of C(1) a *d* at 92.4 ppm. H–C(1) of the thioglycoside **39** appears at 5.97 ppm (*d*, $J(1,2) = 10.7$ Hz), the signals of the Et group are found at 2.67 and 1.3 ppm in the ^{1}H-NMR and at 24.4 and 15 ppm in the ^{13}C-NMR spectrum.

3. *Regioselective Glycosidation of* **35**. Before continuing with the synthesis of the disaccharide of allosamidin, we examined if the protection of OH–C(3) could be avoided by effecting a regioselective glycosidation of the diol **35**. To study the influence of the leaving group on yield and regioselectivity of the glycosidation, we examined three glycosyl donors of different reactivity, *viz.* the β-D-acetate **38**, the thiogylcoside **39**, and the more reactive trichloroimidate **40**. Me_3SiOTf [50] was used as promoter in the glycosidation with **38** and **40**, and methyl triflate (MeOTf) and dimethyl(methylthio)sulfonium triflate ([Me_2(MeS)S]OTf) [51] in the glycosidations with the thioglycoside **39**. The solvent was CH_2Cl_2, except when the promoter was MeOTf which was reported to give better yields in Et_2O [52]. All glycosidations were very regioselective and proceeded highly diastereoselectively (*cf. Table 1*). In each case, the β-D-configurated, 1,3-linked disaccharide **42** (*Scheme 5*) was the main product, and only traces of its anomer, of (1–4)-disaccharides, or of trisaccharides were observed. The high degree of regioselectiv-

Scheme 5[a])



[a]) Conditions and yields are summarized in *Table 1*.

Table 1. *Glycosidation of the Diol* **35**

Donor (1.2 equiv.)	Promoter	Solvent	Temp.	Time	Yield of **42**	Yield of **41**	Recovered **35**
38	Me_3SiOTf (1.2 equiv.)	CH_2Cl_2	r.t.	48 h	17%	61%	57%
39	MeOTf (5 equiv.)	Et_2O	r.t.	12 h	33%	40%	35%
39	[Me_2(MeS)S]OTf (4 equiv.)	CH_2Cl_2	r.t.	12 h	37%	41%	37%
40	Me_3SiOTf (1.2 equiv.)	CH_2Cl_2	0°	20 min	41%	34%	26%

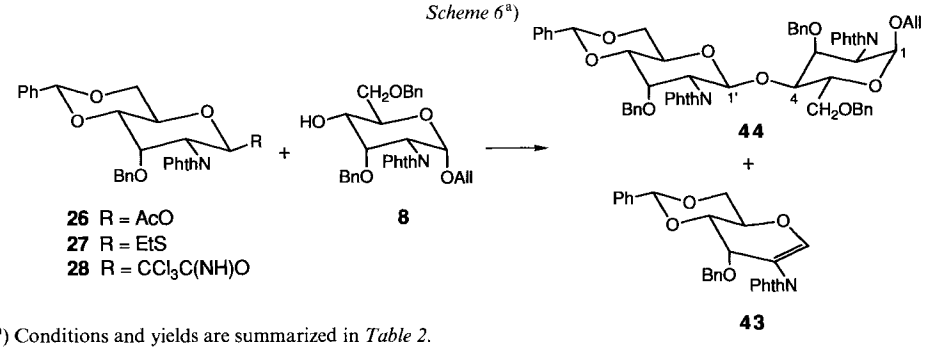
ity, favoring glycosidation of the axial OH group is surprising when compared to the preferred glycosidation of the equatorial OH group in 3,4-unsubstituted galactoside derivatives [53]. It is, however, in keeping with the higher nucleophilicity of the OH–C(3) group, as expected from its involvement, as a H-donor, in a H-bond either to the O–C(1) or to the phthaloyl group. This is evidenced by the chemical shifts and the coupling constant of the OH–C(3) signal, whereas, according to the same criteria, OH–C(4) is not involved in an (intramolecular) H-bond. As expected, the β-D-acetate **38** was the poorest

glycosyl donor and led to low yields of **42**, while the thioglycoside **39** and the imidate **40** gave **42** in higher (and similar) yields (*ca.* 40%). For all glycosidations, the recovery of the glycosyl acceptor was high (more than 34%), and the unsatisfactory yields of **42** were mainly due to the competing formation of **41**. Such amino-glycals are well known side products of glycosidation with 2-phthalimidoglycosyl donors [22] [27] [54] [55]. For 2-phthalimido-D-allopyranose derivatives, elimination could be further facilitated by the antiperiplanar orientation of H–C(2) and O–C(3).

H–C(1) of **41** appears as a *s* at 6.81 ppm. In the ^{13}C-NMR spectrum of **41**, C(1) resonates as a *d* at 149.6 ppm, and C(2) appears at 105.5 ppm as a *s*. The OH group of the disaccharide **42** absorbs at 3470 cm^{-1}. H–C(1′) resonates at 5.96 ppm a *d* (J(1′,2′) = 8.3 Hz) typical for 1,2-*trans* glycosidic bonds. The signal of H–C(3) is shifted to lower field by 0.4 ppm as compared to **35** and resonates as a *t* at 4.77 ppm. OH–C(4) appears at 3.78 ppm as a large *d* (J(4,O*H*–C(4)) = 10.7 Hz), as already observed in **35**. The coupling constants are in agreement with a $^4C_1$ conformation for both monosaccharide units of **42**.

4. *The Disaccharide Moiety of Allosamidin. Scheme 6* and *Table 2* summarize the results of the glycosidation of the acceptor **8** with the donors **26–28**. In each case, we only obtained the expected β-D-configurated disaccharide **44**, besides the elimination product **43**. The *a priori* least reactive donor, the acetate **26**, gave the lowest yields of **44**. Yields were more than doubled, when the thioglycoside **27** was used in the presence of [Me_2(MeS)S]OTf. Somewhat lower yields of **44** were obtained, when MeOTf was the promotor, although the reaction was about as fast as with [Me_2(MeS)S]OTf. No *O*-methylation [51] of **8** was detected. The best yields of **44** (80%) were realized with the imidate **28** and Me_3SiOTf, resulting in a convergent and quite efficient synthesis of the desired disaccharide.

Scheme 6[a])



[a]) Conditions and yields are summarized in *Table 2*.

Table 2. *Glycosidation of* **8**

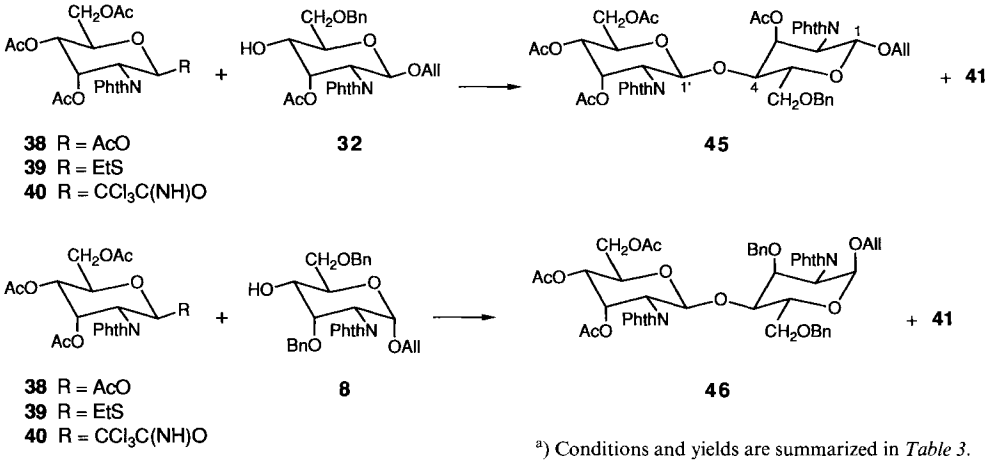
Donor (1.2 equiv.)	Promoter	Solvent	Temp.	Time	Yield of **44**	Yield of **43**	Recovered **8**
26	Me_3SiOTf (1.2 equiv.)	CH_2Cl_2	r.t.	48 h	28%	72%	30%
27	MeOTf (4.5 equiv.)	Et_2O	r.t.	6 h	54%	36%	15%
27	[Me_2(MeS)S]OTf (4.5 equiv.)	CH_2Cl_2	r.t.	6 h	61%	37%	7%
28	Me_3SiOTf (1.2 equiv.)	CH_2Cl_2	0°	20 min	80%	20%	–

The H–C(1), C(1), and C(2) signals of **43** are very similar to those of **41**. In the ^{1}H-NMR spectrum of **44**, H–C(1′) resonates at 6.27 ppm (J(1′,2′) = 8.45 Hz). The coupling constants of the protons of both pyranose rings are in agreement with a $^4C_1$ conformation. The chemical shifts of H–C(1′) (6.27 ppm) and H–C(3′) (4.21–4.18

ppm) indicate that the 2′-phthalimido group has about the same conformation as the one observed for the 2-deoxy-2-phthalimido-β-D-allopyranosides, whereas the low-field resonances of H–C(1) (5.47 ppm) and H–C(3) (4.94 ppm) show the plane of the phthalimido group to adopt a similar orientation as in the 3-*O*-protected 2-deoxy-2-phthalimido-α-D-allopyranosides. The 2 H–C(6) signals are shielded (3.74 ppm for **8** *vs.* 3.64 and 3.52 ppm for **44**), due to the aromatic ring of the 2′-phthalimido group, as confirmed, for **44**, by NOE's between H–C(1′) and H–C(5′), and between H–C(1′) and H–C(4) (same intensity), suggesting that the torsion angles ψ(H–C(1′)–O–C(4)) and φ(H–C(4)–O–C(1′)) of the glycosidic bond are between *ca.* 0 and −30°.

5. *Influence of the Substituents at C(3) on the Reactivity of OH–C(4).* To study this influence, we examined glycosidations of the acceptors **32** and **8** mainly with the thioglycoside **39** as glycosyl donor. Some experiments were also performed with the imidate **40** and the acetate **38** (*Scheme 7*). The results are summarized in *Table 3*. Glycosidation of **32** with **38**–**40** gave the β-(1–4)-disaccharide **45**. The main side product was again the amino-glycal **41**. As expected from analogous glucose derivatives [56], glycosidation of **32** with the β-D-acetate **38** or the thioglycoside **39** gave **45** in poor yields. Considering the low nucleophilicity of OH–C(4) of **32**, **45** was obtained in a surprisingly good yield (56%) with the imidate **40** as glycosyl donor and Me_3SiOTf as promoter. Glycosidations of **8** with the same donors yielded only the β-D-configurated (1–4)-disaccharide **46**. The main

Scheme 7[a])



[a]) Conditions and yields are summarized in *Table 3*.

Table 3. *Glycosidations of* **32** *and* **8**

Donor	Acceptor	Promoter	Solvent	Temp.	Time	Yield of **45** or **46**, resp.
38 (1.2 equiv.)	**32**	Me_3SiOTf (1.2 equiv.)	CH_2Cl_2	r.t.	48 h	12%
39 (1.2 equiv.)	**32**	MeOTf (5 equiv.)	Et_2O	r.t.	12 h	22%
39 (1.2 equiv.)	**32**	$[Me_2(MeS)S]OTf$ (4 equiv.)	CH_2Cl_2	r.t.	12 h	26%
40 (1.2 equiv.)	**32**	Me_3SiOTf (1.2 equiv.)	CH_2Cl_2	0°	20 min	56%
38 (1.2 equiv.)	**8**	Me_3SiOTf (1.2 equiv.)	CH_2Cl_2	r.t.	48 h	19%
39 (1 equiv.)	**8**	$[Me_2(MeS)S]OTf$ (4.5 equiv.)	CH_2Cl_2	r.t.	12 h	37%
39 (2 equiv.)	**8**	$[Me_2(MeS)S]OTf$ (4.5 equiv.)	CH_2Cl_2	r.t.	12 h	48%
39 (1 equiv.)	**8**	MeOTf (5 equiv.)	Et_2O	r.t.	12 h	34%
39 (2 equiv.)	**8**	MeOTf (5 equiv.)	Et_2O	r.t.	12 h	46%
40 (1.2 equiv.)	**8**	Me_3SiOTf (1.2 equiv.)	CH_2Cl_2	0°	20 min	45%

side product was again the amino-glycal **41**. As expected, except for the glycosidation with the imidate **40**, the benzyl-protected **8** was more reactive then the acetate **32**. With an excess of the thioglycoside **39** (2 equiv.), the yield of **46** was increased by *ca.* 10%, but so was the formation of the amino-glycal **41**. Evidently, the relative reactivity of the per-acetylated glycosyl donors parallels on a lower level the one of the 3-*O*-benzyl-4,6-*O*-benzylidene analogues.

H–C(1′) of **45** appears at 6.05 ppm ($J(1',2') = 8.6$ Hz), and H–C(4) resonates at 3.94 ppm. The coupling constants for both monosaccharide units are again in agreement with a $^4C_1$ conformation. A strong shielding is observed for 2 aromatic protons (7.06–7.03 ppm for **45**; and 7.40–7.33 ppm for **32**), for 2 benzylic protons (4.21–4.10 ppm for **45**; 4.66 and 4.60 ppm for **32**), and for the 2 H–C(6) (3.32 and 3.28 ppm for **45**; 3.8 ppm for **32**), suggesting a conformation of **45** similar to the one deduced for **44**, which is confirmed by NOE experiments. In the ^{1}H-NMR spectrum of **46**, H–C(1′) appears at 6.12 ppm as a d ($J(1',2') = 8.4$ Hz). H–C(4) is shifted to lower field by 0.2 ppm and appears at 4.13 ppm. The coupling constants for the H-atoms of both pyranose rings, the chemical shifts of H–C(1) and of H–C(3), and the shielding of the 2 H–C(6) indicate a conformation similar to the one deduced for the disaccharide **44**.

We thank Mr. *M. Vöhler* and Mr. *D. Nanz* for their help with the NMR experiments, the *Swiss National Science Foundations* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. Extraction: The org. layers were dried ($MgSO_4$) and then evaporated *i.v.* at or below 40°. Qual. TLC: 0.25 mm precoated silica-gel plates (*Merck*, silica gel *60* F_{25}); detection by spraying the plates with a soln. of 0.02M I_2 and 0.30M KI in 10% aq. H_2SO_4 soln. followed by heating at *ca.* 200°, or – for specific detection of the glycosyl donors – with a 2% soln. of 4-(4-nitrobenzyl)pyridine in acetone and heating at 100° [57]. Flash chromatography (FC): silica gel *Merck 60* (0.040–0.063 mm). Medium-pressure liquid chromatography (MPLC): silica gel *Merck 60* (0.015–0.040 mm). M.p.'s: uncorrected. Optical rotations: 1-dm cell at 25° and 365, 436, 546, 578, and 589 nm; values at 589 nm were determined from a regression curve. IR Spectra: 3% $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR Spectra: chemical shifts in ppm rel. to TMS as internal standard; in ambiguous cases, ^{1}H-assignments by selective homonuclear decoupling experiments or ^{1}H,^{1}H-TOCSY (^{1}H, 400 MHz); ^{13}C-assignments by ^{1}H,^{13}C-HMQC spectra (^{1}H, 400 MHz) [58]. Mass spectra: CI (NH_3 or isobutane) at 70 eV on *Varian-112 S*.

1. *Glycosyl Donors and Acceptors. Allyl 2-Amino-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-*D*-allopyranoside* (**12**) *and Propyl 2-Amino-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-*D*-allopyranoside* (**13**). *a*) A mixture of **11** (300 mg, 0.68 mmol) and $NH_2NH_2 \cdot H_2O$ (5 ml) was stirred in an autoclave for 3 days at 140°. After cooling to r.t. and evaporation, FC ($CHCl_3$/MeOH 96:4) gave, besides **11** (90 mg, 30%), a 3:1 mixture of **12**/**13** (177 mg; **12**, 39%; **13**, 26%) that could not be separated. The ratio **12**/**13** was determined by ^{1}H-NMR.

b) Similarly, treatment of **11** (300 mg, 0.68 mmol) with $NH_2NH_2 \cdot H_2O$ (5 ml) yielded after 5 days, **12**/**13** 1.1:1 (200 mg; **12**, 42%; **13**, 39%), besides recovered **11** (15 mg, 5%).

Data of **12**: R_f ($CHCl_3$/MeOH 95:5) 0.29. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.50–7.46 (*m*, 2 arom. H); 7.42–7.31 (*m*, 9 arom. H); 7.29–7.25 (*m*, 1 arom. H); 5.94 (*dddd*, J = 17.2, 10.4, 5.8, 4.8, 1 olef. H); 5.53 (*s*, PhC*H*); 5.34 (*dddd* (= '*dq*'), J = 17.2, 1.7, 1 olef. H); 5.17 (*dddd* (= '*dq*'), J = 10.5, 1.5, 1 olef. H); 5.08 (*d*, J = 12.1, PhC*H*); 4.75 (*d*, J = 4.3, H–C(1)); 4.63 (*d*, J = 12.1, PhC*H*); 4.38–4.32 (*AB* of *ABX*, H_{eq}–C(6), H–C(5)); 4.27 (*dddd* (= '*ddt*'), J = 13.3, 4.8, 1.7, 1 allyl. H); 4.02 (*dddd* (= '*ddt*'), J = 13.3, 5.8, 1.5, 1 allyl. H); 3.96 ('*t*', $J \approx 2.9$, H–C(3)); 3.72 (*X* of *ABX*, H_{ax}–C(6)); 3.66 (*dd*, J = 9.0, 2.5, H–C(4)); 2.98 (*dd*, J = 4.2, 3.4, H–C(2)); 1.52 (br. *s*, exchange with D_2O, NH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): 139.2 (*s*, arom. C); 137.7 (*s*, arom. C); 134.3 (*d*, olef. C); 129 (*d*, arom. C); 128.2 (*d*, 2 arom. C); 128.1 (*d*, arom. C); 128 (*d*, arom. C); 127.4 (*d*, arom. C); 127.1 (*d*, arom. C); 126.2 (*d*, 2 arom. C); 116.6 (*t*, olef. C); 102.0 (*d*, PhCH); 99.1 (*d*, C(1)); 80.7 (*d*, C(4)); 77.0 (*d*, C(3)); 74.4 (*t*, PhCH_2); 69.4, 68.7 (2*t*, allyl. C, C(6)); 57.8 (*d*, C(5)); 52.8 (*d*, C(2)).

Data of **13**: R_f ($CHCl_3$/MeOH 95:5) 0.29. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.50–7.46 (*m*, 2 arom. H); 7.42–7.31 (*m*, 9 arom. H); 7.29–7.25 (*m*, 1 arom. H); 5.53 (*s*, PhC*H*); 5.10 (*d*, J = 12.1, PhC*H*); 4.70 (*d*, J = 4.2, H–C(1)); 4.61 (*d*, J = 12.1, PhC*H*); 4.38–4.32 (*m*, H_{eq}–C(6), H–C(5)); 3.94 ('*t*', $J \approx 2.9$, H–C(3)); 3.72 (*m*, H_{ax}–C(6), 1 H of $CH_3CH_2CH_2$); 3.65 (*dd*, J = 9.0, 2.5, H–C(4)); 3.38 (*dt*, J = 6.4, 9.5, 1 H, $CH_3CH_2CH_2$); 2.97 (*dd*, J = 4.2, 3.4,

H–C(2)); 1.67 (*m*, $CH_3CH_2CH_2$); 1.52 (br. *s*, exchange with D_2O, NH_2); 0.98 (*t*, *J* = 7.4, $CH_3CH_2CH_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): 139.4 (*s*, arom. C); 137.7 (*s*, arom. C); 129–126.2 (several *d*, arom. C); 102.0 (*d*, PhCH); 99.9 (*d*, C(1)); 80.8 (*d*, C(4)); 77.3 (*d*, C(3)); 74.3 (*t*, $PhCH_2$); 70.2, 69.5 (2 *t*, $CH_3CH_2CH_2$, C(6)); 57.7 (*d*, C(5)); 52.9 (*d*, C(2)); 23 (*t*, $CH_3CH_2CH_2$); 10.8 (*q*, $CH_3CH_2CH_2$).

*Allyl 2-Acetamido-2-deoxy-α-*D*-allopyranoside* (**14**). A soln. of **10** (1 g, 2.86 mmol) in CH_2Cl_2 (8 ml) and 80% aq. AcOH (4 ml) was heated under reflux for 3.5 h. Evaporation left an oil, which was dissolved in a minimum of MeOH and adsorbed on silica gel. FC (AcOEt/MeOH 9:1) gave **14** (710 mg, 95%) as a white solid. For analysis, a sample was recrystallized in AcOEt/MeOH. R_f (AcOEt/MeOH 9:1) 0.20. M.p. 138.3–139.4° (AcOEt/MeOH). $[\alpha]_D^{25}$ = +119.2 (*c* = 0.9, MeOH). IR (KBr): 3520*s*, 3490*s* (br.), 3080*w*, 2990*w*, 2965*w*, 2940*m*, 2905*m*, 2880*m*, 2860*w*, 1615*s*, 1535*s*, 1465*m*, 1435*m*, 1410*m*, 1390*m*, 1375*m*, 1370*m*, 1350*m*, 1325*m*, 1280*m*, 1250*m*, 1210*m*, 1170*m*, 1140*m*, 1120*s*, 1110*m* (sh), 1090*s* (sh), 1080*s*, 1055*s*, 1045*s*, 1025*s*, 1010*s*, 980*m*, 965*s*, 940*s*, 910*m*, 880*m*, 840*m*, 815*w*. ^{1}H-NMR (400 MHz, CD_3OD): 5.94 (*dddd*, *J* = 17.2, 10.4, 6.4, 5.2, 1 olef. H); 5.31 (*dddd* ('*dq*'), *J* = 17.2, 1.6, 1 olef. H); 5.19 (*dddd* (= '*dq*'), *J* = 10.4, 1.3, 1 olef. H); 4.84 (*d*, *J* = 3.9, H–C(1)); 4.23 (*dddd* (= '*ddt*'), *J* = 13.0, 5.2, 1.5, 1 allyl. H); 4.06 (*dd* (= '*t*'), *J* ≈ 3.6, H–C(2)); 4.03 (*dddd* (= '*ddt*'), *J* = 13.0, 6.4, 1.3, 1 allyl. H); 3.92 ('*t*', *J* ≈ 3.1, H–C(3)); 3.85 (*dd*, *J* = 11.4, 2.3, H–C(6)); 3.8 (*ddd*, *J* = 10.0, 5.4, 2.3, H–C(5)); 3.72 (*dd*, *J* = 11.4, 5.3, H–C(6)); 3.54 (*dd*, *J* = 9.9, 3.2, H–C(4)); 2.01 (*s*, Ac). ^{13}C-NMR (50 MHz, CD_3OD): 173.3 (*s*, CO); 135.6 (*d*, olef. C); 118.3 (*t*, olef. C); 97.8 (*d*, C(1)); 71.7 (*d*); 69.9 (*t*, allyl. C); 69.5 (*d*); 68.5 (*d*); 63 (*t*, C(6)); 51.8 (*d*, C(2)); 22.8 (*q*, Me). CI-MS (NH_3): 262 (100, $[M + 1]^+$), 204 (45, $[M - OAll]^+$). Anal. calc. for $C_{11}H_{19}NO_6$ (261.274): C 50.57, H 7.33, N 5.36; found: C 50.43, H 7.30, N 5.20.

*Allyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*-allopyranoside* (**15**). A vigorously stirred soln. of **14** (500 mg, 1.91 mmol) in DMF (10 ml) was treated with BaO (1.93 g, 12.6 mmol), $Ba(OH)_2 \cdot 8\ H_2O$ (505 mg, 1.6 mmol), and $PhCH_2Br$ (888 µl, 7.5 mmol) and stirred under N_2 for 16 h at r.t. Filtration through *Celite* and evaporation under h.v. afforded a slightly yellow oil which was purified by FC (AcOEt/hexane 1:1) to give **15** (924 mg, 91%) as a colourless oil which crystallized under h.v. after 12 h. R_f (AcOEt/hexane 1:1) 0.25. M.p. 56–57°. $[\alpha]_D^{25}$ = +31.7 (*c* = 0.6, $CHCl_3$). IR ($CHCl_3$): 3440*w*, 3090*w*, 3070*w*, 3030*w*, 3000*m*, 2910*w*, 2870*w*, 1665*s*, 1655*s* (sh), 1510*w*, 1495*m*, 1455*m*, 1375*w*, 1350*w*, 1315*w*, 1250*m*, 1125*s*, 1060*s* (br.), 1040*s* (sh), 1030*s*, 995*m* (sh), 950*m*, 930*w*, 920*w*, 860*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.24 (*m*, 15 arom. H); 5.95–5.85 (*m*, 1 olef. H, NH); 5.28 (*dddd* (= '*dq*'), *J* = 17.2, 1.7, 1 olef. H); 5.15 (*dddd* (= '*dq*'), *J* = 10.5, 1.5, 1 olef. H); 4.98 (*d*, *J* = 12.3, PhC*H*); 4.78 (*d*, *J* = 4.5, H–C(1)); 4.66 (*d*, *J* = 11.5, PhC*H*); 4.65 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 12.1, PhC*H*); 4.52 (*d*, *J* = 11.5, PhC*H*); 4.45 (*d*, *J* = 12.3, PhC*H*); 4.29–4.22 (*m*, 1 allyl. H, H–C(5)); 4.19 (*ddd*, *J* = 9.3, 4.4, 3.6, H–C(2)); 4.07 ('*t*', *J* ≈ 3.1, H–C(3)); 3.96 (*dddd* (= '*ddt*'), *J* = 13.4, 5.8, 1.6, 1 allyl. H); 3.81 (*dd*, *J* = 10.6, 3.8, H–C(6)); 3.75–3.72 (*m*, H–C(4), H–C(6)); 1.76 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.3 (*s*, CO); 139.1 (*s*, arom. C); 138.2 (*s*, arom. C); 137.9 (*s*, arom. C); 134.1 (*s*, olef. C); 128.4–127.5 (several *d*, arom. C); 116.6 (*t*, olef. C); 96 (*d*, C(1)); 75.6 (*d*), 75.1 (*d*, C(4), C(3)); 75 (*t*, $PhCH_2$); 73.5 (*t*, $PhCH_2$); 72.2 (*t*, $PhCH_2$); 68.9, 68.2 (2*t*, allyl. C, C(6)); 66 (*d*, C(5)); 49.2 (*d*, C(2)); 23.1 (*q*, Me). CI-MS (NH_3): 532 (100, $[M + 1]^+$). Anal. calc. for $C_{32}H_{37}NO_6$ (531.649): C 72.29, H 7.01, N 2.63; found: C 72.27, H 6.86, N 2.82.

*Allyl 2-Amino-3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*-allopyranoside* (**16**) *and Propyl 2-Amino-3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*-allopyranoside* (**17**). A mixture of **15** (300 mg, 0.564 mmol) and of $NH_2NH_2 \cdot H_2O$ (5 ml) was stirred in an autoclave for 3 days at 140°. After cooling to r.t., the mixture was evaporated. FC ($CHCl_3$/MeOH 96:4) of the residue gave **15** (51 mg, 17%) and a mixture of **16** (104 mg, 38%) and **17** (105 mg, 38%) which could not be separated. The ratio **16**/**17** was determined by ^{1}H-NMR.

Data of **16**: R_f ($CHCl_3$/MeOH 95:5) 0.31. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.21 (*m*, 15 arom. H); 5.92 (*dddd*, *J* = 17.2, 10.4, 5.6, 4.7, 1 olef. H); 5.30 (*dddd* (= '*dq*'), *J* = 17.2, 1.8, 1 olef. H); 5.12 (*dddd* (= '*dq*'), *J* = 10.4, 1.5, 1 olef. H); 5.03 (*d*, *J* = 12.1, PhC*H*); 4.70 (*d*, *J* = 4.2, H–C(1)); 4.66 (*d*, *J* = 11.6, PhC*H*); 4.65 (*d*, *J* = 12.1, PhC*H*); 4.59 (*d*, *J* = 12.1, PhC*H*); 4.54 (*d*, *J* = 11.6, PhC*H*); 4.53 (*d*, *J* = 12.1, PhC*H*); 4.29–4.20 (*m*, H–C(5), 1 allyl. H); 3.98 (*ddt*, *J* = 13.3, 5.7, 1.5, 1 allyl. H); 3.93 ('*t*', *J* ≈ 2.9, H–C(3)); 3.82 (*dd*, *J* = 10.6, 3.6, H–C(6)); 3.72 (*dd*, *J* = 10.6, 2.1, H–C(6)); 3.66 (*dd*, *J* = 9.9, 2.8, H–C(4)); 2.87 (*dd*, *J* = 4.2, 3.3, H–C(2)); 1.49 (br. *s*, exchange with D_2O, NH_2).

Data of **17**: R_f ($CHCl_3$/MeOH 95:5) 0.31. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.21 (*m*, 15 arom. H); 5.02 (*d*, *J* = 12, PhC*H*); 4.75 (*d*, *J* = 4.2, H–C(1)); 4.66 (*d*, *J* = 11.6, PhC*H*); 4.65 (*d*, *J* = 12.1, PhC*H*); 4.60 (*d*, *J* = 12, PhC*H*); 4.54 (*d*, *J* = 11.6, PhC*H*); 4.53 (*d*, *J* = 12.1, PhC*H*); 4.24 (*ddd*, *J* = 9.9, 3.6, 2.1, H–C(5)); 3.94 ('*t*', *J* ≈ 3.0, H–C(3)); 3.82 (*dd*, *J* = 10.6, 3.6, H–C(6)); 3.74–3.70 (*m*, H–C(6), 1 H of $CH_3CH_2CH_2$); 3.67 (*dd*, *J* = 9.9, 2.9, H–C(4)); 3.35 (*dt*, *J* = 9.5, 6.4, 1 H, $CH_3CH_2CH_2$); 2.88 (*dd*, *J* = 4.2, 3.3, H–C(2)); 1.69–1.60 (*m*, $CH_3CH_2CH_2$); 1.49 (br. *s*, exchange with D_2O, NH_2); 0.94 (*t*, *J* = 7.4, $CH_3CH_2CH_2$).

*Allyl 2-Amino-4,6-*O*-benzylidene-2-deoxy-α-*D*-allopyranoside* (**18**). A suspension of **10** (8 g, 22.9 mmol) in 1N aq. NaOH (160 ml) was vigorously stirred and heated under reflux for 6 d. The resultant clear soln. was cooled to

r.t. and extracted 3× with CH_2Cl_2. The combined org. phases were washed with H_2O and processed as usual to give a white solid which was recrystallized in boiling EtOH: **18** (5.2 g, 74%). A 2nd and 3rd crop of crystals (same m.p.) were obtained by crystallization of the mother liquors. Total yield of **18**, 6.91 g (98%). R_f (AcOEt) 0.04. M.p. 115–117° (EtOH). $[\alpha]_D^{25} = +119.4$ ($c = 0.9$, MeOH). IR (KBr): 3600*w*, 3530*w*, 3400*w*, 2980*w*, 2940*m*, 2875*m*, 1630*w*, 1470*w* (sh), 1460*w*, 1405*w* (sh), 1385*m*, 1370*w* (sh), 1335*w*, 1320*w*, 1285*w*, 1150*m* (sh), 1125*s*, 1105*s*, 1090*s*, 1060*s*, 1030*s*, 1025*s* (sh), 1000*s*, 965*m* (sh), 940*m*, 925*m* (sh), 885*w*, 850*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.55–7.45 (*m*, 2 arom. H); 7.40–7.30 (*m*, 3 arom. H); 5.93 (*dddd*, $J = 17.1, 10.3, 6.1, 5.3$, 1 olef. H); 5.59 (*s*, PhC*H*); 5.35 (*dddd* (= '*dq*'), $J = 17.1, 1.5$, 1 olef. H); 5.25 (*dddd* (= '*dq*'), $J = 10.3, 1.2$, 1 olef. H); 4.84 (*d*, $J = 3.8$, H–C(1)); 4.36 (*dd*, $J = 10.0, 5.0$, H_{eq}–C(6)); 4.27 (*dddd* (= '*ddt*'), $J = 12.9, 5.3, 1.3$, 1 allyl. H); 4.20–4.04 (*m*, H–C(3), H–C(5)); 4.04 (*dddd* (= '*ddt*'), $J = 12.9, 6.1, 1.2$, 1 allyl. H); 3.76 (*t*, $J = 10.0$, H_{ax}–C(6)); 3.56 (*dd*, $J = 9.9, 2.6$, H–C(4)); 3.00 (br. *s*, H–C(2)); 1.96 (br. *s*, exchange with D_2O, OH–C(3), NH_2). ^{13}C-NMR (50 MHz, CD_3OD): 137.2 (*s*, arom. C); 133.3 (*d*, olef. C); 129.1 (*d*, arom. C); 128.2 (*d*, 2 arom. C); 126.2 (*d*, 2 arom. C); 118.3 (*t*, olef. C); 101.9 (*d*, PhCH); 100.0 (*d*, C(1)); 79.4 (*d*, C(4)); 70.8 (*d*, C(3)); 69.3, 69.2 (2*t*, allyl. C, C(6)); 57.5 (*d*, C(5)); 52.4 (*d*, C(2)). CI-MS: 308 (100, $[M + 1]^+$), 250 (67, $[M - OAll]^+$). Anal. calc. for $C_{32}H_{37}NO_6$ (307.349): C 62.53, H 6.89, N 4.56; found: C 62.55, H 6.86, N 4.51.

*Allyl 4,6-*O*-Benzylidene-2-(2-carboxybenzamido)-2-deoxy-*α*-*D*-allopyranoside* (**19**). A mixture of freshly sublimed phthalic anhydride (9.64 g, 65.07 mmol) and **18** (20 g, 65.07 mmol) in dry MeOH (400 ml) was vigorously shaken for 10 min. After addition of Et_3N (9.07 ml, 65.07 mmol) and additional phthalic anhydride (9.64 g, 65.07 mmol), shaking was continued for 10 min. Evaporation and FC (AcOEt/MeOH 10:1) afforded white, crystalline acid **19** (28.16 g, 95%) which was recrystallized in boiling AcOEt. R_f (AcOEt/MeOH 10:1) 0.18. M.p. 158–160.5° (AcOEt). $[\alpha]_D^{25} = +82.3$ ($c = 0.9$, MeOH). IR (KBr): 3600*m* (sh), 3440*m* (br.), 3300*m* (sh), 3270*m*, 3070*m*, 3040*m*, 3010*m*, 2980*m*, 2920*m*, 2860*m*, 1710*s*, 1695*s*, 1660*m* (sh), 1640*s*, 1600*m*, 1585*w*, 1530*s*, 1490*w*, 1455*m*, 1425*w*, 1410*w*, 1385*m*, 1370*m*, 1335*m*, 1315*w*, 1305*m* (sh), 1290*m* (sh), 1270*m*, 1245*m*, 1220*w*, 1180*w*, 1170*w*, 1145*m* (sh), 1135*m*, 1120*s*, 1105*m*, 1080*m*, 1065*s*, 1050*m*, 1020*s*, 995*s*, 965*m*, 945*m*, 920*m*, 890*w*, 850*w*, 800*w*, 765*w* (sh), 750*m*, 725*m*, 710*m*, 700*m*, 665*m*. ^{1}H-NMR (400 MHz, CD_3OD): 7.99 (*m*, arom. H); 7.62 (*m*, arom. H); 7.56–7.45 (*m*, 4 arom. H); 7.4–7.3 (*m*, 3 arom. H); 5.97 (*dddd*, $J = 17.25, 10.4, 6.3, 5.5$, 1 olef. H); 5.68 (*s*, PhC*H*); 5.31 (*dddd* (= '*dq*'), $J = 17.2, 1.6$, 1 olef. H); 5.17 (*dddd* (= '*dq*'), $J = 10.4, 1.2$, 1 olef. H); 5.0 (*d*, $J = 4.2$, H–C(1)); 4.42 (*dd*, $J = 3.3, 4.2$, H–C(2)); 4.30 (*dd* (= '*t*'), $J \approx 2.9$, H–C(3)); 4.29 (*dd*, $J = 9.9, 5.0$, H_{eq}–C(6)); 4.25–4.18 (*m*, H–C(5), 1 allyl. H); 4.09 (*dddd* (= '*ddt*'), $J = 12.9, 6.3, 1.3$, 1 allyl. H); 3.8 (*dd* (= '*t*'), $J = 10.1$, H_{ax}–C(6)); 3.76 (*dd*, $J = 9.6, 2.7$, H–C(4)). ^{13}C-NMR (50 MHz, CD_3OD): 172.4 (*s*, CO_2H); 169.3 (*s*, NHC*O*); 139.5 (*s*); 139.3 (*s*); 135.7 (*s*, *d*); 133.3 (*d*); 131.6 (*d*); 130.95 (*d*); 130.2 (*d*); 129.3 (*d*, 2 C); 128.9 (*d*); 127.8 (*d*); 118.3 (*t*, olef. C); 103.1 (*d*, PhCH); 98.4 (*d*, C(1)); 80.0 (*d*, C(4)); 70.7, 70.3 (2*t*, allyl. C, C(6)); 68.8 (*d*, C(3)); 59.1 (*d*, C(5)); 51.9 (*d*, C(2)). CI-MS: 456 (10, $[M + 1]^+$). Anal. calc. for $C_{24}H_{25}NO_8$ (455.463): C 63.29, H 5.53, N 3.07; found: C 63.04, H 5.76, N 2.79.

*Allyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*α*-*D*-allopyranoside* (**20**) *and Allyl 4,6-*O*-Benzylidene-2-deoxy-2-phthalimido-*α*-*D*-allopyranoside* (**21**). *a*) At 0°, Ac_2O (35 ml) was added dropwise to a stirred soln. of **19** (10 g, 21.95 mmol) in pyridine (100 ml). After 18 h at r.t., the mixture was processed as usual. FC (toluene/AcOEt 8:1) afforded **21** (4.226 g, 44%) and **20** (5.685 g, 54%).

b) A soln. of **19** (10 g, 21.95 mmol) and 4-$(Me_2N)C_5H_4N$ (269 mg, 2.2 mmol) in pyridine (100 ml) and Ac_2O (35 ml) was stirred for 16 h at r.t. Usual workup and FC (toluene/AcOEt 8:1) gave **20** (10.317 g, 98%).

Data of **20**: R_f (toluene/AcOEt 6:1) 0.38. M.p. 205.5–207° (CH_2Cl_2/hexane). $[\alpha]_D^{25} = +132.7$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3080*w* (sh), 3070*w* (sh), 3030*w*, 3000*w*, 2980*w* (sh), 2930*w*, 2870*w*, 1790*w*, 1740*s* (sh), 1725*s*, 1610*w*, 1470*w*, 1455*w*, 1385*m* (sh), 1370*s*, 1350*m*, 1330*m*, 1310*w* (sh), 1240*w* (br.), 1160*w*, 1140*m*, 1120*m* (sh), 1110*m*, 1095*m* (sh), 1080*w*, 1060*m*, 1040*m* (sh), 1030*m*, 995*m*, 970*w* (sh), 960*w* (sh), 925*w*, 915*w* (sh), 885*w*, 860*w*, 690*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.86–7.84 (*m*, 2 arom. H); 7.74–7.72 (*m*, 2 arom. H); 7.46–7.43 (*m*, 2 arom. H); 7.37–7.34 (*m*, 3 arom. H); 5.86 (*dd* (= '*t*'), $J \approx 2.7$, H–C(3)); 5.83 (*dddd*, $J = 17.2, 10.55, 4.9, 4.35$, 1 olef. H); 5.61 (*s*, PhC*H*); 5.46 (*dddd* (= '*dq*'), $J = 17.2, 1.9$, 1 olef. H); 5.14 (*dddd* (= '*dq*'), $J = 10.55, 1.7$, 1 olef. H); 4.9 (*d*, $J = 3.85$, H–C(1)); 4.81 (*dd*, $J = 3.85, 2.7$, H–C(2)); 4.48 (*ddd* (= '*td*'), $J = 10.1, 5.2$, H–C(5)); 4.36 (*dd*, $J = 5.15, 10.4$, H_{eq}–C(6)); 4.28 (*dddd* (= '*ddt*'), $J = 4.4, 13.7, 1.9$, 1 allyl. H); 3.93 (*dddd* (= '*ddt*'), $J = 13.7, 5.0, 1.7$, 1 allyl. H); 3.90 (*dd*, $J = 9.6, 2.9$, H–C(4)); 3.80 (*dd* (= '*t*'), $J = 10.4$, H_{ax}–C(6)); 2.25 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 171.5 (*s*, Ac); 167.2 (*s*, 2 CO); 137.1 (*s*); 134.1 (*d*, 2 C); 133.5 (*d*); 131.5 (*s*, 2 C); 129.0 (*d*); 128.2 (*d*, 2 C); 126.1 (2*d*); 123.5 (*d*, 2 C); 116.3 (*t*, olef. C); 101.3 (*d*, PhCH); 97.2 (*d*, C(1)); 77.6 (*d*, C(4)); 69.1, 68.6 (2*t*, allyl. C, C(6)); 67.1 (*d*, C(3)); 59.0 (*d*, C(5)); 52.5 (*d*, C(2)); 21.5 (*q*, Me). Anal. calc. for $C_{26}H_{25}NO_8$ (479.485): C 65.13, H 5.26, N 2.92; found: C 64.85, H 5.50, N 3.14.

Data of **21**: R_f (toluene/AcOEt 6:1) 0.46. M.p. 205.5–207° (CH_2Cl_2/hexane). $[\alpha]_D^{25} = +115.2$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3460*m* (sh), 3440*m* (br.), 3080*w* (sh), 3070*w* (sh), 3030*w*, 3000*w*, 2980*w* (sh), 2930*w*, 2865*w*, 1770*w*,

1715*s*, 1610*w*, 1470*w*, 1455*w*, 1390*m*, 1370*m*, 1360*w* (sh), 1345*m*, 1330*m*, 1310*w*, 1295*w* (sh), 1260*w* (br.), 1145*w*, 1135*m* (sh), 1125*m* (sh), 1105*s*, 1095*m* (sh), 1085*m*, 1060*m*, 1025*m* (br.), 1010*m*, 995*m*, 980*w* (sh), 960*w*, 930*m* (br.), 915*w* (sh), 890*w*, 860*w*, 690*w*, 645*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.92–7.89 (*m*, 2 arom. H); 7.80–7.78 (*m*, 2 arom. H); 7.56–7.53 (*m*, 2 arom. H); 7.37–7.3 (*m*, 3 arom. H); 6.13 (*m*, exchange with D_2O, OH–C(3)); 5.74 (*dddd*, J = 17.2, 10.5, 5.7, 4.65, 1 olef. H); 5.62 (*s*, PhC*H*); 5.25 (*dddd* (= '*dq*'), J = 17.2, 1.65, 1 olef. H); 5.07 (*dddd* (= '*dq*'), J = 10.5, 1.5, 1 olef. H); 4.89 (*d*, J = 3.7, H–C(1)); 4.65 (*ddd* (= '*td*'), $J \approx$ 10.0, 5.1, H–C(5)); 4.6 (*dd*, J = 3.7, 2.2, H–C(2)); 4.56 (br. *s*, after addn. of D_2O, *t*, J = 2.3, H–C(3)); 4.39 (*dd*, J = 10.35, 5.3, H_{eq}–C(6)); 4.24 (*dddd* (= '*ddt*'), J = 13.4, 4.7, 1.7, 1 allyl. H); 3.88 (*dddd* (= '*ddt*'), J = 13.4, 5.7, 1.5, 1 allyl. H); 3.81 (*dd*, J = 9.3, 2.4, H–C(4)); 3.8 (*dd* (= '*t*'), J = 10.4, H_{ax}–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.8 (*s*, 2 CO); 137.2 (*s*); 134.7 (*d*, 2 C); 133.3 (*d*); 131.9 (*s*, 2 C); 128.9 (*d*); 128.1 (*d*, 2 C); 126.4 (*d*, 2 C); 123.8 (*d*, 2 C); 117.0 (*t*, olef. C); 102.0 (*d*, PhCH); 97.2 (*d*, C(1)); 80.0 (*d*, C(4)); 69.0 (2*t*, C(6), allyl. C); 67.2 (*d*, C(3)); 58.3 (*d*, C(5)); 55.4 (*d*, C(2)). CI-MS: 438 (10, $[M + 1]^+$), 380 (100, $[M - 57]^+$). Anal. calc. for $C_{24}H_{23}NO_7$ (437.448): C 65.89, H 5.30, N 3.20; found: C 65.89, H 5.47, N 3.08.

*Allyl 4,6-*O*-Benzylidene-2-deoxy-2-[2-(methoxycarbonyl)benzamido]-*α*-*D*-allopyranoside* (**22**). A soln. of **20** (250 mg, 0.52 mmol) in MeOH (15 ml) was treated with a 1 mM soln. of MeONa in MeOH (5 ml) and stirred for 5 h at r.t. Addition of *Dowex-1* (H^+ form), filtration, evaporation of the filtrate, and FC (toluene/AcOEt 1:1) of the residue yielded **22** (215 mg, 88%). Oil. R_f (toluene/AcOEt 1:1) 0.26. IR ($CHCl_3$): 3600*w*, 3520*w* (br.), 3435*m*, 3070*w*, 3020*w*, 3000*m*, 2940*w*, 2875*w*, 1730*s*, 1670*s*, 1600*w*, 1580*w*, 1510*m*, 1485*m*, 1450*w*, 1435*w*, 1380*m* (sh), 1370*m*, 1325*m*, 1295*s*, 1280*s*, 1175*s*, 1120*s*, 1005*s*, 1080*s*, 1060*s*, 1040*s* (sh), 1020*s*, 995*s*, 970*m*, 935*w*, 920*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.93 (*m*, 1 arom. H); 7.59–7.47 (*m*, 5 arom. H); 7.41–7.36 (*m*, 3 arom. H); 6.58 (*d*, J = 9.2, NH); 5.91 (*dddd*, J = 17.2, 10.4, 6.3, 5.5, 1 olef. H); 5.65 (*s*, PhC*H*); 5.30 (*dq*, J = 17.2, 1.5, 1 olef. H); 5.22 (*dq*, J = 10.4, 1.2, 1 olef. H); 5.08 (*d*, J = 4.0, H–C(1)); 4.52 (*ddd*, J = 9.2, 4.0, 3.3, H–C(2)); 4.42–4.37 (*m*, H–C(3), H_{eq}–C(6)); 4.26 (*ddt*, J = 12.9, 5.5, 1.3, 1 allyl. H); 4.22 (*ddd* (= '*td*'), $J \approx$ 10.1, 5.1, H–C(5)); 4.09 (*ddt*, J = 12.9, 6.3, 1.2, 1 allyl. H); 3.88 (*s*, MeO); 3.82 (*t*, J = 10.3, H_{ax}–C(6)); 3.73 (*dd*, J = 9.8, 2.8, H–C(4)); 2.92 (*d*, J = 6.7, exchange with D_2O, OH–C(3)). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.1 (*s*, CO); 166.5 (*s*, CO); 138.0 (*s*, arom. C); 137.0 (*s*, arom. C); 133.0 (*d*); 132.0 (*d*); 130.1 (*d*, arom. C); 129.6 (*d*, 2 arom. C); 128.6 (*s*, arom. C); 128.2 (*d*, 2 arom. C); 127.5 (*d*, arom. C); 126.2 (*d*, 2 arom. C); 118.1 (*t*, olef. C); 101.8 (*d*, PhCH); 97.1 (*d*, C(1)); 78.4 (*d*, C(4)); 69.3, 69.1 (2*t*, C(6), allyl. C); 67.8 (*d*, C(3)); 57.6 (*d*, C(5)); 52.4 (*d*, C(2)); 49.8 (*q*, MeO).

*Allyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-[2-(benzyloxycarbonyl)benzamido]-2-deoxy-*α*-*D*-allopyranoside* (**23**) *and Allyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*α*-*D*-allopyranoside* (**9**). NaH (2.2 g, 92.22 mmol) and $PhCH_2Br$ (14.25 ml, 119.89 mmol) were added under N_2 to a stirred soln. of **19** (21 g, 46.11 mmol) in anh. DMF (600 ml). The mixture was stirred for 24 h, diluted with AcOEt (800 ml), and washed with ice-cold 4% aq. HCl soln., sat. aq. $NaHCO_3$ soln., and H_2O. The org. layer was dried and evaporated. FC of the residue (AcOEt/hexane 1:2) gave **9** (12.6 g, 52%) and crystalline **23** (12.9 g, 44%).

Transformation of **23** into **9**: A soln. of **23** (12.9 g, 20.3 mm) in dioxane (200 ml) and 1M aq. NaOH (200 ml) was stirred for 5 h at r.t. Evaporation of dioxane left a white suspension which was extracted with AcOEt (400 ml). The org. layer was washed with ice-cold 4% aq. HCl soln., and H_2O (2×), dried, and evaporated. A soln. of the residue in pyridine (210 ml) and Ac_2O (70 ml) was stirred for 2 d at r.t., evaporated and purified by FC (toluene/AcOEt 12:1): **9** (7.82 g, 73%).

Data for **23**: R_f (AcOEt/hexane 1:1) 0.5. M.p. 81–84°. $[\alpha]_D^{25}$ = +20.4 (c = 1, $CHCl_3$). IR ($CHCl_3$): 3430*w* (br.), 3060*w*, 3030*w*, 3000*w*, 2940*w*, 2860*w*, 1720*m*, 1660*m*, 1600*w*, 1580*w*, 1510*m* (sh), 1500*m*, 1480*m*, 1450*w*, 1370*w*, 1350*w* (sh), 1310*w*, 1280*m* (sh), 1260*m*, 1200*s*, 1120*s*, 1110*m* (sh), 1070*m*, 1040*s*, 1025*s*, 990*m* (sh), 960*w*, 925*m*, 880*w*, 845*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.96 (*m*, arom. H); 7.5–7.45 (*m*, 5 arom. H); 7.42–7.34 (*m*, 8 arom. H); 7.21–7.16 (*m*, 3 arom. H); 6.36 (*d*, J = 9.5, NH); 5.88 (*dddd*, J = 17.25, 10.5, 5.7, 4.85, 1 olef. H); 5.58 (*s*, PhC*H*); 5.28 (*dddd* (= '*dq*'), J = 17.25, 1.7, 1 olef. H); 5.27, 5.23 (*AB*, J = 12.3, $PhCH_2$); 5.14 (*dddd* (= '*dq*'), J = 10.5, 1.4, 1 olef. H); 4.99 (*d*, J = 12.2, PhC*H*); 4.83 (*d*, J = 4.4, H–C(1)); 4.49 (*d*, J = 12.2, PhC*H*); 4.44–4.33 (*m*, H–C(2), H–C(5), H_{eq}–C(6)); 4.21 (*dddd* (= '*ddt*'), J = 13.3, 4.85, 1.7, 1 allyl. H); 3.99 (*m*, H–C(3)); 3.97 (*dddd* (= '*ddt*'), J = 13.3, 5.7, 1.4, 1 allyl. H); 3.78 (*dd* (= '*t*'), J = 10.0, H_{ax}–C(6)); 3.70 (*dd*, J = 9.35, 2.4, H–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.5 (*s*, CO); 165.9 (*s*, CO); 138.9 (*s*); 138.1 (*s*); 137.6 (*s*); 135.5 (*s*); 134.1 (*d*); 132.0 (*d*); 130.3 (*d*); 129.6 (*d*); 129.0 (*d*); 128.9 (*s*); 128.5 (*d*, 4 C); 128.4 (*d*); 128.3 (*d*, 2 C); 128.2 (*d*, 2 C); 127.5 (*d*, 2 C); 127.3 (*d*); 127.2 (*d*); 126.2 (*d*, 2 C); 116.8 (*t*, olef. C); 102 (*d*, PhCH); 96.3 (*d*, C(1)); 80.0 (*d*, C(4)); 74.6 (*d*, C(3)); 74.4 (*t*); 69.3 (*t*); 68.7 (*t*); 67.3 (*t*); 57.9 (*d*, C(5)); 49.3 (*d*, C(2)). CI-MS: 636.9 (100, $[M + 1]^+$). Anal. calc. for $C_{38}H_{37}NO_8$ (635.713): C 71.80, H 5.87, N 2.20; found: C 71.67, H 5.73, N 2.30.

Data for **9**: R_f (toluene/AcOEt 6:1) 0.37. Oil. $[\alpha]_D^{25}$ = +53.1 (c = 1, $CHCl_3$). IR ($CHCl_3$): 3090*w* (sh), 3070*w*, 3030*w*, 3005*w*, 2930*w*, 2870*w*, 1782*w*, 1720*s*, 1610*w*, 1495*w*, 1470*w*, 1455*w*, 1385*m*, 1370*m*, 1350*m*, 1325*m*, 1312*w*,

1310*w*, 1160*w* (sh), 1140*m*, 1125*m* (sh), 1110*s*, 1090*m* (sh), 1055*s*, 1030*s*, 995*m*, 965*w* (sh), 910*m*, 880*w*, 690*w*, 660*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.80–7.04 (*m*, 14 arom. H); 5.88 (*dddd*, *J* = 17.25, 10.5, 5.7, 4.9, 1 olef. H); 5.7 (*s*, PhC*H*); 5.5 (*d*, *J* = 3.7, H–C(1)); 5.30 (*dddd* (= '*dq*'), *J* = 17.25, 1.65, 1 olef. H); 5.07 (*dddd* (= '*dq*'), *J* = 10.5, 1.5, 1 olef. H); 5 (*d*, *J* = 12.0, PhC*H*); 4.86 (*dd* (= '*t*'), *J* = 2.65, H–C(3)); 4.68 (*d*, *J* = 12.0, PhC*H*); 4.65 (*ddd* (= '*td*'), *J* ≈ 10.1, 5.1, H–C(5)); 4.36 (*dd*, *J* = 3.7, 2.65, H–C(2)); 4.34 (*dd*, *J* = 10.4, 5.1, H_{eq}–C(6)); 4.3 (*dddd* (= '*ddt*'), *J* = 13.25, 4.9, 1.65, 1 allyl. H); 4.1 (*dddd* (= '*ddt*'), *J* = 13.25, 5.7, 1.5, 1 allyl. H); 3.83 (*dd*, *J* = 9.6, 2.7, H–C(4)); 3.77 (*dd* (= '*t*'), *J* = 10.4, H_{ax}–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 168 (*s*, 2 CO); 139.1 (*s*); 137.6 (*s*); 134.2 (*d*); 133.8 (*d*, 2 C); 131.7 (*s*, 2 C); 129. (*d*); 128.25 (*d*, 2 C); 127.7 (*d*, 2 C); 127.6 (*d*, 2 C); 126.7 (*d*); 126.5 (*d*, 2 C); 123 (*d*, 2 C); 116.6 (*t*, olef. C); 102.1 (*d*, PhCH); 96.1 (*d*, C(1)); 80.5 (*d*, C(4)); 73.6 (*t*, PhCH); 72.7 (*d*, C(3)); 69.3, 69.2 (2*t*, allyl. C, C(6)); 58.6 (*d*, C(5)); 55.8 (*d*, C(2)). CI-MS: 528 (7, $[M + 1]^+$). Anal. calc. for $C_{31}H_{29}NO_7$ (527.573): C 70.04, H 5.54, N 2.66; found: C 69.78, H 5.54, N 2.57.

*Allyl 3,6-Di-*O*-benzyl-2-deoxy-2-phthalimido-*α*-*D*-allopyranoside* (**8**) *and Allyl 3,4-Di-*O*-benzyl-2-deoxy-2-phthalimido-*α*-*D*-allopyranoside* (**24**). *a*) A mixture of **9** (5.00 g, 9.48 mmol), $NaBH_3CN$ (3.6 g, 57 mmol), and powdered 4-Å molecular sieves (2 g) in THF (200 ml) was stirred at 0° under Ar for 2 h. A sat. HCl soln. in Et_2O was added dropwise, until TLC showed that **9** had disappeared. The mixture was diluted with $CHCl_3$ (500 ml) and filtered. The filtrate was washed with sat. aq. $NaHCO_3$ soln. and H_2O and dried. Filtration, evaporation, and FC (toluene/AcOEt 5:1) of the residue gave **8** (2.96 g, 59%) and **24** (1.05 g, 21%) as colourless oils.

b) A mixture of **9** (1.00 g, 1.9 mmol), $BH_3 \cdot Et_3N$ (1.3 g, 11.4 mmol), and powdered 4-Å molecular sieves (400 mg) in THF (60 ml) was stirred for 30 min at r.t. After the addition of $AlCl_3$ (1.658 g, 11.4 mmol), the mixture was stirred for 14 h, and filtered. Evaporation of the filtrate and FC (toluene/AcOEt 5:1) of the residue yielded **8** (843 mg, 84%) and **24** (50 mg, 5%).

Data of **8**: R_f (toluene/AcOEt 5:1) 0.24. $[\alpha]_D^{25} = +71.5$ (*c* = 0.8, $CHCl_3$). IR ($CHCl_3$): 3690*w* (br.), 3600*w*, 3540*w*, 3400*w* (br.), 3090*w*, 3070*w*, 3035*w*, 3000*w*, 2960*w* (sh), 2925*w*, 2870*w*, 1780*w* (br.), 1715*s* (br.), 1610*w*, 1495*w*, 1470*w* (sh), 1450*m*, 1410*w* (sh), 1370*m*, 1350*m* (sh), 1325*m*, 1305*w* (sh), 1260*m*, 1230*m* (br.), 1145*m* (sh), 1115*s*, 1000*s*, 1045*s*, 1030*s*, 930*w*, 910*w* (sh), 885*w*, 865*w*, 810*w*, 690*w*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.83–7.79 (*m*, 2 arom. H); 7.73–7.68 (*m*, 2 arom. H); 7.37–7.11 (*m*, 10 arom. H); 5.86 (*dddd*, *J* = 17.25, 10.5, 5.6, 5.1, 1 olef. H); 5.27 (*dddd* (= '*dq*'), *J* = 17.25, 1.7, 1 olef. H); 5.26 (*d*, *J* = 4.6, H–C(1)); 5.08 (*dddd* (= '*dq*'), *J* = 10.5, 1.4, 1 olef. H); 4.66 (*d*, *J* = 12.2, PhC*H*); 4.65 (*m*, H–C(5)); 4.61 (*d*, *J* = 12.2, PhC*H*); 4.6 (*d*, *J* = 12.15, PhC*H*); 4.55 (*d*, *J* = 12.15, PhC*H*); 4.46 (*dd* (= '*t*'), *J* ≈ 4.8, H–C(3)); 4.3–4.24 (*m*, 1 allyl. H, H–C(2)); 4.06 (*dddd* (= '*ddt*'), *J* = 13.25, 5.6, 1.5, 1 allyl. H); 3.94 (*ddd*, *J* = 10.7, 4.4, 7.6, with D_2O *dd*, *J* = 4.4, 7.6, H–C(4)); 3.74 (*AB*, 2 H–C(6)); 3.57 (*d*, *J* = 10.7, exchange with D_2O, OH–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.6 (*s*, 2 CO); 138.1 (*s*); 138.0 (*s*); 134.0 (*d*); 133.9 (*d*, 2 C); 131.6 (*s*, 2 C); 128.3 (*d*, 2 C); 128.3 (*d*, 2 C); 128.2 (*d*, 2 C); 127.6 (*d*, 2 C); 127.5 (*d*, 2 C); 123.2 (*d*, 2 C); 116.5 (*t*, olef. C); 95.3 (*d*, C(1)); 74.5 (*d*); 73.4 (2*t*, PhCH_2); 71.1 (*d*); 70.2 (*t*); 68.8 (*t*); 66.8 (*d*, C(5)); 52.1 (*d*, C(2)). Anal. calc. for $C_{31}H_{31}NO_7$ (529.589): C 70.31, H 5.90, N 2.65; found: C 70.32, H 5.90, N 2.87.

Data of **24**: R_f (toluene/AcOEt 5:1) 0.1. $[\alpha]_D^{25} = +84.1$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3640*w* (br.), 3600*w*, 3570*w*, 3090*w*, 3070*w*, 3035*w*, 3000*w*, 2930*w*, 2870*w*, 1780*w* (br.), 1715*s* (br.), 1610*w*, 1495*w*, 1470*w* (sh), 1450*w*, 1410*w* (sh), 1385*m*, 1370*m*, 1350*m* (sh), 1325*m*, 1310*w* (sh), 1135*m*, 1100*s*, 1090*s* (sh), 1060*s* (sh), 1450*s*, 1030*s*, 1000*m* (sh), 970*w* (sh), 930*w*, 885*w*, 850*w*, 690*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.83–7.65 (*m*, 4 arom. H); 7.43–7.24 (*m*, 8 arom. H); 7.07–6.96 (*m*, 2 arom. H); 5.91 (*dddd*, *J* = 17.2, 10.4, 5.5, 5.1, 1 olef. H); 5.55 (*d*, *J* = 3.7, H–C(1)); 5.3 (*dddd* (= '*dq*'), *J* = 17.2, 1.7, 1 olef. H); 5.07 (*dddd* (= '*dq*'), *J* = 10.5, 1.5, 1 olef. H); 5.01 (*t*, *J* = 2.7, H–C(3)); 4.96 (*d*, *J* = 12.1, PhC*H*); 4.80 (*d*, *J* = 11.6, PhC*H*); 4.63 (*m*, 2 PhC*H*); 4.42 (*ddd* (= '*dt*'), *J* ≈ 9.9, 4.0, H–C(5)); 4.27 (*ddt*, *J* = 12.5, 5.0, 1.5, 1 allyl. H); 4.13 (*dd*, *J* = 3.7, 2.6, H–C(2)); 4.1 (*dddd* (= '*ddt*'), *J* = 12.5, 5.5, 1.7, 1 allyl. H); 3.87 (*m*, with D_2O *dd*, *J* = 11.55, 2.8, H–C(6)); 3.83 (*m*, with D_2O *dd*, *J* = 11.55, 3.85, H–C(6)); 3.71 (*dd*, *J* = 9.9, 2.65, H–C(4)); 1.77 (*dd*, *J* = 7.35, 5.4, exchange with D_2O, OH–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.2 (*s*, 2 CO); 139.3 (*s*); 137.7 (*s*); 134.3 (*d*); 133.7 (*d*, 2 C); 131.6 (*s*, 2 C); 128.4 (*d*, 2 C); 127.8 (*d*); 127.7 (*d*, 2 C); 127.6 (*d*, 2 C); 127.1 (*d*, 2 C); 126.5 (*d*); 122.8 (*d*, 2 C); 116.2 (*t*, olef. C); 95.6 (*d*, C(1)); 75.9 (*d*); 73.9 (*t*, PhCH_2); 72.5 (*d*); 71.7 (*t*, PhCH_2); 69.0 (*t*, allyl. C); 67.0 (*d*, C(5)); 62.0 (*t*, C(6)); 56.2 (*d*, C(2)). CI-MS: 472 (100, $[M - OAll]^+$). Anal. calc. for $C_{31}H_{31}NO_7$ (529.589): C 70.31, H 5.90, N 2.65; found: C 70.05, H 6.10, N 2.51.

*3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranose* (**25**). [Ir(cycloocta-1,5-diene)-$(PMePh_2)_2$]PF_6 (0.1 equiv.) was added under N_2 to a stirred soln. of **9** (6 g, 11.35 mmol) in dry THF (500 ml). The orange soln. was degassed and left *ca.* 1 min under H_2 until the colour turned yellow. The soln. was then degassed again and kept under N_2 for 3 h. Evaporation of the solvent gave a foam which was dissolved in a mixture of acetone (360 ml) and H_2O (40 ml). After the addition of HgO (4.6 g, 21.2 mmol) and $HgCl_2$ (5.14 g, 18.9 mmol), the mixture was stirred for 1 h and filtered through *Celite*. Evaporation of acetone left an aq. suspension which was

extracted with AcOEt. The org. layer was washed with a sat. aq. KI soln. (2×) and with H_2O, dried, filtered, and evaporated. FC (toluene/AcOEt 4:1) of the residue afforded **25** (4.2 g, 76%) which was recrystallized in Et_2O/hexane. R_f (toluene/AcOEt 3:1) 0.27. M.p. 149–150.3° (Et_2O/hexane). $[\alpha]_D^{25} = -114.1$ ($c = 0.8$, $CHCl_3$). IR ($CHCl_3$): 3600*w* (br.), 3090*w*, 3070*w*, 3040*w*, 3005*w*, 2960*w* (sh), 2940*w*, 2865*w*, 1775*m*, 1715*s*, 1610*w*, 1495*w*, 1470*w*, 1450*w*, 1400*m* (sh), 1370*m* (sh), 1350*m* (sh), 1325*w*, 1310*w*, 1250*m*, 1230*m* (br.), 1170*m*, 1145*m*, 1100*s*, 1080*m*, 1070*m* (sh), 1040*m*, 1025*m*, 1005*m*, 995*m* (sh), 965*m*, 950*m*, 915*m*, 890*w*, 860*w*, 690*m*, 635*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.73–7.67 (*m*, 4 arom. H); 7.53–7.50 (*m*, 2 arom. H); 7.42–7.37 (*m*, 3 arom. H); 7.07–7.03 (*m*, 2 arom. H); 6.88–6.83 (*m*, 3 arom. H); 6.41 (*dd*, $J = 8.75$, 6.0, with D_2O $J = 8.75$, H–C(1)); 5.57 (*s*, PhC*H*); 4.83 (*d*, $J = 12.3$, PhC*H*); 4.47 (*d*, $J = 12.3$, PhC*H*); 4.43 (*dd*, $J = 10.35$, 5.1, H_{eq}–C(6)); 4.3 (*ddd* (= '*td*'), $J \approx 9.95$, 5.1, H–C(5)); 4.25 (*dd* (= '*t*'), $J \approx 2.5$, H–C(3)); 4.06 (*dd*, $J = 8.75$, 2.8, H–C(2)); 3.86 (*dd*, $J = 9.4$, 2.4, H–C(4)); 3.83 (*dd* (= '*t*'), $J = 10.1$, H_{ax}–C(6)); 3.81 (*d*, $J = 6$, exchange with D_2O, OH–C(1)). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.1 (*s*, 2 CO); 137.5 (*s*); 137.4 (*s*); 133.8 (2*d*); 131.6 (*s*, 2 C); 129.1 (*d*); 128.4 (*d*, 2 C); 128.3 (*d*, 2 C); 127.9 (*d*, 2 C); 127.3 (*d*, 2 C); 126.2 (*d*, 2 C); 123.1 (*d*, 2 C); 102 (*d*, PhCH); 91.2 (*d*, C(1)); 79.8 (*d*, C(4)); 74 (*t*, PhCH_2); 73.9 (*d*, C(3)); 69.1 (*t*, C(6)); 64.4 (*d*, C(5)); 58.0 (*d*, C(2)). Anal. calc. for $C_{28}H_{25}NO_7$ (487.508): C 68.98, H 5.17, N 2.87; found: C 68.87, H 5.12, N 2.97.

*1-O-Acetyl-3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-*D*-allopyranose* (**26**). A cooled (0°) soln. of **25** (1.00 g, 2.05 mmol) in pyridine (30 ml) was treated with Ac_2O (10 ml), stirred for 12 h, at r.t., diluted with cold $CHCl_3$, washed with an ice-cold 4% aq. HCl soln., sat. aq. $NaHCO_3$ soln., and H_2O, and dried. FC (AcOEt/hexane 1:2) of the residue yielded **26** (1.053 g, 97%) which was recrystallized in AcOEt/hexane. R_f (AcOEt/hexane 1:2) 0.3. M.p. 167–168° (AcOEt/hexane). $[\alpha]_D^{25} = -112.7$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3080*w* (sh), 3060*w* (sh), 3030*w*, 3000*w*, 2960*w* (sh), 2940*w*, 2910*w* (sh), 2860*w*, 1780*m* (sh), 1765*m*, 1715*s*, 1685*w* (sh), 1610*w*, 1495*w*, 1465*w*, 1450*w*, 1375*m* (br.), 1365*m* (sh), 1350*w* (sh), 1325*w* (sh), 1310*w*, 1260*w*, 1170*w* (sh), 1160*w*, 1130*m*, 1105*m*, 1075*s* (br.), 1050*s* (sh), 1025*s* (sh), 1010*m*, 970*w*, 910*w*, 890*w*, 865*w*, 690*w*, 650*w*, 625*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.72–7.69 (*m*, 4 arom. H); 7.53–7.51 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.19 (*d*, $J = 9.2$, H–C(1)); 7.05–7.03 (*m*, 2 arom. H); 6.87–6.81 (*m*, 3 arom. H); 5.57 (*s*, PhC*H*); 4.85 (*d*, $J = 12.3$, PhC*H*); 4.47 (*d*, $J = 12.3$, PhC*H*); 4.45 (*ddd* (= '*td*'), $J \approx 9.8$, 5.2, H–C(5)); 4.40 (*dd*, $J = 10$, 5.2 H_{eq}–C(6)); 4.3 (*dd* (= '*t*'), $J \approx 2.5$, H–C(3)); 4.21 (*dd*, $J = 9.2$, 2.8, H–C(2)); 3.85 (*dd*, $J = 9.3$, 2.3, H–C(4)); 3.79 (*dd* ('*t*'), $J = 10$, H_{ax}–C(6)); 1.99 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.1 (*s*, 2 CO); 167.3 (*s*, CO); 137.1 (*s*, 2 C); 133.7 (*d*, 2 C); 131.4 (*s*); 128.9 (*d*); 128.3 (*d*, 2 C); 128.1 (*d*, 2 C); 127.8 (*d*, *s*, 2 C); 127.2 (*d*); 126 (*d*, 2 C); 123.1 (*d*, 2 C); 101.9 (*d*, PhCH); 89 (*d*, C(1)); 79.5 (*d*, C(4)); 73.8 (*t*, PhCH_2); 73.3 (*d*, C(3)); 68.74 (*t*, C(6)); 64.6 (*d*, C(5)); 55.3 (*d*, C(2)); 20.6 (*q*, Ac). CI-MS: 530.4 (25, $[M + 1]^+$). Anal. calc. for $C_{30}H_{27}NO_8$ (529.545): C 68.05, H 5.14, N 2.65; found: C 68.00, H 5.29, N 2.86.

*Ethyl 3-O-Benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-*D*-allopyranoside* (**27**). A mixture of **26** (360 mg, 0.68 mmol), Me_3SiSEt (330 µl, 2.04 mmol), and 4-Å molecular sieves (300 mg), in CH_2Cl_2 (25 ml) was stirred for 20 min at r.t. The suspension was cooled to 0°, treated with a soln. of Me_3SiOTf (123 µl, 0.68 mmol) in CH_2Cl_2 (1 ml), allowed to warm up, and left for 12 h at r.t. After the addition of Et_3N (0.5 ml) and stirring for 5 min, the mixture was filtered through *Celite*. Washing of the filtrate with H_2O, normal workup, and FC (AcOEt/hexane 1:3) yielded **27** (195.6 mg, 53%). Colourless oil. R_f (AcOEt/hexane 1:4) 0.31. $[\alpha]_D^{25} = -125.3$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3070*w*, 3040*w*, 3000*w*, 2960*w*, 2940*w*, 2875*w*, 1780*m*, 1715*s*, 1685*w* (sh), 1610*w*, 1495*w*, 1465*w*, 1455*w*, 1380*s*, 1370*m* (sh), 1325*w*, 1310*w*, 1295*w*, 1260*w*, 1170*w*, 1140*s*, 1120*s*, 1105*s*, 1070*s*, 1040*m*, 1030*m*, 1015*m*, 1000*m*, 990*m*, 970*m* (sh), 915*w*, 860*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.82–7.80 (*m*, 1 arom. H); 7.74–7.67 (*m*, 3 arom. H); 7.54–7.50 (*m*, 2 arom. H); 7.43–7.37 (*m*, 3 arom. H); 7.10–7.08 (*m*, 2 arom. H); 6.89–6.87 (*m*, 3 arom. H); 6.17 (*d*, $J = 10.9$, H–C(1)); 5.58 (*s*, PhC*H*); 4.85 (*d*, $J = 12.2$, PhC*H*); 4.52 (*d*, $J = 12.2$, PhC*H*); 4.44 (*dd*, $J = 10.4$, 5.2, H_{eq}–C(6)); 4.30 (*td*, $J = 9.8$, 5.2, H–C(5)); 4.25 (*dd*, $J = 10.9$, 3.0, H–C(2)); 4.21 ('*t*', $J \approx 2.6$, H–C(3)); 3.85 (*dd*, $J = 9.5$, 2.6, H–C(4)); 3.82 (*t*, $J = 10.4$, H_{ax}–C(6)); 2.75 (*q*, $J = 7.4$, CH_3CH_2S); 1.27 (*t*, $J = 7.4$, CH_3CH_2S). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.4 (*s*, CO); 167 (*s*, CO); 137.4 (*s*, arom. C); 137.2 (*s*, arom. C); 133.8 (*d*, arom. C); 133.4 (*d*, arom. C); 132.2 (*s*, arom. C); 130.8 (*s*, arom. C); 128.9 (*d*, arom. C); 128.4 (*d*, 2 arom. C); 128.1 (*d*, 2 arom. C); 127.8 (*d*, 2 arom. C); 127.2 (*d*, arom. C); 126 (*d*, 2 arom. C); 123 (*d*, arom. C); 122.9 (*d*, arom. C); 101.7 (*d*, PhCH); 79.7, 79.4 (2 *d*, C(1), C(4)); 73.9 (*t*, PhCH_2); 73.8 (*d*, C(3)); 69.0 (*t*, C(6)); 66.6 (*d*, C(5)); 55.4 (*d*, C(2)); 24.5 (*t*, CH_3CH_2S); 14.8 (*q*, CH_3CH_2S). Anal. calc. for $C_{30}H_{29}NO_6S$ (531.623): C 67.78, H 5.50, N 2.63; found: C 67.87, H 5.61, N 2.51.

*3-O-Benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-*D*-allopyranosyl Trichloroacetimidate* (**28**). A mixture of **25** (2 g, 4.1 mmol), CCl_3CN (2.07 ml, 20.5 mmol), and powdered anh. K_2CO_3 (2.72 g, 19.7 mmol) in CH_2Cl_2 (40 ml) was stirred for 6 h at r.t. and filtered through *Celite*. Evaporation of the filtrate and FC (toluene/AcOEt 10:1) gave **28** (1.996 g, 77%), which was recrystallized in CH_2Cl_2/hexane. R_f (toluene/AcOEt 10:1) 0.39. M.p. 164–166.5° (CH_2Cl_2/hexane). $[\alpha]_D^{25} = -105.6$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3440*w*, 3090*w* (sh), 3060*w*, 3040*w*, 3000*w*, 2960*w*

(sh), 2940*w*, 2910*w* (sh), 2865*w*, 1780*m*, 1720*s*, 1680*m*, 1610*w*, 1495*w*, 1470*w*, 1450*w*, 1385*s*, 1370*m* (sh), 1350*m* (sh), 1310*m* (sh), 1295*m*, 1280*m* (sh), 1160*w*, 1130*m*, 1105*m* (sh), 1070s (br.), 1050*s* (sh), 1025*s*, 1010*m*, 970*w*, 910*w*, 900*w*, 870*w*, 835*w*, 690*w*, 660*w*, 640*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.78 (*s*, NH); 7.77–7.68 (*m*, 4 arom. H); 7.54–7.51 (*m*, 2 arom. H); 7.44–7.39 (*m*, 3 arom. H); 7.36 (*d*, J = 9.1, H–C(1)); 7.09–7.07 (*m*, 2 arom. H); 6.96–6.84 (*m*, 3 arom. H); 5.59 (*s*, PhC*H*); 4.88 (*d*, J = 12.3, PhC*H*); 4.55–4.45 (*m*, H–C(5), H_{eq}–C(6)); 4.48 (*d*, J = 12.3, PhC*H*); 4.38 (*dd*, J = 9.1, 2.8, H–C(2)); 4.33 (*dd* (= '*t*'), $J \approx 2.5$, H–C(3)); 3.93 (*dd*, J = 9.2, 2.2, H–C(4)); 3.88 (*dd* (= '*t*'), J = 9.8, H_{ax}–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.2 (*s*, CO); 159.9 (*s*, C=N); 137.4 (*s*); 137.3 (*s*); 134.1 (*d*); 133.9 (*d*); 132.0 (*s*); 130.3 (*s*); 129.1 (*d*); 128.4 (*d*, 2 C); 128.3 (*d*, 2 C); 127.9 (*d*, 2 C); 127.6 (*d*, 2 C); 126.2 (*d*); 123.2 (*d*, 2 C); 102.1 (*d*, PhCH); 93.1 (*d*, C(1)); 79.6 (*d*, C(4)); 74.1 (*t*, PhCH_2); 73.9 (*d*, C(3)); 69.0 (*t*, C(6)); 65.0 (*d*, C(5)); 55.7 (*d*, C(2)). Anal. calc. for $C_{30}H_{25}Cl_3N_2O_7$ (631.896): C 57.02, H 3.99, N 4.43; found: C 57.07, H 3.90, N 4.52.

*Allyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranoside* (**29**). MPLC (CH_2Cl_2/MeOH 97:3) of the mother liquor of a large-scale preparation of **10** [31] gave **29** which was recrystallized in boiling AcOEt. R_f (CH_2Cl_2/MeOH 97.5:2.5) 0.2. M.p. 251–252° (AcOEt). $[\alpha]_D^{25} = -90.4$ (c = 0.8, $CHCl_3$). IR ($CHCl_3$): 3590*w*, 3440*m*, 2990*w*, 2960*w*, 2900*w*, 2870*w*, 1670*s*, 1650*m* (sh), 1510*w* (sh), 1500*m*, 1465*w*, 1450*w*, 1390*w* (sh), 1370*m*, 1310*w*, 1155*w* (sh), 1120*m* (sh), 1085*s*, 1030*m* (sh), 1000*s* (br.), 935*w*, 915*w*, 855*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.50–7.47 (*m*, 2 arom. H); 7.40–7.37 (*m*, 3 arom. H); 5.99 (*d*, J = 9.1, exchange with D_2O, NH); 5.87 (*dddd*, J = 17.2, 10.4, 6.0, 4.8, 1 olef. H); 5.60 (*s*, PhC*H*); 5.29 (*dddd* (= '*dq*'), J = 17.2, 1.7, 1 olef. H); 5.19 (*dddd* (= '*dq*'), J = 10.4, 1.4, 1 olef. H); 4.71 (*d*, J = 8.5, H–C(1)); 4.38 (*dd*, J = 10.6, 5.0, H_{eq}–C(6)); 4.35 (*dddd* (= '*ddt*'), J = 13.2, 4.8, 1.6, 1 allyl. H); 4.27 (br. *s*, after addn. of D_2O '*t*', $J \approx 2.9$, H–C(3)); 4.21 (*dddd*, J = 9.1, 8.5, 2.9, 1.1, after addn. of D_2O J = 9.1, 8.5, 2.9, H–C(2)); 4.07 (*dddd* (= '*ddt*'), J = 13.2, 6.0, 1.4, 1 allyl. H); 3.97 (*td*, $J \approx 10$, 5.0, H–C(5)); 3.80 (*t*, J = 10.3, H_{ax}–C(6)); 3.66 (*dd*, J = 9.4, 2.5, H–C(4)); 2.52 (*t*, J = 1.2, exchange with D_2O, OH–C(3)); 2.03 (*s*, Ac). ^{13}C-NMR (50 MHz, CD_3OD); 172.8 (*s* CO); 139.2 (*s*, arom. C); 135.6 (*d*, olef. C); 129.9 (*d*, arom. C); 129 (*d*, 2 arom. C); 127.5 (*d*, 2 arom. C); 117.1 (*t*, olef. C); 102.9 (*d*, PhCH); 100.5 (*d*, C(1)); 80.4 (*d*, C(4)); 71.1 (*t*, allyl. C); 70.1 (*t*, C(6)); 69.3 (*d*, C(3)); 64.6 (*d*, C(5)); 54.7 (*d*, C(2)); 22.6 (*q*, Me). CI-MS (NH_3): 350 (100, $[M + 1]^+$), 292 (45, $[M - OAll]^+$). Anal. calc. for $C_{18}H_{23}NO_6$ (349.383): C 61.88, H 6.64, N 4.01; found: C 61.95, H 6.69, N 3.85.

*Allyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranoside* (**30**). A vigorously stirred soln. of **29** (1 g, 2.9 mmol) in dry DMF (15 ml) was treated with BaO (1.00 g, 6.5 mmol), $Ba(OH)_2 \cdot 8\,H_2O$ (0.24 g, 0.76 mmol), and BnBr (447 µl, 3.8 mmol), and stirred under N_2 for 4 h at r.t. Filtration through *Celite*, evaporation of the filtrate under h.v., and FC (AcOEt/hexane 5:1) yielded **30** (1.19 g, 95%). Colourless oil. R_f (AcOEt) 0.5. IR ($CHCl_3$): 3440*m*, 3070*w*, 3000*m*, 2940*m*, 2860*m*, 1670*s*, 1500*m*, 1455*m*, 1375*m*, 1310*m*, 1120*s*, 1100*s*, 1070*s*, 1025*s*, 995*s*, 950*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.5–7.48 (*m*, 2 arom. H); 7.4–7.32 (*m*, 8 arom. H); 5.85 (*dddd*, J = 17.2, 10.4, 5.7, 4.5, 1 olef. H); 5.73 (*d*, J = 9.2, NH); 5.53 (*s*, PhC*H*); 5.24 (*dddd* (= '*dq*'), J = 17.2, 1.6, 1 olef. H); 5.14 (*dddd* (= '*dq*'), J = 10.4, 1.3, 1 olef. H); 5.03 (*d*, J = 11.6, PhC*H*); 4.78 (*d*, J = 8.7, H–C(1)); 4.53 (*d*, J = 11.6, PhC*H*); 4.41 (*dd*, J = 10.4, 5.2, H_{eq}–C(6)); 4.29 (*dddd* (= '*ddt*'), J = 13.1, 5.7, 1.6, 1 allyl. H); 4.16–4.03 (*m*, H–C(3), H–C(2), H–C(5), 1 allyl. H); 3.81 (*t*, J = 10.4, H_{ax}–C(6)); 3.77 (*dd*, J = 9.5, 2.4, H–C(4)); 1.85 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.9 (*s*, CO); 138.6 (*s*, arom. C); 137.4 (*s*, arom. C); 133.7 (*d*, olef. C); 128.8 (*d*, arom. C); 128.1 (*d*, 2 arom. C); 128 (*d*, 2 arom. C); 127.6 (*d*, 2 arom. C); 127.3 (*d*, arom. C); 125.9 (*d*, 2 arom. C); 116.1 (*t*, olef. C); 101.2 (*d*, PhC*H*); 98.5 (*d*, C(1)); 80.1 (*d*, C(4)); 74.2 (*t*, PhCH_2); 73.9 (*d*, C(3)); 69.2, 68.3 (2*t*, C(6), allyl. C); 63.7 (*d*, C(5)); 52.1 (*d*, C(2)); 22.8 (*q*, Me).

*Allyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-*D*-allopyranoside* (**31**). A suspension of **29** (5.68 g, 16.26 mmol) in 1N aq. NaOH (160 ml) was vigorously stirred and kept under reflux for 6 days. The resultant clear soln. was cooled to r.t. and extracted 3× with CH_2Cl_2. The combined org. phases were washed with H_2O and processed as usual to give the crude amine as a white solid. Freshly sublimated phthalic anhydride (2.408 g, 16.26 mmol) was added to a soln. of the amine in dry MeOH (100 ml), and the suspension was vigorously shaken for 10 min at r.t. After addition of Et_3N (2.27 ml, 16.26 mmol) and of additional phthalic anhydride (2.408 g, 16.26 mmol), the clear soln. was shaken for further 10 min and evaporated. The residue was dissolved in pyridine (80 ml), cooled to 0°, treated with Ac_2O (25 ml), and stirred for 16 h at r.t. Normal workup and FC (toluene/AcOEt 12:1) gave **31** (7.07 g, 95%). Colourless oil. R_f (toluene/AcOEt 6:1) 0.5. $[\alpha]_D^{25} = -46$ (c = 1, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3070*w*, 3040*w*, 3010*w*, 2930*w*, 2870*w*, 1770*m*, 1740*s*, 1715*s*, 1685*w* (sh), 1610*w*, 1470*w*, 1455*w*, 1375*s*, 1355*m* (sh), 1330*m*, 1310*w*, 1260*w*, 1165*m* (sh), 1145*m* (sh), 1130*s*, 1105*s*, 1085*s*, 1045*m*, 1015*s*, 995*s*, 975*m* (sh), 930*w*, 915*w* (sh), 900*w*, 870*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.87–7.85 (*m*, arom. H); 7.82–7.79 (*m*, arom. H); 7.74–7.70 (*m*, 2 arom. H); 7.46–7.41 (*m*, 2 arom. H); 7.37–7.34 (*m*, 3 arom. H); 6.04 (*d*, J = 8.7, H–C(1)); 5.82 (*dddd*, J = 17.2, 10.4, 5.7, 4.5, 1 olef. H); 5.74 (*dd* (= '*t*'), $J \approx 2.6$, H–C(3)); 5.59 (*s*, PhC*H*); 5.2 (*dddd* (= '*dq*'), J = 17.2, 1.6, 1 olef. H); 5.12 (*dddd* (= '*dq*'), J = 10.4, 1.3, 1 olef. H); 4.44 (*dd*, J = 10.5, 5.1, H_{eq}–C(6)); 4.4 (*dd*, J = 8.7, 2.6, H–C(2)); 4.35

(*dddd* (= '*ddt*'), J = 12.5, 5.7, 1.6, 1 allyl. H); 4.24–4.12 (*m*, 1 allyl. H, H–C(5)); 3.89 (*dd*, J = 9.6, 2.8, H–C(4)); 3.85 (*dd* (= '*t*'), J = 10.4, H_{ax}–C(6)); 2.06 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.4 (*s*, CH_3CO); 167.8 (*s*, CO); 167.7 (*s*, CO); 136.9 (*s*, arom. C); 134.0 (*d*, 1 arom. C, 1 olef. C); 133.6 (*d*, arom. C); 131.7 (*s*, arom. C); 131.3 (*s*, arom. C); 129 (*d*, arom. C); 128.2 (*d*, 2 arom. C); 126 (*d* 2 arom. C); 123.5 (*d*, arom. C); 123.1 (*d*, arom. C); 117.6 (*t*, olef. C); 101.5 (*d*, PhCH); 96.6 (*d*, C(1)); 76.9 (*d*, C(4)); 70.7 (*t*); 69.7 (*d*, C(3)); 69.1 (*t*); 64.7 (*d*, C(5)); 55.1 (*d*, C(2)); 20.8 (*q*, Me). Anal. calc. for $C_{26}H_{25}NO_8$ (479.485): C 65.13, H 5.26, N 2.92; found: C 64.95, H 5.48, N 3.14.

*Allyl 3-*O*-Acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-allopyranoside* (**32**). Similarly as described for the preparation of **8**, a mixture of **31** (698 mg, 1.458 mmol), $NaBH_3CN$ (553 mg, 8.75 mmol), and powdered 4-Å molecular sieves (400 mg) in THF (60 ml) gave, after FC (AcOEt/hexane 1:1), **32** (588 mg, 83%). Oil. R_f (AcOEt/hexane 1:1) 0.41. $[\alpha]_D^{25} = -36.1$ (c = 0.9, $CHCl_3$): IR ($CHCl_3$): 3590*w*, 3505*w* (sh), 3485*w*, 3080*w* (sh), 3040*w*, 3000*w*, 2960*w* (sh), 2920*w*, 2870*w*, 1775*w*, 1740*m*, 1715*s*, 1685*w* (sh), 1610*w*, 1470*w*, 1450*w*, 1380*m* (br.), 1320*w*, 1255*w* (sh), 1240*m* (br.), 1190*m*, 1155*m*, 1120*m* (sh), 1075*m* (br.), 1025*m* (br.), 990*m* (sh), 960*w*, 910*w* (sh), 870*w*, 690*w*, 640*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.89–7.81 (*m*, 2 arom. H); 7.73–7.69 (*m*, 2 arom. H); 7.4–7.33 (*m*, 5 arom. H); 5.89 (*d*, J = 8.65, H–C(1)); 5.83 (*dddd*, J = 17.2, 10.35, 6.2, 5.6, 1 olef. H); 5.55 (*dd* (= '*t*'), $J \approx$ 2.5, H–C(3)); 5.17 (*dddd* (= '*dq*'), J = 17.2, 1.6, 1 olef. H); 5.09 (*dddd* (= '*dq*'), J = 10.35, 1.3, 1 olef. H); 4.66 (*d*, J = 11.95, PhC*H*); 4.60 (*d*, J = 12.95, PhC*H*); 4.33 (*dddd* (= '*ddt*'), J = 12.4, 5.6, 1.4, 1 allyl. H); 4.29 (*dd*, J = 8.65, 2.6, H–C(2)); 4.12 (*dddd* (= '*ddt*'), J = 12.4, 6.2, 1.3, 1 allyl. H); 4.02–3.96 (*m*, H–C(4), H–C(5), OH–C(4)); 3.8 (*AB*, 2 H–C(6)); 2.05 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 171.1 (*s*, Ac); 167.9 (*s*, 2 CO); 137.7 (*s*); 134.0 (*d*, 2 C); 133.9 (*d*); 131.55 (*s*, 2 C); 128.4 (*d*, 2 C); 127.8 (*d*, 2 C); 127.7 (*d*, 2 C); 123.3 (*d*); 117.4 (*t*, olef. C); 95.9 (*d*, C(1)); 73.7 (*t*, PhCH_2); 73.1 (*d*); 72.1 (*d*); 70.4 (*t*); 70.3 (*t*); 68.2 (*d*, C(5)); 54.7 (*d*, C(2)); 20.8 (*q*, Me). Anal. calc. for $C_{24}H_{25}NO_7$ (439.464): C 64.86, H 5.65, N 2.91; found: C 64.68, H 5.80, N 2.96.

*Allyl 4-*O*-Acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-α-*D*-allopyranoside* (**34**). Similarly as described for the preparation of **8**, a mixture of **20** (105 mg, 0.219 mmol), $NaBH_3CN$ (82.5 mg, 1.31 mmol), and powdered 4-Å molecular sieves (100 mg), in THF (10 ml) gave, after FC (AcOEt/hexane 1:1), **34** (66.4 mg, 63%). Colourless oil. R_f (AcOEt/hexane 1:1) 0.25. IR ($CHCl_3$): 3410*m* (br.), 3090*w*, 3070*w*, 3040*w*, 3010*m*, 2960*m*, 2930*m*, 2870*m*, 1790*m*, 1770*s*, 1735*s*, 1720*s*, 1610*w*, 1495*w*, 1470*m*, 1450*m*, 1430*m*, 1400*s*, 1375*s*, 1365*s* (sh), 1345*m*, 1330*s*, 1200*s*, 1140*m* (sh), 1100*s*, 1080*s*, 1050*s*, 1030*s* (sh), 990*m* (sh), 935*m*, 910*w*, 890*m*, 875*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.90–7.87 (*m*, 2 arom. H); 7.78–7.65 (*m*, 2 arom. H); 7.36–7.28 (*m*, 5 arom. H); 6.06 (*m*, exchange with D_2O, OH–C(3)); 5.75 (*dddd*, J = 17.2, 10.5, 5.5, 4.8, 1 olef. H); 5.23 (*dddd* (= '*dq*'), J = 17.2, 1.7, 1 olef. H); 5.10 (*ddd*, J = 10.2, 2.4, 0.9, H–C(4)); 5.50 (*dddd* (= '*dq*'), J = 10.5, 1.6, 1 olef. H); 4.95 (*d*, J = 3.7, H–C(1)); 4.70 (*d*, J = 12.3, PhC*H*); 4.66 (*ddd*, J = 3.7, 2.4, 0.7, H–C(2)); 4.61–4.57 (*m*, H–C(3), H–C(5)); 4.47 (*d*, J = 12.3, PhC*H*); 4.23 (*dddd* (= '*ddt*'), J = 13.4, 4.7, 1.7, 1 allyl. H); 3.88 (*dddd* (= '*ddt*'), J = 13.4, 5.6, 1.5, 1 allyl. H); 3.66 (*AB* of *ABX*, 2 H–C(6)); 1.99 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.7 (*s*, CO); 168.7 (*s*, 2 CO); 137.9 (*s*, arom. C); 134.6 (*d*, 2 arom. C); 133.3 (*d*, olef. C); 131.2 (*s*, arom. C); 128.3 (*d*, 2 arom. C); 127.8 (*d*, 2 arom. C); 127.6 (*d*, arom. C); 124 (*d*, 2 arom. C); 116.8 (*t*, olef. C); 97.1 (*d*, C(1)); 73.3 (*t*, PhCH_2); 70.1 (*d*, C(4)); 68.9, 67.8 (2*t*, C(6), allyl. C); 66.9 (*d*, C(3)); 64.9 (*d*, C(5)); 54.5 (*d*, C(2)); 20.8 (*q*, Me).

*Allyl 6-*O*-Benzyl-2-deoxy-2-phthalimido-α-*D*-allopyranoside* (**35**). Similarly as described for the preparation of **8**, a mixture of **21** (358 mg, 0.818 mmol), $NaCNBH_3$ (308 mg, 4.91 mmol), and powdered 4-Å molecular sieves (300 mg) in THF (50 ml) gave, after FC (toluene/AcOEt 5:1), **35** (273 mg, 76%). Oil. R_f (toluene/AcOEt 4:1) 0.24. $[\alpha]_D^{25} = +98$ (c = 1, $CHCl_3$). IR ($CHCl_3$): 3450*w*, 3370*w* (sh), 3380*w* (br.), 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2960*w* (sh), 2920*w*, 2900*w*, 2875*w*, 1785*w* (sh), 1770*m* , 1720*s* (sh), 1710*s*, 1685*w* (sh), 1610*w*, 1495*w*, 1470*w*, 1450*w*, 1385*m*, 1350*s*, 1330*m*, 1255*w*, 1130*m* (sh), 1110*m* (sh), 1095*s* (sh), 1070*s*, 1050*s*, 1030*m* (sh), 960*w*, 935*w*, 890*w*, 860*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.93–7.88 (*m*, 2 arom. H); 7.81–7.77 (*m*, 2 arom. H); 7.41–7.29 (*m*, 5 arom. H); 6.09 (*m*, exchange with D_2O, OH–C(3)), 5.76 (*dddd*, J = 17.2, 10.5, 5.6, 4.7, 1 olef. H); 5.23 (*dddd* (= '*dq*'), J = 17.2, 1.7, 1 olef. H); 5.06 (*dddd* (= '*dq*'), J = 10.5, 1.5, 1 olef. H); 4.92 (*d*, J = 3.7, H–C(1)); 4.67 (*d*, J = 12.3, PhC*H*); 4.63 (*d*, J = 12.3, PhC*H*); 4.57 (*ddd*, J = 3.7, 2.6, 0.6, with D_2O *dd*, J = 3.7, 2.6, H–C(2)); 4.36 (*m*, with D_2O '*t*', $J \approx$ 2.7, H–C(3)); 4.23 (*dddd* (= '*ddt*'), J = 13.4, 4.7, 1.7, 1 allyl. H); 4.19 (*ddd*, J = 2.6, 4.5, 9.9, H–C(5)); 3.89 (*dddd* (= '*ddt*'), J = 13.4, 5.6, 1.5, 1 allyl. H); 3.88–3.80 (*m*, H–C(4), 2 H–C(6)); 2.81 (*d*, J = 10.8, OH–C(4)). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.9 (*s*, 2 CO); 138.3 (*s*); 134.6 (*d*, 2 C); 133.5 (*d*); 131.3 (*s*, 2 C); 128.3 (*d*, 2 C); 127.5 (*d*, 2 C); 127.5 (*d*); 123.8 (*d*, 2 C); 116.8 (*t*, olef. C); 96.7 (*d*, C(1)); 73.5 (*t*, PhCH_2); 69.4, 68.8 (2*t*, C(6), allyl. C); 68.4 (*d*); 68.3 (*d*); 67.9 (*d*); 58.3 (*d*, C(5)); 54.9 (*d*, C(2)). CI-MS: 440.3 (5, $[M + 1]^+$), 382.3 (100, $[M - 57]^+$). Anal. calc. for $C_{24}H_{25}NO_7$ (439.464): C 65.56, H 5.73, N 3.19; found: C 65.54, H 5.64, N 3.33.

*Allyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-α-*D*-allopyranoside* (**36**). A soln. of **20** (5.4 g, 11.26 mmol) in CH_2Cl_2 (40 ml) and 80% aq. AcOH soln. (20 ml) was kept under reflux for 4.5 h and then evaporated. A cooled (0°) soln. of the residue in pyridine (120 ml) was treated with 4-(Me_2N)C_5H_4N (10.7 mg, 1.3 mmol) and Ac_2O (40 ml)

and left for 12 h at r.t. Normal workup and FC (toluene/AcOEt 6:1) yielded **36** (5.14 g, 96%). White foam. R_f (toluene/AcOEt 4:1) 0.28. $[\alpha]_D^{25} = +138.3$ ($c = 0.9$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3030*w*, 2990*w*, 2920*w*, 2860*w* (sh), 1785*m*, 1755*s* (sh), 1740*s* (sh), 1725*s* (br.), 1685*w* (sh), 1610*w*, 1470*w*, 1450*w*, 1370*s*, 1350*m* (sh), 1325*m*, 1265*w* (sh), 1235*m* (br.), 1120*w*, 1105*w* (sh), 1045*m* (br.), 975*w*, 960*w*, 925*w*, 870*w*, 840*w*, 685*w*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.84–7.81 (*m*, 2 arom. H); 7.73–7.71 (*m*, 2 arom. H); 5.86 (*dd* (= '*t*'), $J \approx 2.7$, H–C(3)); 5.83 (*dddd*, $J = 17.2, 10.6, 5.0, 4.3$, 1 olef. H); 5.44 (*dddd* (= '*dq*'), $J = 17.2, 1.8$, 1 olef. H); 5.13 (*dddd* (= '*dq*'), $J = 10.6, 1.6$, 1 olef. H); 5.07 (*dd*, $J = 10.4, 2.9$, H–C(4)); 5.04 (*d*, $J = 3.7$, H–C(1)); 4.73 (*dd*, $J = 3.7, 2.7$, H–C(2)); 4.49 (*ddd*, $J = 10.4, 4.3, 2.0$, H–C(5)); 4.35 (*dd*, $J = 12.2, 4.3$, H–C(6)); 4.25 (*dddd* (= '*ddt*'), $J = 13.8, 4.3, 1.7$, 1 allyl. H); 4.21 (*dd*, $J = 12.2, 2.0$, H–C(6)); 3.94 (*dddd* (= '*ddt*'), $J = 13.8, 5.0, 1.7$, 1 allyl. H); 2.24 (*s*, Ac); 2.12 (*s*, Ac); 2.01 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 171.2 (*s*, Ac); 170.7 (*s*, Ac); 169.3 (*s*, Ac); 167.1 (*s*, 2 CO); 134.1 (*d*, 2 C); 133.4 (*d*); 131.3 (*s*, 2 C); 123.4 (*d*, 2 C); 116.1 (*t*, olef. C); 96.5 (*d*, C(1)); 68.5 (*t*, allyl. C); 67.2 (*d*); 66.7 (*d*); 64.2 (*d*, C(5)); 62.2 (*t*, C(6)); 52.2 (*d*, C(2)); 21.3 (*q*, Me); 20.7 (*q*, Me); 20.5 (*q*, Me). Anal. calc. for $C_{23}H_{25}NO_{10}$ (475.45): C 58.10, H 5.30, N 2.95; found: C 58.30, H 5.53, N 2.81.

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-*D*-allopyranose* (**37**). Similarly as described for the preparation of **25**, a soln. of **36** (5 g, 10.52 mmol) in dry THF (400 ml) was treated with $[Ir(cycloocta\text{-}1,5\text{-}diene)(PMePh_2)_2]PF_6$ and then with HgO (4.25 g, 19.6 mmol) and $HgCl_2$ (4.75 g, 17.5 mmol) in acetone (270 ml) and H_2O (30 ml). FC (toluene/AcOEt 2:1) afforded **37** (3.57 g, 78%). White foam. R_f (toluene/AcOEt 4:1) 0.06. $[\alpha]_D^{25} = +26.8$ ($c = 0.9$, $CHCl_3$). IR ($CHCl_3$): 3550*w*, 3480*w*, 3090*w*, 3030*w*, 2990*w* (sh), 2960*w*, 2920*w*, 2880*w* (sh), 1785*w*, 1755*s* (sh), 1740*s* (sh), 1725*s* (br.), 1685*w* (sh), 1610*w*, 1460*w* (sh), 1450*w*, 1365*w*, 1350*m* (sh), 1325*m*, 1240*m* (br.), 1120*m* (sh), 1105*w* (sh), 1095*m*, 1085*m*, 1070*m*, 1040*m* (br.), 960*w*, 925*w*, 880*w*, 810*w*, 710*w*, 660*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.83–7.78 (*m*, 2 arom. H); 7.71–7.69 (*m*, 2 arom. H); 6.23 (*dd*, $J = 8.6, 6.4$, H–C(1)); 5.61 (*dd* (= '*t*'), $J \approx 2.8$, H–C(3)); 5.08 (*dd*, $J = 9.8, 3.1$, H–C(4)); 4.31 (*dd*, $J = 8.6, 2.6$, H–C(2)); 4.28–4.23 (*m*, H–C(5), 2 H–C(6), OH–C(1)); 2.09 (*s*, Ac); 2.05 (*s*, Ac); 1.99 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.9 (*s*, Ac); 170.2 (*s*, Ac); 169.1 (*s*, Ac); 167.8 (*s*, 2 CO); 134.2 (*d*, 2 C); 131.3 (*s*, 2 C); 123.4 (*d*, 2 C); 90.8 (*d*, C(1)); 70.7 (*d*); 69.6 (*d*); 66.5 (*d*, C(5)); 62.5 (*t*, C(6)); 55.3 (*d*, C(2)); 20.7 (*q*, Me); 20.6 (*q*, Me); 20.4 (*q*, Me). Anal. calc. for $C_{20}H_{21}NO_{10}$ (435.385): C 55.17, H 4.86, N 3.22; found: C 54.91, H 5.10, N 3.12.

*1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-*D*-allopyranose* (**38**). Similarly as described for the preparation of **26**, a soln. of **37** (1.00 g, 2.3 mmol) in pyridine (30 ml) was treated with Ac_2O (10 ml). FC (toluene/AcOEt 4:1) yielded crystalline **38** (1.08 h, 98%) which was recrystallized in AcOEt/hexane. R_f (toluene/AcOEt 4:1) 0.22. M.p. 153.5–154.5°. $[\alpha]_D^{25} = +28.6$ ($c = 0.9$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3025*w* (br.), 2960*w*, 2940*w* (sh), 2920*w* (sh), 2905*w*, 2880*w* (sh), 1780*s* (sh), 1755*s* (br.), 1725*s*, 1685*w* (sh), 1615*w*, 1470*w*, 1455*w*, 1430*w*, 1385*s* (sh), 1370*s*, 1325*w*, 1290*w*, 1240*s* (br.), 1200*w*, 1115*m* (sh), 1085*s*, 1050*s*, 1020*m*, 1000*m*, 970*w* (sh), 950*m*, 910*w*, 885*w*, 870*w*, 640*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.85–7.82 (*m*, 2 arom. H); 7.75–7.73 (*m*, 2 arom. H); 7.06 (*d*, $J = 9.1$, H–C(1)); 5.67 (*dd* (= '*t*'), $J \approx 2.8$, H–C(3)); 5.12 (*dd*, $J = 10.0, 3.1$, H–C(4)); 4.49 (*dd*, $J = 9.1, 2.5$, H–C(2)); 4.39–4.18 (*m*, H–C(5), 2 H–C(6)); 2.11 (*s*, Ac); 2.06 (*s*, Ac); 2.01 (*s*, 2 Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.6 (*s*, Ac); 170.2 (*s*, Ac); 169.0 (*s*, Ac); 168.3 (*s*, Ac); 167.3 (*s*, 2 CO); 134.3 (*d*, 2 C); 131.2 (*s*, 2 C); 123.5 (*d*, 2 C); 88.4 (*d*, C(1)); 71.3 (*d*); 69.0 (*d*); 65.8 (*d*, C(5)); 61.8 (*t*, C(6)); 52.9 (*d*, C(2)); 20.7 (*q*, Me); 20.7 (*q*, Me); 20.6 (*q*, Me); 20.4 (*q*, Me). Anal. calc. for $C_{22}H_{23}NO_{11}$ (477.422): C 55.35, H 4.86, N 2.93; found: C 55.40, H 4.87, N 2.84.

*Ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-*D*-allopyranoside* (**39**). Similarly as described for the preparation of **27**, a mixture of **38** (600 mg, 1.26 mmol), Me_3SiSEt (610 µl, 3.77 mmol), and 4-Å molecular sieves (500 mg) in CH_2Cl_2 (30 ml) was treated with a soln. of Me_3SiOTf (227 µl, 1.26 mmol) in CH_2Cl_2 (1 ml). FC (toluene/AcOEt 5:1) yielded **39** (458 mg, 76%). Slightly yellow oil. R_f (toluene/AcOEt 6:1) 0.32. $[\alpha]_D^{25} = +12.3$ ($c = 1$, $CHCl_3$). IR ($CHCl_3$): 3040*w*, 3000*w* (sh), 2960*w*, 2930*w*, 1780*w* (sh), 1745*s* (br.), 1720*s*, 1705*w* (sh), 1610*w*, 1470*w*, 1450*w*, 1430*w*, 1380*m* (sh), 1370*m*, 1350*w* (sh), 1330*w*, 1290*w* (sh), 1230*m* (br.), 1135*w*, 1095*w* (sh), 1080*m*, 1055*m* (sh), 1045*m* (sh), 1025*m*, 995*w* (sh), 960*w*, 940*w*, 900*w*, 875*w*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.88–7.69 (*m*, 4 arom. H); 5.97 (*d*, $J = 10.7$, H–C(1)); 5.63 (*dd* (= '*t*'), $J \approx 1.8$, H–C(3)); 5.09 (*dd*, $J = 9.85, 3.05$, H–C(4)); 4.49 (*dd*, $J = 10.7, 2.5$, H–C(2)); 4.28–4.19 (*m*, H–C(5), 2 H–C(6)); 2.74 (*dd*, $J = 7.4, 2.2$, 1 H, CH_3CH_2S); 2.67 (*dd*, $J = 7.4, 2.2$, 1 H, CH_3CH_2S); 2.11 (*s*, Ac); 2.09 (*s*, Ac); 2.01 (*s*, 2 Ac); 1.3 (*t*, $J = 7.4$, CH_3CH_2S). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.7 (*s*, Ac); 170.3 (*s*, Ac); 169.0 (*s*, Ac); 167.4 (*s*, CO); 167.2 (*s*, CO); 134.2 (*d*, 2 C); 131.7 (*s*); 131.0 (*s*); 123.7 (*d*); 123.3 (*d*); 79.0 (*d*, C(1)); 72.9 (*d*); 69.4 (*d*); 66.6 (*d*, C(5)); 62.6 (*t*, C(6)); 53.2 (*d*, C(2)); 24.4 (*t*, CH_3CH_2S); 20.7 (*q*, 2 Me); 150.0 (*q*, CH_3CH_2S). Anal. calc. for $C_{22}H_{25}NO_9S$ (479.5): C 55.11, H 5.26, N 2.92; found: C 55.19, H 5.49, N 2.98.

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-*D*-allopyranosyl Trichloroacetimidate* (**40**). CCl_3CN (578 µl, 5.74 mmol) and powdered anh. K_2CO_3 (762 mg, 5.51 mmol) were added to a stirred soln. of **37** (500 mg, 1.15 mmol) in CH_2Cl_2 (6 ml). After 6 h at r.t., the suspension was filtered through *Celite*. Evaporation of the filtrate and FC

(AcOEt/hexane 1:1) of the residue gave **40** (493 mg, 74%). Oil. R_f (AcOEt/hexane 1:1) 0.29. IR ($CHCl_3$): 3340*w*, 3040*w*, 3000*w* (sh), 2960*w*, 2940*w* (sh), 1780*w*, 1745*s*, 1720*s*, 1680*w*, 1610*w*, 1470*w* (sh), 1450*w* (sh), 1340*w*, 1370*m*, 1290*w*, 1240*m* (br.), 1120*m* (sh), 1110*m* (sh), 1075*s* (br.), 1040*s*, 1020*m* (sh), 960*w*, 950*w* (sh), 900*w*, 870*w*, 835*w*, 635*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.68 (*s*, NH); 7.76–7.7 (*m*, 2 arom. H); 7.69–7.62 (*m*, 2 arom. H); 7.11 (*d*, $J = 9.0$, H–C(1)); 5.65 (*dd* (= '*t*'), $J \approx 2.8$, H–C(3)); 5.13 (*dd*, $J = 10.2, 3.1$, H–C(4)); 4.59 (*dd*, $J = 9.0, 2.5$, H–C(2)); 4.44–4.15 (*m*, C(5), 2 H–C(6)); 2.05 (*s*, Ac); 2.03 (*s*, Ac); 1.95 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.7 (*s*, Ac); 170.2 (*s*, Ac); 169.1 (*s*, Ac); 167.4 (*s*, 2 CO); 160.2 (*s*, C=N); 134.4 (*d*, 2 C); 131.3 (*s*, 2 C); 123.5 (*d*, 2 C); 92.4 (*d*, C(1)); 71.6 (*d*); 69.5 (*d*); 66.0 (*d*, C(5)); 61.9 (*t*, C(6)); 53.2 (*d*, C(2)); 20.7 (*q*, 2 Me); 20.5 (*q*, Me).

2. *Glycosidation. General Procedure for the Glycosidation.* All reactions were performed under Ar and in the presence of activated powdered 4-Å molecular sieves. CH_2Cl_2 and Et_2O were distilled over CaH_2. Trimethylsilyltriflate (Me_3SiOTf) and methyltriflate (MeOTf, *Fluka*) were used without further purification. Dimethyl(methylthio)sulfonium triflate ([Me_2(MeS)S]OTf) was prepared according to [59]. The yields of disaccharides are based upon the glycosyl acceptor and those of the amino-glycals upon the glycosyl donor.

2.1. *Glycosidation of* **35** *by* **38**–**40**. 2.1.1. A mixture of **35** (100 mg, 0.228 mmol), **38** (130.3 mg, 0.273 mmol), and 4-Å molecular sieves (150 mg) in CH_2Cl_2 (3 ml) was stirred for 20 min at r.t. The suspension was cooled to 0° and treated with a soln. of Me_3SiOTf (49.5 µl, 0.273 mmol) in CH_2Cl_2 (0.5 ml). The mixture was allowed to warm up, left for 48 h at r.t, treated with Et_3N (0.5 ml), kept for 10 min at r.t, and filtered through *Celite*. The residue obtained after evaporation of the filtrate was dissolved in a minimum of $CHCl_3$ and adsorbed on silica gel. FC (AcOEt/hexane 1:4→1:2) gave **41** (69.5 mg, 61%), **35** (57 mg, 57%), and **42** (33 mg, 17%).

2.1.2. A mixture of **35** (90 mg, 0.205 mmol), **39** (118 mg, 0.246 mmol), and 4-Å molecular sieves (150 mg) in Et_2O (5 ml) was stirred for 20 min at r.t., treated with MeOTf (135 µl, 1.23 mmol), stirred for 24 h at r.t., and processed as described in *2.1.1*. FC (AcOEt/hexane 1:4→1:2) gave **41** (41 mg, 40%), **35** (31.5 mg, 35%), and **42** (58 mg, 33%).

2.1.3. A mixture of **35** (90 mg, 0.205 mmol), **39** (118 mg, 0.246 mmol), and 4-Å molecular sieves (150 mg) in CH_2Cl_2 (4 ml) was stirred for 20 min at r.t. and treated with a soln. of [Me_2(MeS)S]OTf (254 mg, 0.984 mmol) in CH_2Cl_2 (1 ml). The mixture was stirred for 24 h at r.t. and processed as described in *2.1.1*. FC (AcOEt/hexane 1:4→1:2) gave **41** (42 mg, 41%), **35** (29.7 mg, 33%), and **42** (65 mg, 37%).

2.1.4. A mixture of **35** (95 mg, 0.216 mmol), **40** (150.4 mg, 0.259 mmol), and 4-Å molecular sieves (150 mg) in CH_2Cl_2 (5 ml) was stirred for 20 min at r.t. The suspension was cooled to 0°, and a soln. of Me_3SiOTf (47 µl, 0.259 mmol) in CH_2Cl_2 (0.5 ml) was added. After 20 min at 0°, TLC showed that **40** had disappeared. Et_3N (0.5 ml) was added and the mixture treated as described in *2.1.1*. FC (AcOEt/hexane 1:4→1:2) gave **41** (37 mg, 34%), **35** (24.7 mg, 26%), and **42** (76 mg, 41%).

*3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-deoxy-2-phthalimido-*D-ribo*-hex-1-enitol* (**41**). R_f (AcOEt/hexane 4:1) 0.25. Oil. $[\alpha]_D^{25} = +269.7$ ($c = 0.8$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3070*w*, 3020*m*, 2960*w*, 2930*w*, 2860*w*, 1780*s* (sh), 1760*s* (sh), 1720*s*, 1670*m*, 1610*w*, 1590*w*, 1470*m*, 1430*m* (sh), 1395*s*, 1370*s*, 1330*w*, 1300*m*, 1250*s* (br.), 1175*m* (sh), 1100*s*, 1085*s*, 1075*s* (sh), 1050*s*, 1020*m*, 960*m*, 910*m*, 880*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.91–7.84 (*m*, 2 arom. H); 7.80–7.73 (*m*, 2 arom. H); 6.81 (*s*, H–C(1)); 5.79 (*d*, $J = 3.8$, H–C(3)); 5.45 (*dd*, $J = 11.0, 3,8$, H–C(4)); 4.49 (*X* of *ABX*, H–C(5)); 4.41 (*AB* of *ABX*, 2 H–C(6)); 2.13 (*s*, 2 Ac); 2.05 (*s*, 2 Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.5 (*s*, 3 CH_3CO); 168.8 (*s*, CO); 167.5 (*s*, CO); 149.6 (*d*, C(1)); 143.3 (*d*, 2 arom. C); 131.6 (*s*, 2 arom. C); 123.7 (*d*, 2 arom. C); 105.5 (*s*, C(2)); 71.2 (*d*, C(4)); 65.3 (*d*); 64.4 (*d*); 61.3 (*t*, C(6)); 20.8 (*q*, Me); 20.7 (*q*, Me); 20.5 (*q*, Me). Anal. calc. for $C_{20}H_{19}NO_9$ (417.376): C 57.56, H 4.59, N 3.36; found: C 57.49, H 4.82, N 3.56.

*Allyl-6-*O*-Benzyl-2-deoxy-2-phthalimido-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-*D*-allopyranosyl)-α-*D*-allopyranoside* (**42**). R_f (AcOEt/hexane 1:1) 0.22. Oil. $[\alpha]_D^{25} = -23.5$ ($c = 0.8$, $CHCl_3$). IR ($CHCl_3$): 3470*w*, 3090*w*, 3030*w*, 3000*w*, 2910*w* (br.), 2860*w*, 1780*m*, 1745*s*, 1720*s*, 1610*w*, 1465*w*, 1450*w*, 1390*m* (sh), 1370*s*, 1350*m* (sh), 1325*w*, 1235*m*, 1115*m* (sh), 1085*s*, 1050*m* (sh), 1020*s*, 945*w*, 905*m*, 885*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.88–7.83 (*m*, 3 arom. H); 7.77–7.68 (*m*, 6 arom. H); 7.34–7.28 (*m*, 4 arom. H); 5.96 (*d*, $J = 8.3$, H–C(1′)); 5.61 (*dddd*, $J = 17.2, 10.5, 6.1, 4.5$, 1 olef. H); 5.54 ('*t*', $J \approx 2.8$, H–C(3′)); 5.15 (*dddd* (= '*dq*'), $J = 17.2, 1.9$, 1 olef. H); 5.06 (*d*, $J = 3.8$, H–C(1)); 4.77 ('*t*', $J \approx 3.4$, H–C(3)); 4.71 (*dddd* (= '*dq*'), $J = 10.5, 1.6$, 1 olef. H); 4.69 (*dd*, $J = 10.4, 3.2$, H–C(4′)); 4.58 (*t*, $J = 3.7$, H–C(2)); 4.56 (*m*, PhCH_2); 4.37 (*dd*, $J = 8.3, 2.3$, H–C(2′)); 4.04–3.99 (*m*, H–C(5′), 1 allyl. H); 3.88–3.80 (*m*, 1 allyl. H, H–C(4), H–C(5)); 3.78 (*d*, $J = 10.7$, exchange with D_2O, OH–C(4)); 3.76 (*dd*, $J = 11.9, 2.1$, H–C(6′)); 3.75 (*dd*, $J = 10.7, 2.6$, H–C(6)); 3.71 (*dd*, $J = 10.7, 4.7$, H–C(6)); 3.05 (*dd*, $J = 11.9, 7.4$, H–C(6′)); 1.97 (*s*, Ac); 193 (*s*, Ac); 1.91 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.2 (*s*, CH_3CO); 169.8 (*s*, CH_3CO); 169.4 (*s*, CO); 168.8 (*s*, CH_3CO); 167.3 (*s*, 2 CO); 167.0 (*s*, CO); 138.1 (*s*, arom. C); 134.3 (*d*, arom. C); 133.7 (*d*, 2 arom. C); 133.6 (*d*, arom. C); 131.7 (*s*, 2 arom. C); 131.4 (*s*, arom. C); 130.9 (*s*, arom. C); 128 (*d*, 3 arom. C); 127.2 (*d*, 3 arom. C); 123.5 (*d*, arom. C); 123.1 (*d*, arom. C); 122.8 (*d*, 2 arom. C); 114.7 (*t*, olef. C); 96, 95.8 (2*d*,

C(1'), C(1)); 73.5 (*d*); 73.1 (*t*, PhCH$_2$); 70.3 (*d*); 69.4 (*t*); 69.2 (*d*); 67.9 (*d*); 67.6 (*t*); 67.5 (*d*); 66.6 (*d*); 62.5 (*t*, C(6')); 54.7 (*d*, C(2)); 53.3 (*d*, C(2')); 20.4 (*q*, Me); 20.3 (*q*, Me); 20.2 (*q*, Me). Anal. calc. for $C_{44}H_{44}N_2O_{16}$ (856.834): C 61.69, H 5.18, N 3.27; found: C 61.59, H 5.10, N 3.11.

2.2. *Glycosidation of* **8** *by* **26**–**28**. According to *2.1.1*, the reaction of **8** (50 mg, 0.094 mmol) with **26** (59.8 mg, 0.113 mmol) and Me_3SiOTf (20.5 µl, 0.113 mmol) and 2 FC (each time: AcOEt/toluene 1:20→1:12) gave **43** (38.2 mg, 72%), **8** (15 mg, 30%), and **44** (26.4 mg, 28%).

According to *2.1.2*, the reaction of **8** (35 mg, 0.066 mmol) with **27** (42.2 mg, 0.079 mmol) and MeOTf (39 µl, 0.357 mmol) and 2 FC (each time: AcOEt/toluene 1:20→1:12) gave **43** (37.2 mg, 36%), **8** (5.3 mg, 15%), and **44** (35.7 mg, 54%).

According to *2.1.3*, the reaction of **8** (44 mg, 0.083 mmol) with **27** (53 mg, 0.097 mmol) and [Me_2(MeS)S]OTf (116 mg, 0.448 mmol) and FC (AcOEt/toluene 1:20→1:12) gave **43** (17.3 mg, 37%), **8** (3 mg, 7%), and **44** (50.6 mg, 61%).

According to *2.1.4*, the reaction of **8** (38 mg, 0.072 mmol) with **28** (54.3 mg, 0.086 mmol) and Me_3SiOTf (15 µl, 0.085 mmol) and FC (AcOEt/toluene 1:20→1:12) gave **43** (8 mg, 20%) and **44** (57.3 mg, 80%).

*1,5-Anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*D*-ribo-hex-1-enitol* (**43**). R_f (toluene/AcOEt 10:1) 0.39. M.p. 161.3–163.4° (CH_2Cl_2/hexane). $[\alpha]_D^{25} = +32$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3090*w* (sh), 3060*w*, 3040*w*, 3000*w*, 2940*w*, 2920*w*, 2870*w*, 2840*w* (sh), 1780*m*, 1770*m*, 1720*s*, 1665*m*, 1655*w* (sh), 1610*w*, 1590*w*, 1490*w*, 1465*w*, 1450*w*, 1390*m*, 1380*m* (sh), 1355*m* (sh), 1310*w*, 1290*w*, 1275*w*, 1260*w*, 1190*w*, 1140*m*, 1115*s*, 1100*s*, 1085*m*, 1050*m*, 1035*m* (sh), 1020*s*, 970*w*, 940*w*, 915*w*, 900*w*, 875*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.8–7.71 (*m*, 4 arom. H); 7.57–7.54 (*m*, 2 arom. H); 7.44–7.37 (*m*, 3 arom. H); 7.11–7.08 (*m*, 2 arom. H); 6.88–6.81 (*m*, 3 arom. H); 6.61 (*s*, H–C(1)); 5.65 (*s*, PhC*H*); 4.83 (*d*, *J* = 12,5, PhC*H*); 4.57 (*dd*, *J* = 10.2, 5.4, H_{eq}–C(6)); 4.52–4.47 (*m*, H–C(5)); 4.47 (*d*, *J* = 12.5, PhC*H*); 4.41 (*d*, *J* = 3.5, H–C(3)); 4.22 (*dd*, *J* = 10.3, 3.5, H–C(4)); 3.92 (*t*, *J* = 10.1, H_{ax}–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.4 (*s*, 2 CO); 146.8 (*d*, C(1)); 138.4 (*s*); 137.3 (*s*); 133.9 (*d*, 2 C); 131.7 (*s*); 129.1 (*d*); 128.3 (*d*, 2 C); 128.1 (*d*, 2 C); 127.9 (*d*, *s*, 2 C); 127.1 (*d*); 126.2 (*d*, 2 C); 123.4 (*d*, 2 C); 108.6 (*s*, C(2)); 101.7 (*d*, PhCH); 78.3 (*d*, C(4)); 73.7 (*t*, PhCH_2); 68.4 (*t*, C(6)); 67.7 (*d*, C(3)); 64.8 (*d*, C(5)). CI-MS: 469 (M^+), 362 (100, [M – OBn]$^+$). Anal. calc. for $C_{28}H_{23}NO_6$ (469.493): C 71.63, H 4.94, N 2.98; found: C 71.57, H 4.96, N 3.00.

*Allyl 3,6-Di-*O*-benzyl-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-*D*-allopyranoside)-2-deoxy-2-phthalimido-α-*D*-allopyranoside* (**44**). R_f (toluene/AcOEt 10:1) 0.3. Oil. $[\alpha]_D^{25} = -55.7$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3090*w* (sh), 3060*w*, 3040*w*, 3000*w*, 2960*m*, 2920*w*, 2860*w*, 1780*m*, 1715*s*, 1685*w* (sh), 1610*w*, 1495*w*, 1470*w* (sh), 1455*w*, 1385*m*, 1375*m*, 1350*m* (sh), 1325*m*, 1310*m*, 1260*m*, 1110*w* (sh), 1185*m* (sh), 1100–1085*s* (br.), 1005*s*, 970*m* (sh), 945*w* (sh), 915*w*, 900*w*, 885*w*, 865*w*, 820*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.76–6.87 (*m*, 28 arom. H); 6.27 (*d*, *J* = 8.45, H–C(1')); 5.86 (*dddd*, *J* = 12.2, 10.5, 5.6, 5.2, 1 olef. H); 5.58 (*s*, PhC*H*); 5.47 (*d*, *J* = 3.7, H–C(1)); 5.22 (*dddd* (= '*dq*'), *J* = 17.2, 1.7, 1 olef. H); 4.98 (*dddd* (= '*dq*'), *J* = 10.5, 1.4, 1 olef. H); 4.94 (*dd* (= '*t*'), *J* ≈ 2.7, H–C(3)); 4.85 (*d*, *J* = 12.1, PhC*H*); 4.84 (*d*, *J* = 12.4, PhC*H*); 4.58 (*d*, *J* = 12.4, PhC*H*); 4.53 (*d*, *J* = 11.8, PhC*H*); 4.49 (*d*, *J* = 12.0, PhC*H*); 4.47 (*m*, H_{eq}–C(6')); 4.39 (*ddd*, *J* = 10.1, 5.5, 2.0, H–C(5)); 4.31 (*d*, *J* = 12.3, PhC*H*); 4.28–4.23 (*m*, H–C(5'), H–C(2)); 4.21–4.18 (*m*, H–C(3'), 1 allyl. H); 4.14 (*dd*, *J* = 8.45, 2.9, H–C(2')); 4.09 (*dd*, *J* = 10.15, 2.7, H–C(4)); 4.03 (*dddd* (= '*ddt*'), *J* = 13.2, 5.6, 1.5, 1 allyl. H); 3.85 (*m*, H–C(4')); 3.84 (*t*, *J* = 10.1, H_{ax}–C(6')); 3.64 (*dd*, *J* = 10.7, 5.5, H–C(6)); 3.52 (*dd*, *J* = 2.0, 10.7, H–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 168 (*s*, 2 CO); 167.7 (*s*, CO); 167.4 (*s*, CO); 139.4 (*s*); 138.5 (*s*); 137.4 (*s*); 134–122.9 (*m*, olef. and arom. C); 116.4 (*t*, 1 olef. C); 102 (*d*, PhCH); 97.4 (*d*, C(1')); 95.6 (*d*, C(1)); 80.0 (*d*, C(4')); 76.2 (*d*, C(3)); 75.5 (*d*, C(4)); 74.4 (*d*, C(3')); 74.3 (*t*, PhCH_2); 74.15 (*t*, PhCH_2); 72.8 (*t*; PhCH_2); 69.5 (*t*, C(6)); 69.1 (*t*, C(6')); 69.0 (*t*, allyl. C); 66.0 (*d*, C(5)); 63.9 (*d*, C(5')); 56.8 (*d*, C(2')); 55.4 (*d*, C(2)). Anal. calc. for $C_{59}H_{54}N_2O_8$ (999.082): C 70.93, H 5.45, N 2.80; found: C 71.03, H 5.15, N 2.65.

2.3. *Glycosidation of* **32** *by* **38**–**40**. According to *2.1.1*, the reaction of **32** (113 mg, 0.257 mmol) with **38** (147 mg, 0.309 mmol), and Me_3SiOTf (56 µl, 0.309 mmol) in CH_2Cl_2 (4 ml) gave, after FC (CH_2Cl_2/MeOH 99.5:0.5→96:4), **41** (96.6 mg, 75%), **32** (50.8 mg, 45%), and **45** (27.7 mg, 12%).

According to *2.1.2*, the reaction of **32** (131 mg, 0.298 mmol) with **39** (171 mg, 0.357 mmol) and MeOTf (195 µl, 1.78 mmol) in Et_2O (5 ml) gave, after FC (CH_2Cl_2/MeOH 99.5:0.5→96:4), **41** (70 mg, 47%), **32** (32.7 mg, 25%), and **45** (69.6 mg, 26%).

According to *2.1.3*, the reaction of **32** (80 mg, 0.182 mmol) with **39** (105 mg, 0.218 mmol) and [Me_2(MeS)S]OTf (225 mg, 0.872 mmol) in CH_2Cl_2 (4 ml) gave, after FC (CH_2Cl_2/MeOH 99.5:0.5→96:4), **41** (32.7 mg, 36%), **32** (18.4 mg, 23%), and **45** (36 mg, 22%).

According to *2.1.4*, the reaction of **32** (120 mg, 0.273 mmol) with **40** (190 mg, 0.327 mmol) and Me_3SiOTf (59 µl, 0.327 mmol) in CH_2Cl_2 (5 ml) gave, after FC (CH_2Cl_2/MeOH 99.5:0.5→96:4), **41** (31.4 mg, 23%), **32** (25 mg, 21%), and **45** (137 mg, 56%).

Allyl 3-O-Acetyl-6-O-benzyl-2-deoxy-2-phthalimido-4-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-allopyranosyl)-β-D-allopyranoside (**45**). R_f (AcOEt/hexane 1:1) 0.20. Oil. $[\alpha]_D^{25} = +9.5$ ($c = 0.8$, $CHCl_3$). IR ($CHCl_3$): 3080*w*, 3060*w* (sh), 3035*w*, 3000*w*, 2940*w*, 2900*w*, 2870*w*, 1775*m*, 1740*s*, 1720*s*, 1675*w* (sh), 1610*w*, 1470*w*, 1450*w*, 1430*w*, 1375*s* (br.), 1335*m* (sh), 1320*w*, 1230*s* (br.), 1150*m*, 1110*s*, 1085*s* (sh), 1075*s*, 1030*s*, 995*m* (sh), 945*m*, 900*w*, 885*w*, 870*w* ^{1}H-NMR (400 MHz, $CDCl_3$): 7.88–7.83 (*m*, 3 arom. H); 7.77–7.68 (*m*, 8 arom. H); 7.28–7.23 (*m*, 3 arom. H); 7.06–7.03 (*m*, 2 arom. H); 6.05 (*d*, $J = 8.6$, H–C(1′)); 5.80 (*d*, $J = 8.7$, H–C(1)); 5.79 (*dddd*, $J = 17.25$, 10.5, 6.2, 5.4, 1 olef. H); 5.75 (*t*, $J \approx 2.7$, H–C(3)); 5.56 (*t*, $J \approx 2.7$, H–C(3′)); 5.14 (*dddd* (= '*dq*'), $J = 17.25$, 1.6, 1 olef H); 5.07 (*dddd* (= '*dq*', $J = 10.5$, 1.4, 1 olef. H); 4.98 (*dd*, $J = 10.2$, 3.0, H–C(4′)); 4.33 (*dd*, $J = 8.6$, 2.5, H–C(2′)); 4.28 (*dddd* (= '*ddt*'), $J = 12.6$, 5.4, 1.4, 1 allyl. H); 4.27 (*dd*, $J = 8.7$, 2.5, H–C(2)); 4.21–4.10 (*m*, H–C(5′), H–C(6′), PhCH); 4.08 (*dddd* (= '*ddt*'), $J = 12.6$, 6.2, 1.5, 1 allyl. H); 4.05–3.99 (*m*, H–C(6′), H–C(5), PhC*H*); 3.94 (*dd*, $J = 9.9$, 3.1, H–C(4)); 3.32 (*dd*, $J = 11.0$, 5.0, H–C(6)); 3.28 (*dd*, $J = 11.0$, 2.4, H–C(6)); 2.09 (*s*, Ac); 2.01 (*s*, Ac); 1.97 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.5 (*s*, CO); 170.4 (*s* CO); 170.1 (*s*, CO); 168.9 (*s*, CO); 167.9 (*s*, 2 CO); 167.7 (*s*, CO); 167.2 (*s*, CO); 138 (*s*, arom. C); 134.2 (*d*); 134.1 (*d*); 133.8 (*d*, 2 arom. C); 131.7 (*s*, arom. C); 131.5 (*s*, arom. C); 131.3 (*s*, arom. C); 130.8 (*s*, arom. C); 127.9 (*d*, 3 arom. C); 127.1 (*d*, arom. C); 126.9 (*d*, 3 arom. C); 123.5 (*d*, arom. C); 123.1 (*d*, 2 arom. C); 117.2 (*t*, olef. C); 96.4, 95.6 (2*d*, C(1′), C(1)); 74.6 (*d*); 72.7 (*d*); 72.6 (*t*, PhCH_2); 70.5 (*d*); 70.2 (*t*); 70.1 (*d*); 69.4 (*d*); 68.8 (*t*); 65.8 (*d*); 54.6, 53.9 (2*d*, C(2), C(2′)); 20.6 (*q*, Me); 20.5 (*q*, Me); 20.4 (*q*, Me); 20.3 (*q*, Me). Anal. calc. for $C_{46}H_{46}N_2O_{17}$ (898.871): C 61.47, H 5.16, N 3.12; found: C 61.49, H 5.33, N 3.21.

2.4. *Glycosidation of* **8** *by* **38**–**40**. According to *2.1.1*, the reaction of **8** (97.1 mg, 0.183 mmol) with **38** (105 mg, 0.22 mmol) and Me_3SiOTf (40 µl, 0.22 mmol) in CH_2Cl_2 (4 ml) and 2 FC (each time: AcOEt/toluene 1:6→1:3) gave **41** (62 mg, 68%), **8** (50.5 mg, 52%), and **46** (33 mg, 19%).

According to *2.1.2*, the reaction of **8** (88 mg, 0.166 mmol) with **39** (176 mg, 0.332 mmol) and MeOTf (91 µl, 0.83 mmol) and 2 FC (each time: AcOEt/toluene 1:6→1:3) gave **41** (89 mg, 64%), **8** (31 mg, 35%), and **46** (72.4 mg, 46%).

According to *2.1.3*, the reaction of **8** (101.7 mg, 0.192 mmol) with **39** (204 mg, 0.384 mmol) and $[Me_2(MeS)S]OTf$ (223 mg, 0.864 mmol) and 2 FC (each time: AcOEt/toluene 1:6→1:3) gave **41** (98 mg, 61%), **8** (36.6 mg, 36%), and **46** (87.3 mg, 48%).

According to *2.1.4*, the reaction of **8** (28.7 mg, 0.054 mmol) with **40** (41 mg, 0.065 mmol) and Me_3SiOTf (7 µl, 0.065 mmol) gave, after 2 FC (each time: AcOEt/toluene 1:6→1:3), **41** (18 mg, 66%), **8** (10 mg, 35%), and **46** (23 mg, 45%).

Allyl 3,6-Di-O-benzyl-2-deoxy-2-phthalimido-4-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-allopyranosyl)-α-D-allopyranoside (**46**). R_f (toluene/AcOEt 4:1) 0.15. Oil. $[\alpha]_D^{25} = +0.5$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3060*w*, 3040*w*, 3000*w*, 2920*w*, 2860*w*, 1775*w* (sh), 1740*s*, 1715*s*, 1685*w* (sh), 1610*w*, 1590*w*, 1555*w*, 1490*w*, 1465*w*, 1450*w*, 1370*m*, 1350*m* (sh), 1320*w*, 1230*m*, 1160*w*, 1145*w*, 1100*m*, 1085*m*, 1035*m* (sh), 1025*s*, 945*w*, 900*w*, 885*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.85–7.62 (*m*, 8 arom. H); 7.37–7.22 (*m*, 7 arom. H); 6.98–6.94 (*m*, 2 arom. H); 6.89–6.86 (*m*, 1 arom. H); 6.12 (*d*, $J = 8.4$, H–C(1′)); 5.85 (*dddd*, $J = 17.2$, 10.5, 5.5, 4.8, 1 olef. H); 5.61 (*t*, $J \approx 2.7$, H–C(3′)); 5.44 (*d*, $J = 3.7$, H–C(1)); 5.24 (*dddd* (= '*dq*'), $J = 17.2$, 1.7, 1 olef. H); 5.11 (*dd*, $J = 10.1$, 3.1, H–C(4′)); 4.99 (*dddd* (= '*dq*'), $J = 10.5$, 1.5, 1 olef. H); 4.97 (*t*, $J \approx 2.7$, H–C(3)); 4.86 (*d*, $J = 12.4$, PhC*H*); 4.59 (*d*, $J = 12.4$, PhC*H*); 4.55 (*d*, $J = 11.7$, PhC*H*); 4.42 (*dd*, $J = 8.4$, 2.4, H–C(2′)); 4.36 (*ddd*, $J = 10.1$, 4.6, 2.0, H–C(5)); 4.35 (*d*, $J = 11.7$, PhC*H*); 4.31–4.21 (*m*, 2 H–C(6′), H–C(5′), H–C(2)); 4.20 (*dddd* (= '*ddt*'), $J = 13.1$, 4.8, 1.7, 1 allyl. H); 4.13 (*dd*, $J = 10.1$, 2.8, H–C(4)); 4.02 (*dddd* (= '*ddt*'), $J = 13.1$, 5.5, 1.5, 1 allyl. H); 3.55 (*dd*, $J = 10.6$, 4.6, H–C(6)); 3.48 (*dd*, $J = 10.6$, 2.1, H–C(6)); 2.12 (*s*, Ac); 2.08 (*s*, Ac); 2.02 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.5 (*s*, CO); 170.1 (*s*, CO); 169 (*s*, CO); 167.8 (*s*, 2 CO); 167.5 (*s*, CO); 167.1 (*s*, CO); 139.4 (*s*, arom. C); 138.4 (*s*, arom. C); 134.2 (*d*, 2 arom. C); 134.1 (*d*, arom. C); 133.4 (*d*, arom. C); 131.5 (*s*, 2 arom. C); 131.4 (*s*, arom. C); 131 (*s*, arom. C); 128 (*d*, 2 arom. C); 127.4 (*d*, 2 arom. C); 127.2 (*d*, 4 arom. C); 127.1 (*d*, 3 arom. C); 126.2 (*d*, arom. C); 122.6 (*d*, 2 arom. C); 116 (*t*, olef. C); 96.9 (*d*, C(1′)); 95.6 (*d*, C(1)); 75.8, 75.7 (2*d*, C(3′), C(4′)); 74.1 (*t*, PhCH_2); 72.5 (*t*, PhCH_2); 70.4 (*d*); 69.5 (*d*); 69.2, 68.8 (2*t*, allyl. C, C(6)); 66.5, 65.5 (2*d*, C(5), C(5′)); 62.3 (*t*, C(6′)); 55.5 (*d*, C(2′)); 54.2 (*d*, C(2)); 20.5 (*q*, 2 Me); 20.3 (*q*, Me). Anal. calc. for $C_{51}H_{50}N_2O_{16}$ (946.959): C 64.68, H 5.32, N 2.96; found: C 64.92, H 5.43, N 2.75.

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